

**Intramolecular Carbenoid Insertions:
The Reactions of α -Diazoketones Derived From
Furanyl, Thienyl, Benzofuranyl and Benzothienyl Acetic Acids
with Rhodium (II) Acetate**

By
KELVIN HIN-YEONG YONG, B.Sc.

A Thesis Submitted to the Department of Chemistry
in Partial Fulfillment of the Requirements
for the Degree of
Master's of Science

Brock University
January, 1998

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ABSTRACT

A number of synthetically useful ring systems can be prepared *via* the intramolecular insertion of a metal-stabilized carbenoid into a heteroaromatic systems. The chemical outcome of these reactions are dependent not only on the nature of the heteroatom but also on the length of the aliphatic tether linking the carbenoid moiety with the aromatic fragment. Our work with furanyl and thienyl systems containing a single methylene tether have allowed for some rather atypical chemistry. For example, treatment of 1-diazo-3-(2-thienyl)-2-propanone (**6**) with catalytic rhodium (II) acetate yields 5,6-dihydro-4*H*-cyclopenta[*b*]thiophen-5-one (**3**) while, the isomeric 1-diazo-3-(3-thienyl)-2-propanone(**15**) gives a spiro-disulphide (**20**).

Novel chemistry was also exhibited in the analogous furanyl systems. While treatment of 1-diazo-3-(3-furanyl)-2-propanone (**52**) with Rh₂(OAc)₄ resulted in the expected 2-(4-Oxo-2-cyclopentenyliden)acetaldehyde (**54**), isomeric 1-diazo-3-(2-furanyl)-2-propanone (**8**) undergoes vinylogous Wolff rearrangement to give a mixture of 6a-methyl-2,3,3a,6a-tetrahydrofuro[2,3-*b*]furan-2-one (**44**) and 2-(2-methyl-3-furyl)acetic acid (**43**).

Rhodium acetate catalyzed decomposition of 1-diazo-3-(3-benzofuranyl)-2-propanone (**84**) and 1-diazo-3-(2-benzofuranyl)-2-propanone (**69**) also allows for vinylogous Wolff rearrangement, a chemistry unseen in benzofuranyl systems with longer tethers. A number of interesting products were isolated from the trapping of intermediate ketenes.

Decomposition of 1-diazo-3-(3-benzothienyl)-2-propanone (**100**) resulted in the formation of 2,3-dihydro-1*H*-benzo[*b*]cyclopenta[*d*]thiophen-2-one (**102**). However, in addition to (**102**), a dimer was also generated from the decomposition of 1-diazo-3-(2-benzothienyl)-2-propanone (**109**).

The insight into the mechanistic underpinnings of the above reactions are provided by molecular modeling at a PM3 level.

Acknowledgments

I wish to express my acknowledgments to Dr. Fred Capretta for his guidance and helpful insights, making this work possible.

I would also like to express my gratitude to my family for all their encouragement and support, and to Charlotte Khouw (my MTJ), for putting up with me by being very supportive and understanding, as well as an excellent typist and proofreader.

I would also like to thank my supervisory committee Dr. Atkinson and Dr. Miller for their comments and suggestions.

In addition, I would like to express my special thanks to Mr. Tim Jones for being very helpful in running the mass spectra, to everybody in H221 and H224 for keeping me company (especially the night owls), Dr. Jianxin Gu for all his helpful advice, Dr. Carl Turner for proofreading my thesis and Mr. Mohamed Salim for sharing the lab maintenance tasks.

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INTRODUCTION

1. Carbenes and Carbenoids

Carbenes are neutral divalent species of carbon that usually only exist as short-lived intermediates. The carbene carbon is linked to two adjacent groups (R) by covalent bonds, and it possesses two non-bonding electrons, which can have either antiparallel spin (singlet state) or parallel spin

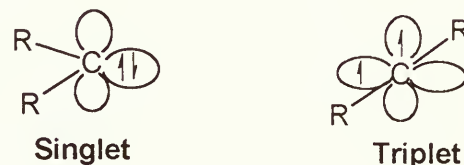
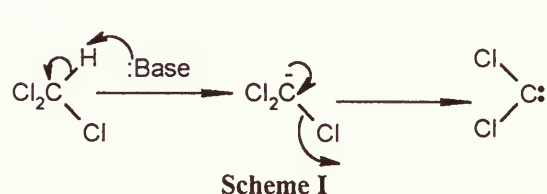


Figure I

(triplet state) as shown in Figure I.¹ With a few exceptions², carbenes can only be trapped in inert matrices at extremely low temperatures ($\leq 77\text{ K}$)³ due to their high reactivity.



There are a number of methods by which free carbenes can be generated; the two most important methods being the α -

elimination of halogenated compounds and the disintegration of compounds containing certain types of double bonds. Scheme I illustrates a typical α -elimination reaction in which chloroform is treated with a strong base. In this two steps process, the base removes a proton to generate the anion (CCl_3^-) which subsequently loses a chloride ion to give the dichlorocarbene shown (Scheme I).⁴ Another common method used to generate free carbenes involves the disintegration of compounds containing certain types of double bonds, for example, ketenes, diazo compounds and diazirines.⁵ These compounds will

¹ Skell, P. S., Woodworth, R. C., *J. Am. Chem. Soc.*, **1956**, *78*, 4496; Skell, P. S., *Tetrahedron*, **1985**, *41*, 1427.

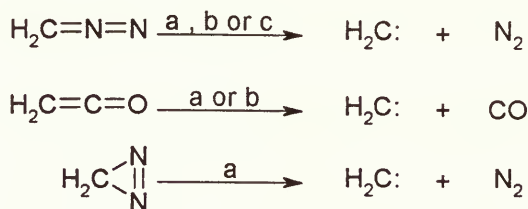
² Regitz, M., *Angew. Chem. Int. Ed. Engl.*, **1991**, *30*, 674.

³ Zuev, P. S., Nefedov, O. M., *Russ. Chem. Rev.*, **1989**, *58*, 636.

⁴ Kirmse, W., *Angew. Chem. Int. Ed. Engl.*, **1965**, *4*, 1; Hoffman, R. W., *Acc. Chem. Res.*, **1985**, *18*, 248.

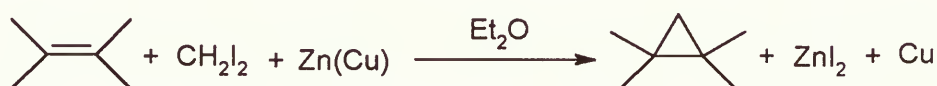
⁵ Regitz, M, Maas, G., Diazo compounds, (New York : Academic Press, 1986) 170-184.

undergo homolytic cleavage of the double bond under various conditions (see Scheme II) to form a carbene and a neutral species.



The term "carbenoid" is a = photolysis ; b = thermolysis ; c = metal-ion catalysis
Scheme II

used to describe species that react like free carbenes but are at least partially bound to another atom (usually a transition metal).⁶ The use of carbenoids in synthesis has recently become quite popular due to the fact that these species are generally less reactive than their free carbene counterparts and hence allow for greater control in synthetic reactions. In addition, these carbenoid species generally require simpler reaction procedures for their preparation and do not involve the use of specialized apparatus. Rather, the use of transition metal catalysts for carbenoid generation allows the reactions to proceed at or near ambient temperature. Furthermore, metal-stabilized carbenoids can be made to offer high degrees chemoselectivity⁷ and stereoselectivity⁸ in the product formed.



Scheme III

Two of the most commonly used carbenoid generation methods are the Simmons-Smith reaction and catalytic decomposition of diazo compounds using transition metal

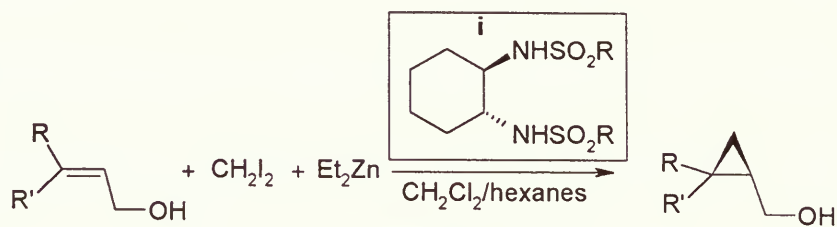
⁶ Nozaki, H., Mariuti, S., Takaya, H., *et al.*, *Tetrahedron Lett.*, 1966, 5239.

⁷ Hubert, A.J., Noels, A.F., Anciaux, A.J., Teyssie, P., *Synthesis*, 1976, 600; Paulissen, R., Hayez, E., Hubert, A.J., Teyssie, P., *Tetrahedron Lett.*, 1972, 1465; Paulissen, R., Reimlinger, H., Hayez, E., Hubert, A.J., Teyssie, P., *Tetrahedron Lett.*, 1973, 2233.

⁸ Doyle, M.P., Griffin, J.H., Bagheri, V., Dorow, R.L., *Organometallics*, 1984, 3, 53; Doyle, M.P., Griffin, J.H., Conceição, J., *J. Chem. Soc., Chem. Commun.*, 1985, 328.

complexes. The Simmons-Smith reaction⁹ was first reported in 1958 and involves the use of diiodomethane and a copper-zinc couple. The organozinc carbenoid generated adds to an alkene in situ allowing for the formation of a cyclopropane product in good yields and with few side products (Scheme III). The Simmons-Smith reaction has been used successfully in numerous organic syntheses.¹⁰

The most recent uses of the Simmons-Smith reaction have involved modifications that allow for the



Scheme IV

cyclopropanations to proceed asymmetrically. In 1992, Kobayashi's group¹¹ reported the first catalytic, enantioselective Simmons-Smith cyclopropanation on various allylic alcohols. The reaction was carried out on allylic alcohols using diethyl zinc, diiodomethane and catalytic amounts of a chiral C₂-symmetric disulfonamide (i) in dichloromethane and

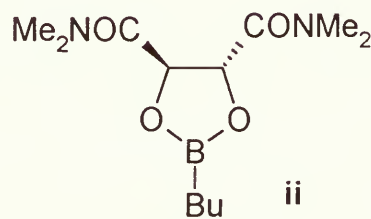


Figure II

resulted in very good yields of the cyclopropane (80 - 100%) and enantiomeric excesses (e.e.) generally in the 70 - 80% range (Scheme IV). Charette *et al.*¹² also reported a similar reaction using a chiral dioxaborolane (ii) as the chiral ligand (see Figure II) and

⁹ Simmons, H.E., Cairns, T. L., Vladuchick, S. A., Hoiness, C. M., *Org. React.*, **1973**, *20*, 1.

¹⁰ For examples see : Wender, P. A., Keenan, R. M., Lee, H. Y., *J. Am. Chem. Soc.*, **1987**, *109*, 4390; Wender, P. A., Howbert, J. J., *J. Am. Chem. Soc.*, **1981**, *103*, 689.

¹¹ Takahashi, H., Yoshioka, M., Ohno, M., Kobayshi, S., *Tetrahedron Lett.*, **1992**, *33*, 2575.

¹² Charette, A.B., Lemay, J., *Angew. Chem. Int. Ed. Engl.*, **1997**, *36*, 1090; Charette, A.B., Juteau, H., *J. Am. Chem. Soc.*, **1994**, *116*, 2651; Charette, A.B., Prescott, S., Brochu, C., *J. Org. Chem.*, **1995**, *60*, 1081.

reported e.e. values in the 90% range with yields of about 80-100%. These enantioselective cyclopropanations of allylic alcohols may be looked upon as modifications of Sharpless's enantioselective epoxidation of allylic alcohols.

2. α -Diazoketones

Much of the recent work in the carbenoid chemistry field has involved the transition metal catalyzed decomposition of α -diazocarbonyl compounds. The popularity of these α -diazocarbonyl compounds is based on their ease of preparation (*vide infra*), facile purification (can be chromatographed on silica gel) and stability (can be stored for a prolonged periods of time without significant decomposition). The use of diazo compounds dominates the carbenoid field and there have been a number of excellent reviews published.¹³

The ability of carbonyl groups to stabilize the carbenoids derived from α -diazocarbonyl compounds has also been demonstrated. It was shown from Molecular Orbital (M.O.)

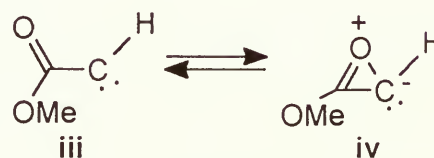


Figure III

calculations¹⁴ that carbomethoxy carbene (iii) possesses a equilibrium structure wherein the carbene is stabilized by the oxygen's lone pair of electrons (iv) as shown in Figure III.

¹³ Doyle, M. P., *Chem. Rev.*, **1986**, *86*, 919; Adams, J., Spero, D.M., *Tetrahedron*, **1991**, *47*, 1765; Padwa, A., Frumpe, K.E., *Tetrahedron*, **1992**, *48*, 5385; Ye, T., McKervey, M.A., *Chem. Rev.*, **1994**, *94*, 1091; Doyle, M.P., McKervey, M.A., *Chem. Commun.*, **1997**, 983.

¹⁴ Noyori, R., Yamanaka, M., *Tetrahedron Lett.*, **1980**, *21*, 2851.

Although ethyl diazoacetate was first synthesized in 1883 by Curtius,¹⁵ work by Arndt and Eistert in the late 1920s allowed for the general preparation of α -diazoketones from the corresponding carboxylic acid.¹⁶ Acylation of diazomethane remains the single most important route to acyclic terminal α -diazoketones. The successful generation of α -diazoketones by the Arndt and Eistert method lies in the use of an excess (>2 equivalents) of diazomethane. The procedure is illustrated in Scheme V. Treatment of the carboxylic acid with a chlorinating agent such as thionyl chloride will result in the corresponding acyl chloride. With the addition of the acyl chloride to a diazomethane solution, a nucleophilic attack by diazomethane onto the acyl chloride, followed by elimination of a chloride ion, generates a diazonium cation species. Proton abstraction by a base yields the desired diazoketone. When the base is diazomethane, the diazonium cation formed then reacts with the chloride ion to

form chloromethane

and nitrogen. (Scheme

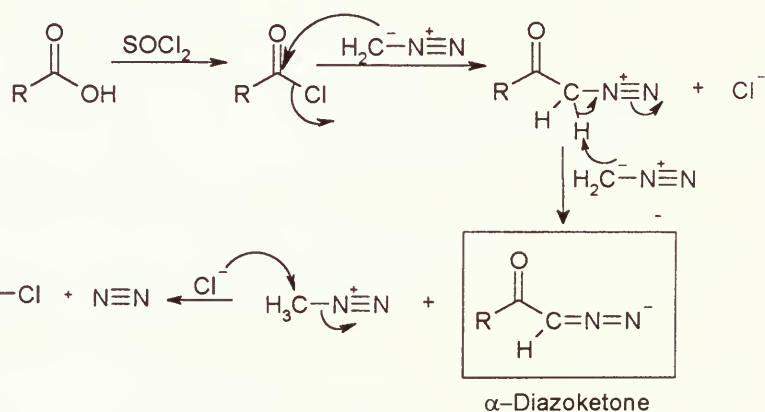
V). Arndt and Eistert¹⁶

used these α -

diazoketones as

intermediates in the

homologation of carboxylic acids.

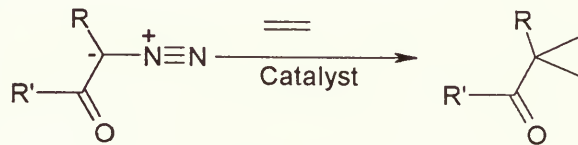


Scheme V

¹⁵ Curtius, T., *Ber.*, **1883**, 16, 2230.

¹⁶ Arndt, F., Eistert, B., *Ber.*, **1935**, 68, 200; Regitz, M., Mass, G., Diazo Compounds: Properties & Synthesis, (Orlando, FL: Academic Press, 1986), 185.

Photolysis or thermolysis of α -diazoketones can lead to the corresponding free carbenes. However, if certain transition metal complexes are introduced, the generation of carbenoids can be induced.



Scheme VI

These in turn can perform a variety of chemical reactions including OH¹⁷, NH¹⁸ and CH¹⁹ insertions, Wolff rearrangements²⁰ and cyclopropanations of double bonds²¹, to name but a few. For the purposes of this thesis, the desired carbenoids reaction is cyclopropane formation (Scheme VI).

3. Catalysts Used for Carbenoid Generation

A survey of the current carbenoid literature reveals that although a number of transition metal complexes (based on palladium,²² iron,²³ cobalt,²⁴ molybdenum,²⁵

¹⁷ Giddings, P. J., John, D. I., Thomas, E. J., *Tetrahedron Lett.*, **1978**, 995; Ganem, B., Ikota, N., Muralidharan, V. B., Wade, W. S., Young, S. D., Yukimoto, Y., *J. Am. Chem. Soc.*, **1982**, *104*, 6787; Teng, C.-Y. P., Ganem, B., *J. Am. Chem. Soc.*, **1984**, *106*, 2463; Marshall, J. R., Walker, J., *J. Chem. Soc.*, **1952**, 467.

¹⁸ Salzmman, T. N., Ratcliffe, R. W., *J. Am. Chem. Soc.*, **1980**, *102*, 6161; Melillo, D. G., Shinkai, I., Liu, T., Ryan, K., Sletzing, M., *Tetrahedron Lett.*, **1980**, *21*, 2783; Aratani, M., Hirai, H., Sawada, K., Yamada, A., Hashimoto, M., *Tetrahedron Lett.*, **1985**, *26*, 223; Evans, D. A., Sjogren, E. B., *Tetrahedron Lett.*, **1986**, *27*, 3119; William, R. M., Lee, B. H., Miller, M. M., Anderson, O. P., *J. Am. Chem. Soc.*, **1989**, *111*, 1073.

¹⁹ Ceccherelli, P., Curini, M., Marcotullio, M. C., Rosati, O. *Tetrahedron*, **1991**, *47*, 7403; Hashimoto, S., Watanabe, N., Ikegami, S., *Tetrahedron Lett.*, **1992**, *33*, 2709.

²⁰ Wolff, L., *Leibigs Ann. Chem.*, **1912**, *394*, 23; Plucinska, K., Liberek, B., *Tetrahedron*, **1987**, *43*, 3509; Nishi, T., Morisawa, Y., *Heterocycles*, **1989**, *29*, 1835.

²¹ Burke, S. D., Grieco, P. A., *Org. React.*, (N.Y.), **1979**, *26*, 361; Hatch, C. E., III, Baum, J. S., *J. Org. Chem.*, **1980**, *45I*, 3281.

²² Paulissen, R., Hubert, A. J., Teyssie, P. *Tetrahedron Lett.* **1972**, 1465; Vallgarda, J., Appelberg, U., Csoregh, I., Hacksell, U., *J. Chem. Soc., Perkin Trans. I*, **1994**, 461.

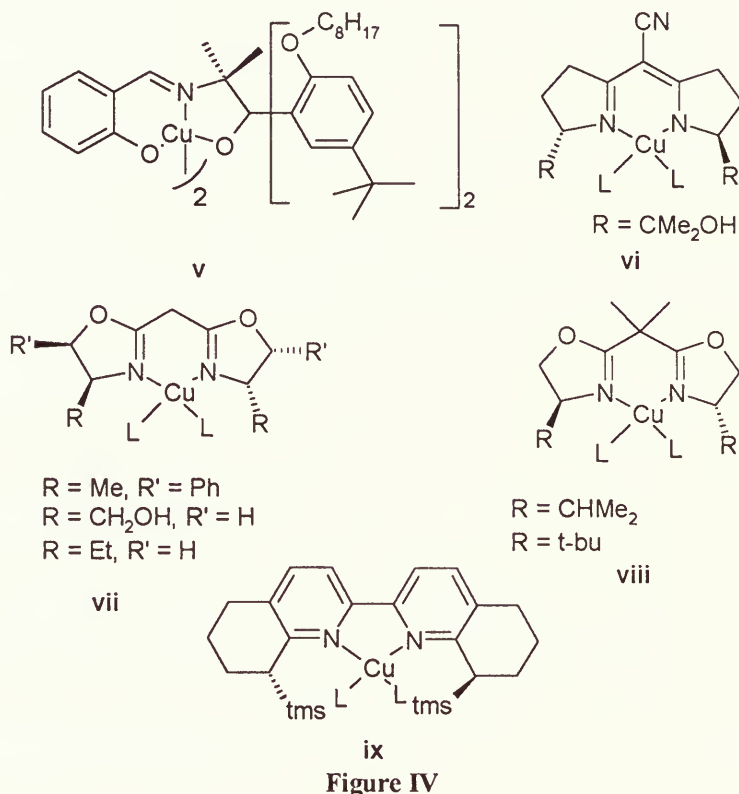
²³ Wolf, I. R., Hamaker, C. G., Djukic, J. P., Kododek, T., Woo, L. K., *J. Am. Chem. Soc.*, **1995**, *117*, 1994.

²⁴ Tatsuno, Y., Konishi, A., Nakamura, A., Otsuka, S., *J. Chem. Soc., Chem. Commun.*, **1974**, 588; Nakamura, A., Konishi, A., Tatsuno, Y., Otsuka, S., *J. Am. Chem. Soc.*, **1978**, *100*, 3443; Nakamura, A., Konishi, A., Tsujitani, R., Kudo, M., Otsuka, S., *ibid.* **1978**, *100*, 3449.

²⁵ Doyle, M. P., Davidson, J. G., *J. Org. Chem.*, **1980**, *45*, 1538; Doyle, M. P., Dorow, R. L., Buhro, W. E., Tambllyn, J. H., Trudell, M. L., *Organometallics*, **1984**, *3*, 44.

osmium²⁶ or ruthenium²⁷) can be used to generate α -carbonyl carbenoids from α -diazoketones, the most popular catalysts are based on either copper or rhodium.

Traditionally, insoluble catalysts such as copper powder, copper bronze, cupric oxide *etc.* have been used to effect carbenoid generation.²⁸ With the advent of homogeneous copper catalysts, however, the use of these catalysts has decreased significantly.



Most recently, a number of chiral copper (II) complexes (some shown in Figure IV) have been investigated extensively for their use in asymmetric cyclopropanations.²⁹

Systematic screening of common transition metal complexes has revealed rhodium (II) species to be the mildest and most efficient catalysts for cyclopropanation.³⁰ Among them,

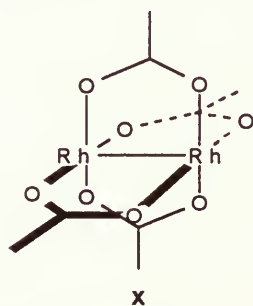


Figure V

²⁶ Demonceau, A., Lemoine, C. A., Noels, A. F., *Tetrahedron Lett.*, **1996**, 37, 1025.

²⁷ Nishiyama, H., Itoh, Y., Sugawara, Y., Matsumoto, H., Aoki, K., Itoh, K., *Bull. Chem. Soc. Jpn.*, **1995**, 68, 1247; Demonceau, A., Simal, F., Noel, A. F., Vinas, L., Nunez, R., Teixidor, F., *Tetrahedron Lett.*, **1997**, 38, 4079.

²⁸ Maas, G., *Top. Curr. Chem.*, **1987**, 137, 75.

²⁹ Ichihyanagi, T., Shimizu, M., Fujisawa, T., *Tetrahedron*, **1997**, 53, 9599.

³⁰ Anciaz, A.J., Hubert, A.J., Noels, A.F. *et. al*, *J. Org. Chem.*, **1980**, 45, 695.

rhodium (II) carboxylates (see Figure V) are the catalysts of choice. Rhodium carboxylates are binuclear compounds with four bridging carboxylate ligands, possessing one vacant axial coordination site per metal atom. Studies have shown rhodium complexes to effectively catalyze cyclopropanation of a wide variety of double bonds (substituted, terminal, *etc.*) with generally good yields.³¹ Furthermore, rhodium (II) carboxylates are thermally and air stable, resistant to carboxylate exchange, not susceptible to redox reactions with diazo compounds, and they generally do not coordinate with the olefin (unlike palladium and some copper catalysts)³².

4. Mechanistic Considerations

The catalytic cycle whereby a metal complex (L_nM) catalyzes the decomposition of a diazo compound (CR_2N_2) is illustrated in Figure VI.³² The sequence begins with electrophilic attack of the catalyst at the diazo carbon with subsequent loss of nitrogen and the formation of a metal stabilized carbene ($L_nM=CR_2$). Transfer of the carbene entity to an electron-rich species ($S:$) completes the cycle.

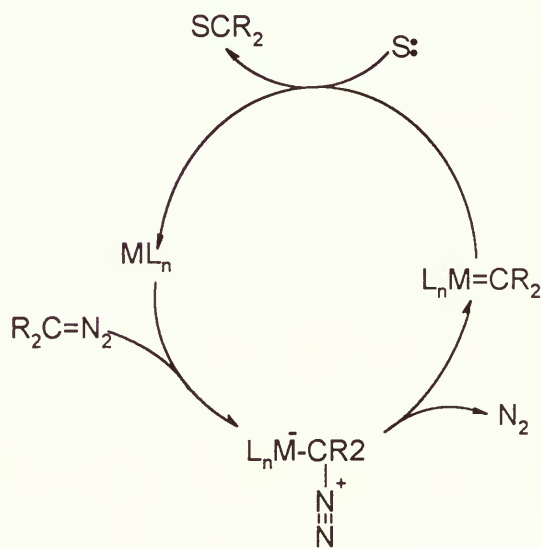


Figure VI

³¹ Doyle, M. P., *Synthesis*, **1981**, 787.

³² Doyle, M. P., *Chem. Rev.*, **1986**, 86, 919.

Metal stabilized carbenes are widely assumed to participate in the transformations catalyzed by complexes of Cu, Rh, Pd, Fe, Co, Mo, Os and Ru. Unfortunately, these carbenoid intermediates have never been isolated, and all evidence concerning their involvement is indirect. For instance, carbene dimer formation is characteristic of carbenoid intermediates, and although such dimers have been isolated from many reactions, their existence cannot be taken as conclusive evidence of metal-carbene participation. A number of transition-metal complexes mentioned above have been shown to provide a degree of enantioselectivity to some cyclopropane forming reaction. Chirality transfer demands the catalyst be intimately involved in the transformation and would seem to imply that free (achiral) carbenes are unlikely.

Perhaps the most convincing evidence as to the nature of the intermediates in these catalytic diazo compound decompositions comes from a mechanistic study conducted by Doyle.⁸ A series of olefins were transformed stoichiometrically using $(\text{CO})_5\text{W}=\text{CHPh}$ ³³ and catalytically using $\text{Rh}_2(\text{OAc})_4/\text{PhCHN}_2$ to their corresponding phenylcyclopropane. The tungsten-stabilized phenyl carbene which is stable and has been characterized, is known to generate phenyl cyclopropanes of predominantly *syn* geometry. The ratio of *syn* to *anti* cyclopropane product obtained from each olefin provides a measurement of the stereoselectivity of cyclopropanation by the two methods. For the same set of substituted alkenes, a linear log-log relationship between the *syn/anti* stereoselectivity for the $(\text{CO})_5\text{W}=\text{CHPh}$ and $\text{Rh}_2(\text{OAc})_4/\text{PhCHN}_2$ reactions was found. Furthermore, a linear correlation was also found between the relative reactivities of $(\text{CO})_5\text{W}=\text{CHPh}$ and $\text{Rh}_2(\text{OAc})_4/\text{N}_2\text{CHPh}$. These results lead to the conclusion that the intermediates in the

³³ Casey, C.P., Polichnowski, S.W., Shusterman, J., Jones, C.R., *J. Am. Chem. Soc.*, 1979, 101, 7282.

Rh(II)-catalyzed reaction are very similar to stable electrophilic carbenes. Additionally, similar selectivity-reactivity correlation between cyclopropanation reactions catalyzed by $\text{Rh}_2(\text{OAc})_4$ and other metal complexes provide these catalysts with a mechanistic link to metal carbene intermediates.²⁵

Two mechanisms that explain the cyclopropanation of an alkene by a carbenoid have appeared in the chemical literature and are presented in Figure VII. The first mechanism involves nucleophilic attack of the

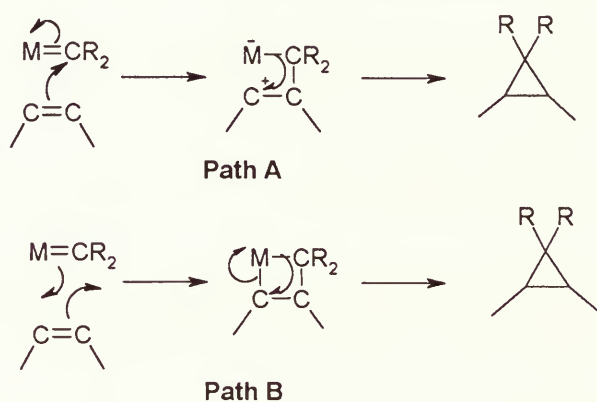
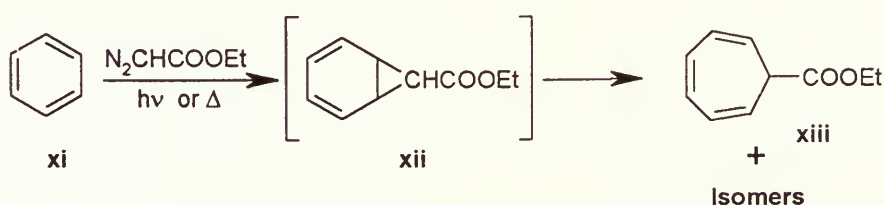


Figure VII

alkene onto the carbenoid, generating a polar intermediate, followed by 1,3-bond formation to give the cyclopropane as shown in *Path A* (Figure VII). As cyclopropanation usually proceeds stereospecifically, with respect to the alkene, this mechanism would require the polar intermediate to collapse forming the product faster than single bond rotation. The other mechanism involves the formation of a four membered metallocycle intermediate by either a concerted [2+2] cycloaddition or a stepwise mechanism (not shown). Reductive elimination of the metallocycle intermediate gives the desired cyclopropane, as shown in *Path B* (Figure VII).

5.0 Carbene and Carbenoid Insertions into Aromatic Systems



Scheme VII

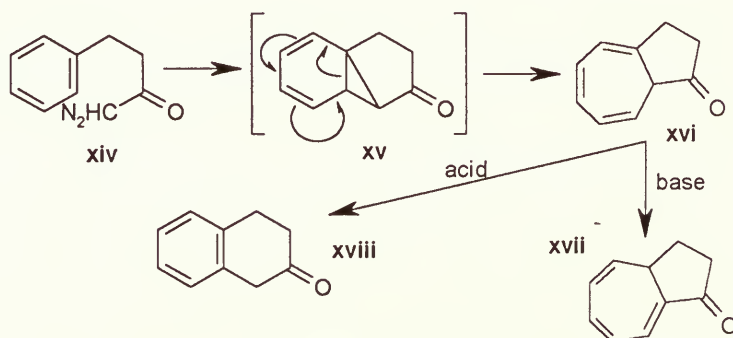
The first carbene insertion into an aromatic system was reported by Buchner in 1896³⁴ and has become known as the Buchner method for ring enlargement (Scheme VII). The reaction involves the treatment of benzene (xi) with ethyl diazoacetate under photolytic or thermal conditions to give the corresponding esters of norcaradiene. The reaction has subsequently been modified to include the use of transition metal catalysts to facilitate the initial cyclopropanation. Heating the intermediate (xii) allows for an electrocyclic ring opening to the cycloheptatriene xiii, which can further isomerize to more highly conjugated isomers.

Intramolecular versions of the Buchner reaction have also appeared in the literature. In these systems, benzene is tethered by a methylene chain to a terminal α -diazoketone. Treatment of this α -diazoketone with a copper catalyst allowed Costantino *et al.*³⁵ to generate the fused

cycloheptatriene xvii in roughly 50% yield (Scheme VIII).

McKervey³⁶ has subsequently repeated the reaction using both

rhodium (II) acetate and



Scheme VIII

rhodium (II) trifluoroacetate as the catalysts and obtained a 95% yield of the initial cycloheptatriene product xvi (Scheme VIII). Treatment of xvi with triethylamine caused

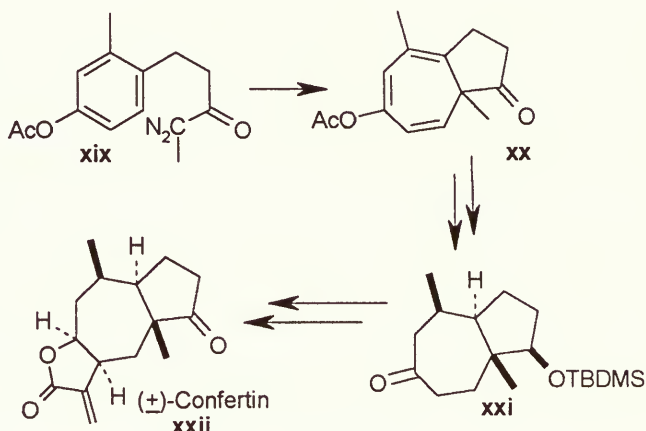
³⁴ Buchner, E., *Ber.*, **1896**, 29, 106.

³⁵ Costantino, A., Linstrumella, G., Julis, S., *Bull. Soc. Chim. Fr.*, **1970**, 907.

³⁶ Kennedy, M., McKervey, M.A., Maguire, A.R., Tuladhar, S.M., Twohig, M.F., *J. Chem. Soc., Perkin Trans. I*, **1990**, 1047.

isomerization to the product that was isolated earlier (**xvii**). Exposure of **xvi** to acid allowed for rearrangement to the β -tetralone (**xviii**).

The synthetic utility of the intramolecular Buchner reaction has been demonstrated by McKervery's group in their synthesis of (\pm)-confertin (**xxii**).³⁷ The key step involves the synthesis of the fused seven-membered ring using the intramolecular Buchner reaction (Scheme IX). After the basic structure is in place, the desired (\pm)-confertin (**xxii**) was obtained in a few steps.



Scheme IX

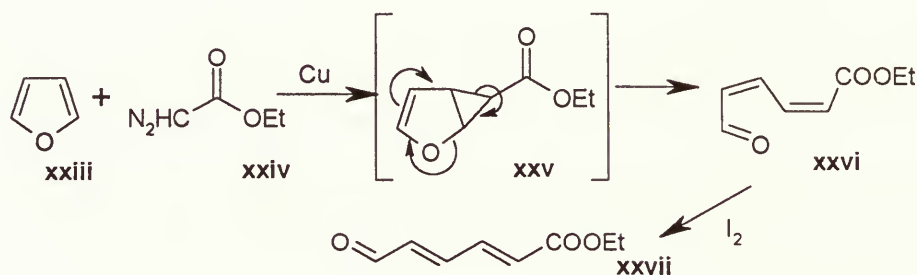
Since the Buchner reaction, carbenes and carbenoids have been inserted into a wide variety of substituted benzene systems including phenolic³⁸ and biphenyl³⁹ systems. For the purposes of this thesis, we will now focus on the inter- and intramolecular insertions of carbenes and carbenoids into 5-membered heteroaromatic systems such as furan, thiophene and pyrrole.

³⁷ Kennedy, M., McKervery, M.A., *J. Chem. Soc., Chem. Commun.*, **1988**, 1028; Kennedy, M., McKervery, M.A., *J. Chem. Soc., Perkin Trans. I*, **1991**, 2565.

³⁸ Iwata, C., Yamada, M., Shinoo, Y., Kobayashi, K., Okada, M., *Chem. Pharm. Bull.*, **1980**, 28, 1932; Iwata, C., Morie, T., *ibid*, **1985**, 33, 944.

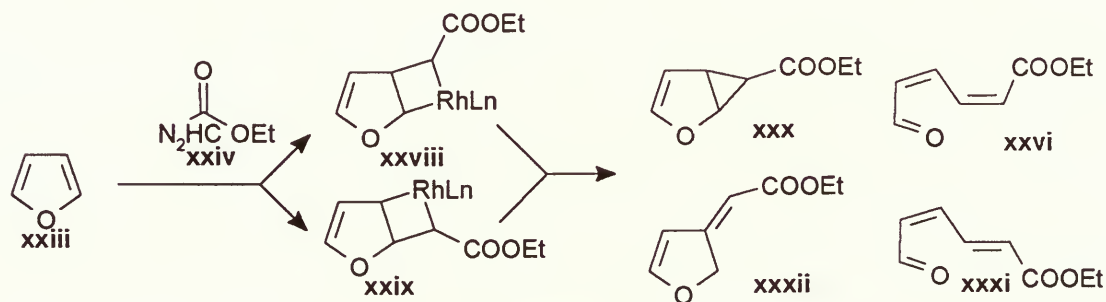
³⁹ Chattergee, J. N., Sinba, A. K., Bhakta, C., *Indian J. Chem., Sect. B*, **1979**, 17, 329; Duddeck, H., Kennedy, M., McKervery, M. A., Twohig, M. F., *J. Chem. Soc., Chem. Commun.*, **1988**, 1586.

5.1 Carbene and Carbenoid Insertions into Furan.



In an early study, Novac and Sorm⁴⁰ observed that cyclopropanation of furan (xxiii) by ethyl diazoacetate (xxiv) under copper catalyzed conditions resulted in an unstable intermediate (xxv) that upon ring opening yielded the *Z,E*-diene xxvi (see Scheme X). Unraveling of the intermediate cyclopropane is thought to proceed *via* a [4+2]-cycloreversion to yield the conjugated ester-aldehyde xxvi. The *Z,E*-diene can be isomerized to the *E,E*-diene xxvii by the addition of a catalytic amount of iodine, making this reaction even more synthetically useful.⁴¹ As will be seen later, this retro-cycloaddition is common in cyclopropanated furan systems.

In a more recent study of this system by Wenkert⁴², intermolecular carbenoid insertion of ethyl diazoacetate into furan in the presence of rhodium (II) acetate resulted in

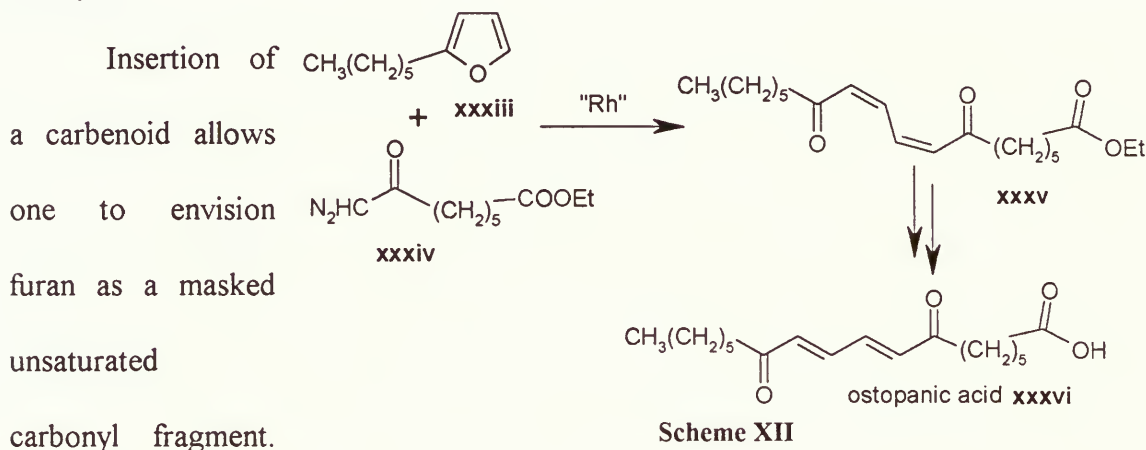


⁴⁰ Novac, J., Sorm, F. L., *Collection of Czechoslovak Chem. Commun.*, **1958**, 23, 1126.

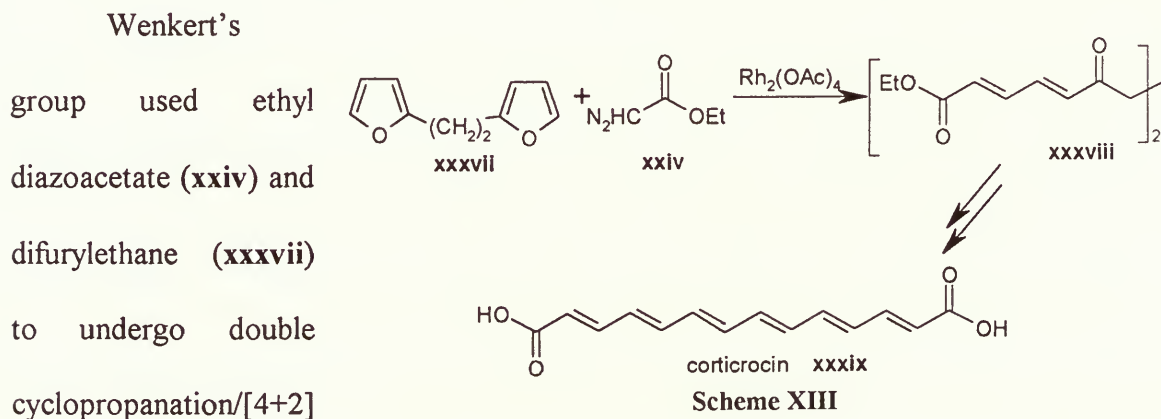
⁴¹ Lurien, T., Guenther, V., *Ger. Offen.* 2,652,356, 18 May, 1978; *Chem. Abst.*, **1978**, 89, 110052.

⁴² Wenkert, E., Guo, M., Lavilla, R., Peter, B., Ramachandran, K., Shue, J.-H., *J. Org. Chem.*, **1990**, 55, 6203.

4 products, **xxx**, **xxvi**, **xxxi** and **xxxii**, in a 17 : 15 : 10 : 1 ratio, respectively (Scheme XI). It was proposed that the observed products were derived from the decomposition of the metallocycle intermediates (**xxviii** and **xxix**). Wenkert also showed that the addition of iodine to the reaction mixture allows for a one pot reaction to the *E,E*-isomer **xxvii** in 68% yield.



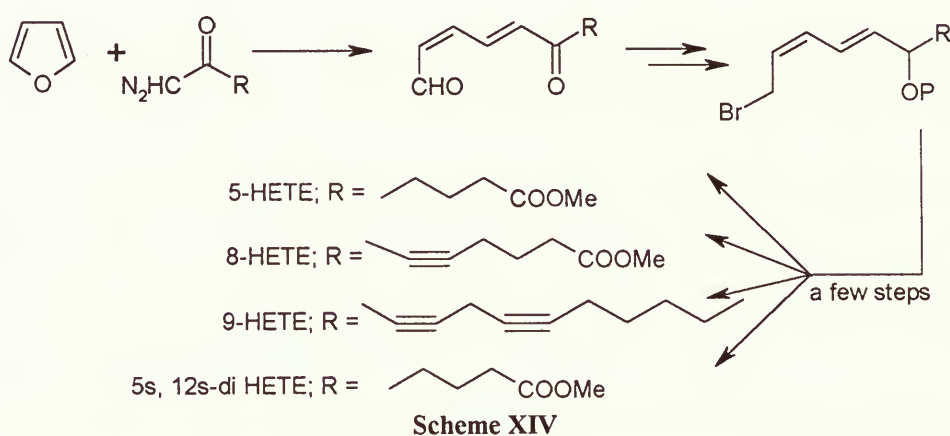
This approach has been applied to the total synthesis of ostopanic acid (**xxxvi**), a plant cytotoxin (see Scheme XII)⁴³ in 3 steps. Treatment of the furan **xxxiii** with diazoketone **xxxiv** in the presence of rhodium catalyst, followed by iodine treatment gave the ethyl ostopanate (**xxxv**). Deprotection of the ester gave the desired ostopanic acid (**xxxvi**).



⁴³ Sheu, J.H., Yen, C.F., Huang, H.C., Hong, Y-L.V., *J. Org. Chem.*, 1989, 54, 5126 .

-cycloreversion unraveling to form the tetraene (**xxxviii**) which can be converted to corticrocin (**xxxix**) by reduction of the two ketone groups followed by dehydration (Scheme XIII).⁴²

Workers at Montreal's Merck Frosst⁴⁴ have also made use of this insertion into furan in the synthesis of a series of hydroxy-6,8,11,14-eicosatetraenoic (HETEs), mono-hydroxylated metabolites of arachidonic acid (Scheme XIV).



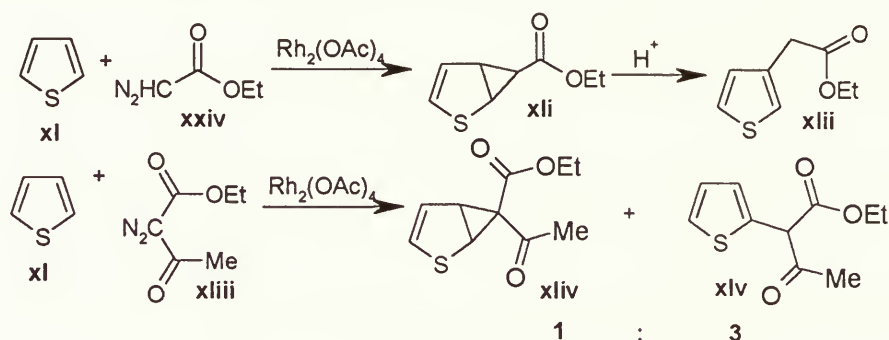
5.2 Carbene and Carbenoid Insertions into Thiophenes

Reactions between thiophenes and diazocarbonyls have been known for several years.⁴⁵ Unlike furanyl systems, however, thiophene (**xl**) reacts with ethyl diazoacetate to give the stable cyclopropanated product (**xli**) which does not undergo [4+2] cycloreversion (see Scheme XV)⁴⁶ and was stable to distillation and chromatography. When treated with ethanolic HCl, **xli** rearomatizes to give ethyl 3-thiophene acetate (**xlii**) in good yield. The chemical outcome of the reaction, however, is dependent upon the

⁴⁴ Rokach, J., Adams, J., Perry, R., *Tetrahedron Lett.*, **1983**, 24, 5185; Adams, J., Rokach, J., *Tetrahedron Lett.*, **1984**, 25, 35; Adams, J., Leblanc, Y., Rokach, J., *Tetrahedron Lett.*, **1984**, 24, 1227.

⁴⁵ Schenck, G.O., Steinmetz, R., *Ann.*, **1963**, 668, 19.

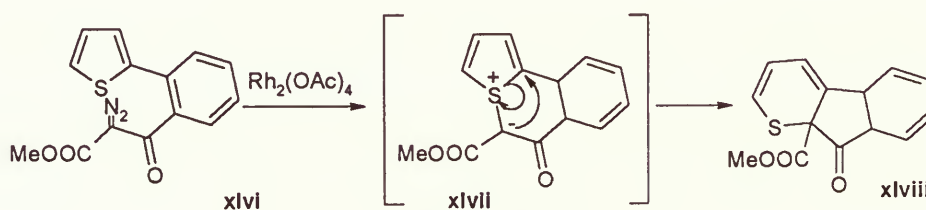
⁴⁶ Gillespie, R.J., Porter, A.E., *J. Chem. Soc., Perkin Trans. I*, **1979**, 2624.



Scheme XV

diazocarbonyl employed. When ethyl diazoacetoacetate (**xlili**) was used, a mixture of the cyclopropanated (**xliv**) and rearomatized product (**xl**v) was obtained in a 1 : 3 ratio, respectively, in 80% total yield.

In addition to cyclopropanation, thiophenes can react with carbenoids to form sulfur ylids. Skramstad has used these intermediates in order to carry out ring contraction/enlargement reactions (Scheme XVI).⁴⁷ Treatment of diazoketone **xlvi** with rhodium acetate allows for intramolecular attack of the sulfur by the carbenoid to result in the formation of ylid **xlvi**i which subsequently undergoes Stevens Rearrangement⁴⁸ to the neutral tricyclic product **xlvi**iii.



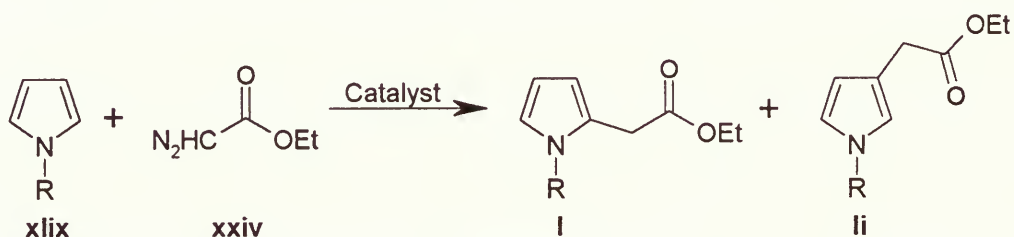
Scheme XVI

⁴⁷ Stoflor, H., Skramstad, J., Nordenson, S., *J. Chem. Soc., Chem. Commun.*, **1984**, 208.

⁴⁸ Stevens, T. S., Creighton, E.M., Gordon, A.B., MacNicol, M., *J. Chem. Soc.*, **1928**, 3193; Stevens, T. S., *J. Chem. Soc.*, **1930**, 2107; Stevens, T. S., Thomson, T., *J. Chem. Soc.*, **1932**, 1932.

5.3 Carbene and Carbenoid Insertions into Pyrrole

Pyrrole and its derivatives exhibit a range of reactivity toward carbenoids derived from diazocarbonyls. These reactions usually result in the isolation of the alkylated pyrrole products rather than cyclopropanated materials. For example, copper-catalyzed reaction of ethyl diazoacetate with pyrrole has long been recognized as one of the most reliable routes to pyrrole-2-acetic acid.⁴⁹ The reaction is generally carried out by addition of ethyl diazoacetate (**xxiv**) to a heated mixture of pyrrole (**xlx**) and copper catalyst at such a rate that a low concentration of the diazoacetate is maintained throughout the reaction. Substitution at the 2-position of unsubstituted pyrrole (**xlx** R=H) is most prevalent, but a



Scheme XVII

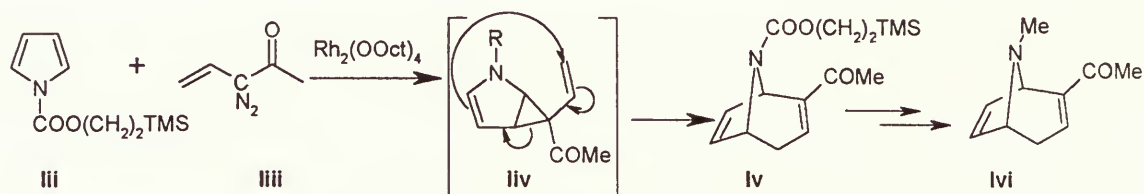
preference for substitution at the 3-position can be promoted by attaching a bulky substituent (R) on the nitrogen. For example, treatment of pyrrole (**xlx** R=H) with ethyl diazoacetate gives >90% 2-substituted product (**I** R=H), while reaction with *N*-*tert*-butyl pyrrole gives >95% 3-substituted product (**II** R=*t*-butyl) (Scheme XVII).⁵⁰ The reversal in selectivity of the reaction, when a bulky substituent is introduced, was explained by a C-H insertion which is sensitive to the steric factor of the pyrrole.

Pyrroles possessing an electron withdrawing carboxylate group on the nitrogen have been shown to undergo a tandem cyclopropanation-Cope rearrangement, providing

⁴⁹ Nenitzescu, C.D., Solomonica, E., *Ber.*, **1931**, *64*, 1924.

⁵⁰ Maryanoff, B.E., *J. Heterocycl. Chem.*, **1977**, *14*, 177; Maryanoff, B. E., *J. Org. Chem.*, **1979**, *44*, 4410; Maryanoff, B. E., *ibid*, **1982**, *47*, 3000.

direct access to the tropane skeleton (**lv**).⁵¹ The reaction proceeds *via* an intermolecular carbenoid insertion into the π -bond of the pyrrole to form a cyclopropanated intermediate (**liv**). This intermediate then undergoes a sigmatropic rearrangement (shown in Scheme XVIII) to form the tropane product **lv**; overall, a net [4+3] reaction.



Scheme XVIII

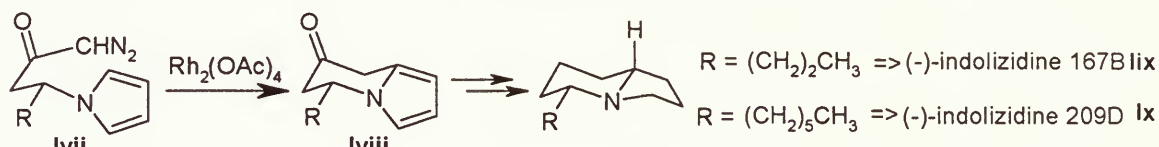
Davies⁵¹ has demonstrated the usefulness of this reaction in a short synthesis of (\pm)-furuginine (**lvi**). The key step of the synthesis used a tandem cyclopropanation-Cope rearrangement to install the base tropane structure (**lv**). (\pm)-Furuginine (**lvi**) was then prepared by reduction of the *N*-formate group to a *N*-methyl group. Note that the use of rhodium octanoate allowed for the reaction to be carried out in hexanes and a higher overall yield was obtained.

The intramolecular version of carbenoid insertion into the pyrrole ring system was first used by Jefford and Johncock⁵² for the synthesis of another important family of alkaloids, the indolizidines. The example given below illustrates the synthesis of optically active indolizidines by using *N*-alkyl pyrroles derived from chiral amino acids.⁵³ Decomposition of the diazoketone **lvii** results in the formation of the desired 2-substituted

⁵¹ Davies, H. M. L., Saikali, E., Young, W. B., *J. Org. Chem.*, **1991**, *56*, 5696.

⁵² Jefford, C.W., Johncock, W. *Helv. Chim. Acta*, **1983**, *66*, 2666; Jefford, C.W., Zaslona, A., *Tetrahedron Lett.*, **1985**, *26*, 6035; Jefford, C.W.; Kubota, T., Zaslona, A., *Helv. Chim. Acta* **1986**, *69*, 2048.

⁵³ Jefford, C. W., Tang, Q., Zoslona, A., *Helv. Chim. Acta*, **1989**, *72*, 1749; Jefford, C. W., Tang, Q., Zoslona, A., *J. Am. Chem. Soc.*, **1991**, *113*, 3513; Jefford, C. W., Wang, J. B., *Tetrahedron Lett.*, **1993**, *34*, 3119.

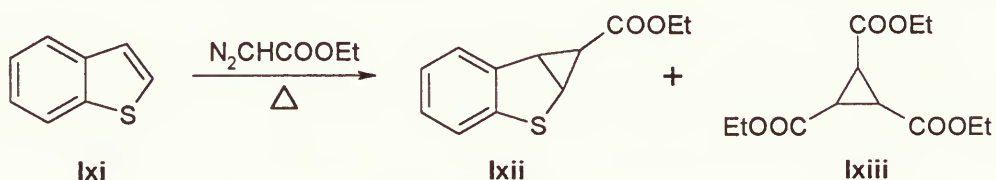


Scheme XIX

product **Iviii** which is thought to be the result of an aromatic substitution. Compound **Iviii** can then be converted to (-)-indolizidine 167B ($R = n\text{-propyl}$, **Iix**) and (-)-indolizidine 209D ($R = n\text{-hexyl}$, **Ix**) by reduction of the carbonyl and pyrrole ring.

5.4 Carbene and Carbenoid Insertions into Indoles, Benzofurans and Benzothiophenes

Reaction of ethyl diazoacetate with benzothiophenes, benzofurans and indoles have been studied by Wenkert.⁵⁴ When the reaction of ethyl diazoacetate and benzothiophene (**Ixi**) was carried out in the presence of copper catalyst, the only isolable



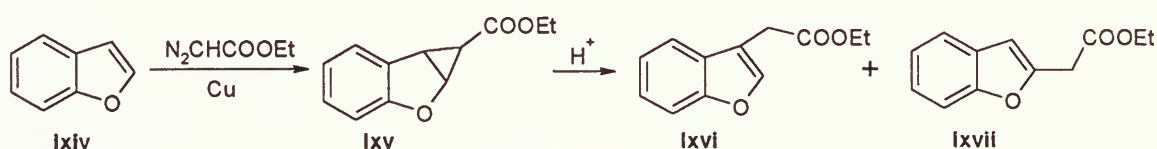
Scheme XX

product was 1,2,3-cyclopropanetricarboxylate (**Ixi**) in 30% yield. Compound **Ixi** was generated from the cyclopropanation of the initially formed alkene dimer. However, thermal decomposition of ethyl diazoacetate in the presence of benzothiophene allowed for the isolation of not only **Ixi**, but also products that resulted from carbene insertion into benzothiophene (in 8% yield). These minor insertion products were the cyclopropanated product (**Ixi**) together with a small amount of the 2- and 3-

⁵⁴ Wenkert, E., Alonso, M.E., Gottlieb, H.E., Sanchez, E.L., Pellicciari, R., Cogolli, P., *J. Org. Chem.*, 1977, 42, 3945.

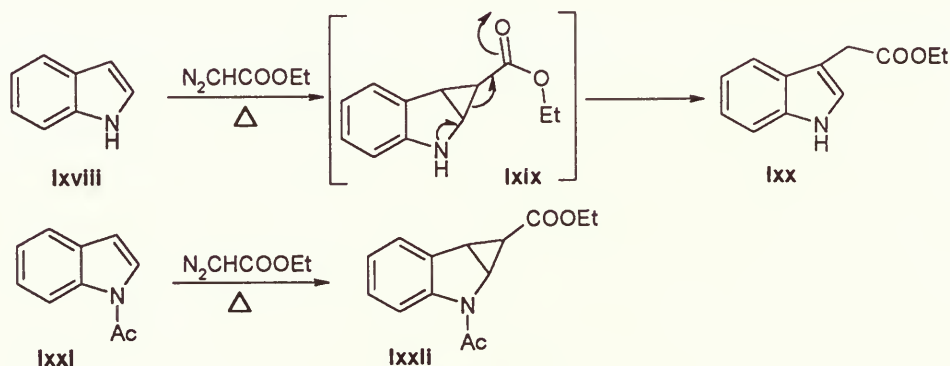
benzothiophene acetate that probably arose from the cyclopropane ring opening and rearomatization of the benzothiophene (Scheme XX).

Unlike the benzothiophene system, addition of ethyl diazoacetate to benzofuran (**lxiv**) in the presence of a copper catalyst allows for the isolation of the cyclopropanated product **lxv** in 62% yield. Subsequent acid catalyzed re-arrangement yields both 3-substituted (**lxvi**) and 2-substituted (**lxvii**) ethyl benzofuran acetate in a 4 : 1 ratio, in a combined 97% yield (Scheme XXI).



Scheme XXI

Substitution at the nitrogen of indoles allows for some control of the reactivity of the cyclopropanes generated by intermolecular carbenoid insertion of ethyl diazoacetate. In the presence of a copper catalyst, ethyl diazoacetate reacts with unsubstituted indole to give ethyl 3-indole acetate in 74% yield.⁵⁵ The intermediate cyclopropane (**lxix**) undergoes spontaneous ring opening facilitated by the electron rich nitrogen. However, with an

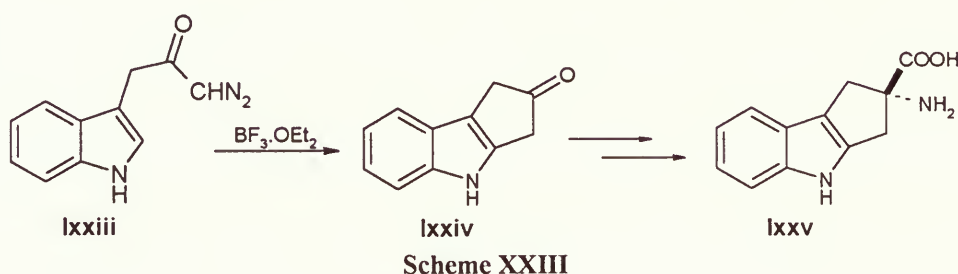


Scheme XXII

⁵⁵ Nametkin, S. S., Mel'nikov, N. N., Bokerev, K. S., *Zh. Prikl. Khim.*, 1956, 29, 459.

electron withdrawing group attached to the nitrogen (e.g. *N*-acetyl indole), intermolecular carbenoid insertion into **lxxi** allows for the isolation of the cyclopropanated product **lxxii**.

The intramolecular version of a carbenoid insertion into an indole system was used by Pellicciari *et al.*⁵⁶ in their preparation of a conformationally restricted analogue of tryptophan (**lxxv**). The indole-based diazoketone **lxxiii** was treated with boron trifluoride etherate to allow for the conversion to **lxxiv**. The desired amino acid **lxxv** can then be synthesized from **lxxiv** by standard procedures in two chemical steps.

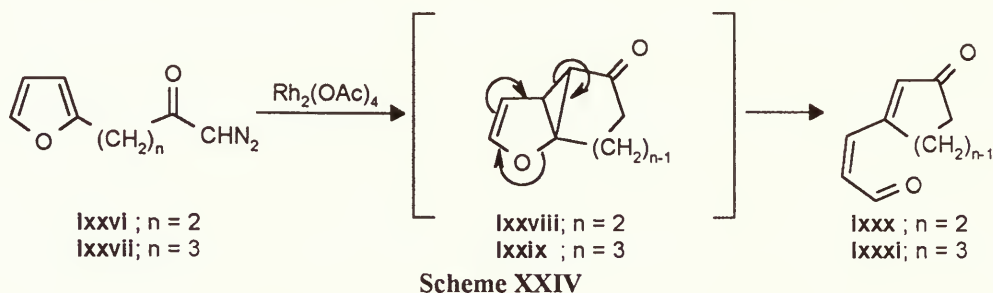


6. Previous Intramolecular Carbenoid Insertion Studies

Much of the work in this thesis augments and carries on from the studies conducted by Albert Padwa at Emory University and subsequent studies by Tony Durst at the University of Ottawa. In his seminal paper published in 1989,⁵⁷ Padwa investigated the chemistry carried out by a series of α -diazoketones tethered to furanyl, thienyl and benzofuranyl systems.

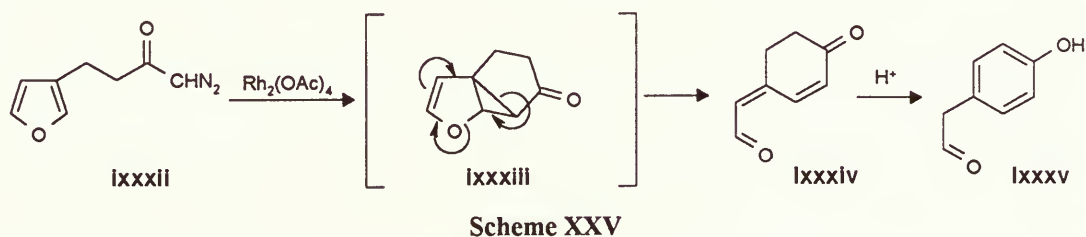
⁵⁶ Franceschetti, L., Garzon-Aburbeh, A., Mahmoud, R. M., Natalini, B., Pellicciari, R., *Tetrahedron Lett.*, **1993**, *34*, 3185.

⁵⁷ Padwa, A., Wisnieff, T. J., Walsh, E. J., *J. Org. Chem.*, **1989**, *54*, 299.



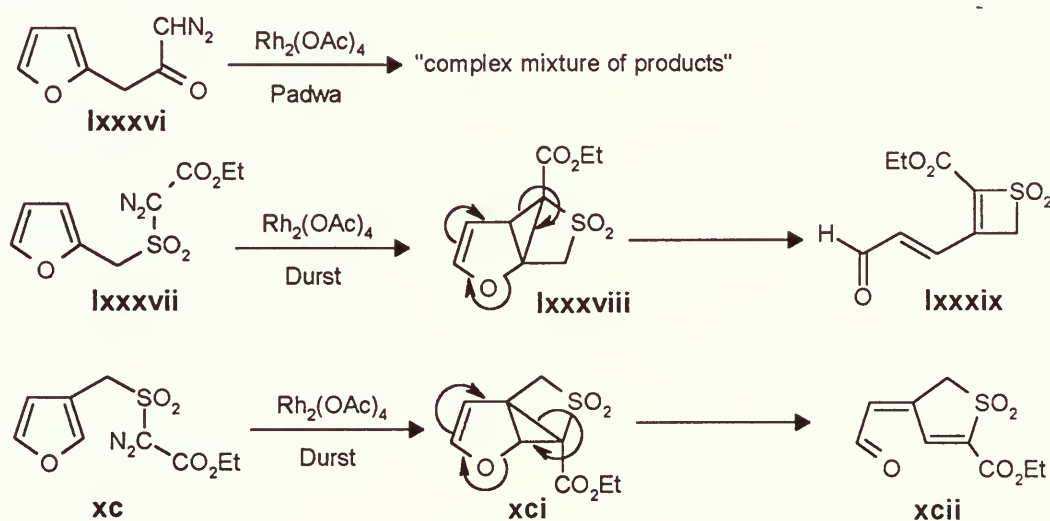
Padwa showed that when 1-diazo-4-(2-furanyl)-2-butanone (**lxxvi**) was exposed to rhodium (II) acetate, the *cis*-keto-aldehyde **lxxx** was isolated in 86% yield. This is in contrast to the work by Nwaji and Onyiriuka who cyclized the same substrate using copper (II) sulfate, as the catalyst in refluxing cyclohexane. In this case, the more thermodynamically stable *trans*-cyclopentenone was isolated in 60% yield.⁵⁸ In both cases the reaction proceeds *via* addition of the keto-carbene to the furanyl π -bond followed by a retro-[4+2] ring opening of the intermediate cyclopropane to give the keto-aldehyde. Padwa's higher yield and ability to isolate the initially formed cisoid product demonstrates the superiority of the rhodium catalyst (Scheme XXIV).

Similar chemistry was exhibited by the isomeric 3-substituted furan, 1-diazo-4-(3-furanyl)-2-butanone (**lxxxii**, see Scheme XXV). Formation of the phenolic product isolated (**lxxxv**) could be rationalized as arising from intramolecular cyclopropanation to form the intermediate (**lxxxiii**) followed by [4+2] cycloreversion to give the keto-aldehyde (**lxxxiv**), which then undergoes acid catalyzed rearomatization to form **lxxxv**.



⁵⁸ Nwaji, M. N., Onyiriuka, O. O., *Tetrahedron Lett.*, 1974, 2255.

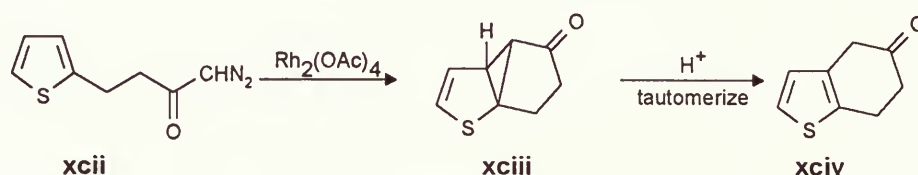
The addition of another methylene to the aliphatic tether linking the α -diazoketone to the furan (for example, **lxxxvii**) results in the same type of chemistry. However, when a substrate containing a single methylene tether was treated with rhodium acetate, the results were different. In fact, Padwa's attempt to cyclize 1-diazo-3-(2-furanyl)-2-propanone (**lxxxvi**) resulted in the formation of a "complex mixture of products."⁵⁷ This is in contrast, however, to Durst's work.⁵⁹ As part of his studies dealing with the rhodium acetate and rhodium trifluoroacetate catalyzed decomposition of α -diazo- β -arylmethanesulfonyl esters, Durst was able to cyclize **lxxxvii** (as shown in Scheme XXVI) to the sulfonylcyclobutenone **lxxxix**. Note that **lxxxvii** differs from **lxxxvi** in that it contains the additional ester functionality and in that the C=O has been replaced with SO₂. This reaction presumably proceeds *via* the intermediate cyclopropane **lxxxviii** which undergoes a [4+2]-cycloreversion. The longer C-S bonds in thiele-S,S-dioxide **lxxxix** allow for considerably less strain than would be expected in the carbocyclic analogue derived from **lxxxvi**. Durst's work has also shown that the isomeric system **xc** carries out



⁵⁹ Babu, S. D., Hrytsak, M. D., Durst, T., *Can. J. Chem.*, **1989**, *67*, 1071.

the standard cyclopropanation/cycloreversion chemistry seen in the other furanyl systems to give **xcii**.

The behavior of the analogous thienyl systems was shown to be quite different to that exhibited by the furans. For example, Padwa's treatment of 1-diazo-4-(2-thienyl)-2-butanone (**xcii**) with rhodium acetate resulted in 4,5,6,7-tetrahydrobenzo[*b*]thiophen-5-



Scheme XXVII

one (**xciv**). The reaction proceeds through a cyclopropane **xciii** which undergoes an acid catalyzed ring opening to form an enol, and then tautomerizes to form the product **xciv**. It is not clear whether or not there is heteroatom participation in this cyclopropane/unraveling (c.f. **Ixix**) although such participation is mechanistically feasible.

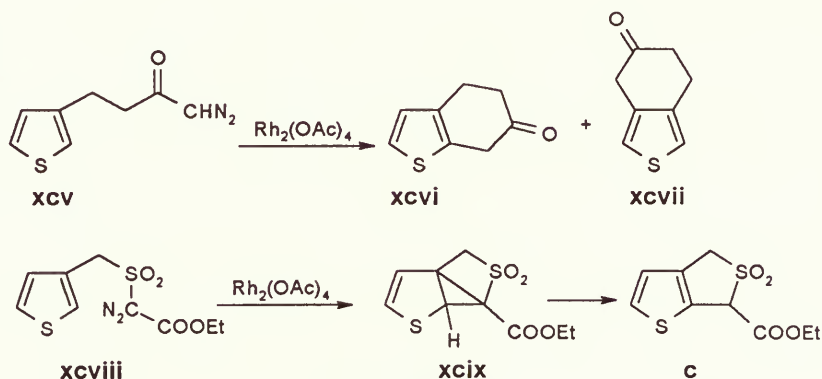
Under similar conditions, the isomeric 1-diazo-4-(3-thienyl)-2-butanone (**xcv**) undergoes cyclopropanation, to give a mixture of 2-isomeric cyclopropane intermediates which then undergoes

acid catalyzed ring opening followed by tautomerization to give

4,5-

dihydrobenzo[*b*]thioph

en-6(7*H*)-one (**xcvi**) as



Scheme XXVIII

the major product and 6,7-dihydrobenzo[*c*]-thiophen-5(4*H*)-one (**xcvii**) as the minor

product. Durst showed that similar chemistry takes place when **xcviii** is exposed to rhodium acetate to give **c**.

It is worth reiterating that the cyclopropane intermediates in the furanyl systems (see **lxxvi** and **lxxxii**) undergo [4+2]-cycloreversion while the acid-catalyzed ring opening route prevails in the thienyl series (see **xcii** and **xcv**). The different chemistry seen may be attributed, in part to the greater bond strength of the aldehyde C=O bond in comparison to the thioaldehyde C=S bond which would be formed if [4+2]-cycloreversion took place in the thienyl series.

7. *Aims and Objectives*

This thesis explores the scope and mechanistic details of the above mentioned intramolecular carbenoid insertions to understand the determining factors by which a particular cyclopropane system unravels, and whether this ring opening can be directed or controlled for synthetic utility. Work has focused on the rhodium (II) acetate decomposition chemistry of systems wherein a terminal α -diazoketone is tethered to a

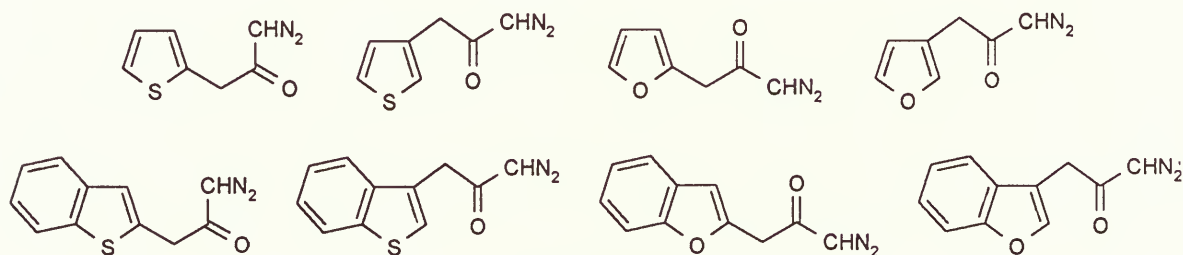


Figure VIII

heteroaromatic moiety by a methylene tether. The α -diazoketones studied (derived from 2- and 3-substituted furanyl, thienyl, benzofuranyl and benzothieryl acetic acids) are shown in Figure VIII. As will be seen, the strain imparted to cyclopropane intermediates

by a single methylene tether has allowed for some rather atypical chemistry to a number of novel ring systems. The experimental work will be correlated to calculations carried out at an PM3 level in an effort to help rationalize the disparate chemistry seen.

RESULTS & DISCUSSION

(i) Rhodium Acetate Catalyzed Decomposition of 1-Diazo-3-(2-Thienyl)-2-Propanone (6)

Antiviral agents based on the 5,6-dihydro-4*H*-cyclopenta[*b*]thiophene-6-one (1) and 5,6-dihydro-4*H*-cyclopenta[*b*]thiophene-4-one (2) ring systems have previously been described in the literature.⁶⁰ As part

of a research effort to prepare isomeric systems, Dr. Alex Alanine of Hoffmann-La Roche (Basel) has

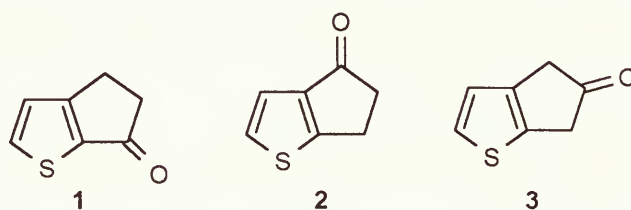
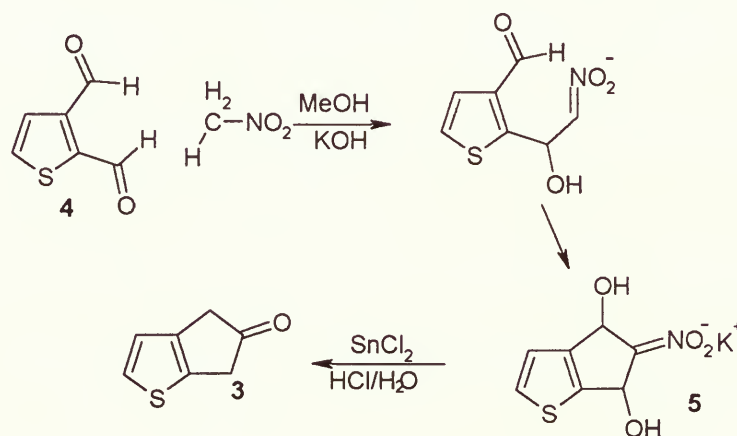


Figure 1

expressed that a straightforward

synthesis to 5,6-dihydro-4*H*-cyclopenta[*b*]thiophene-5-one (3) would be highly desirable since the existing preparative protocol described by Skramstad⁶¹ is rather costly. Skramstad's route involves the use of relatively expensive 2,3-thiophenedicarboxaldehyde



Scheme 1

⁶⁰ Dallemange, P., Alsaidi, A., Boulouard, M., Roul, S., Rabba, M., *Heterocycles*, **1993**, 36, 287; Dallemange, P., Boulouard, M., Roul, S., Rabba, M., *J. Heterocycl. Chem.*, **1993**, 30, 799.

⁶¹ Skramstad, J., *Acta Chem. Scand.*, **1971**, 25, 1287.

as the starting material (\$37/g Aldrich). Treatment of a solution of the dialdehyde in methanolic potassium hydroxide with one equivalent of nitromethane resulted in two consecutive Claisen-Schmidt type reactions to yield potassium-5,6-dihydro-4,6-dihydroxy-4*H*-cyclopenta[*b*]thiophene-5-nitronate (**5**). Exposure of **5** to tin chloride in hydrochloric acid gave the desired product **3** in 50% yield.

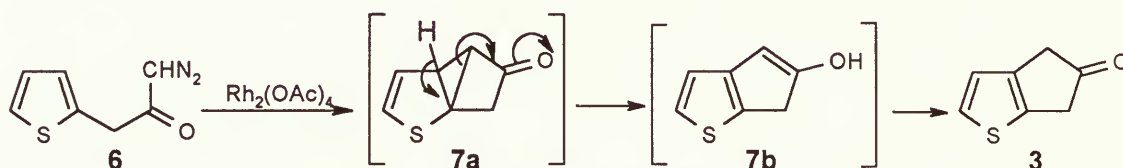
A more direct and economical route to the desired 5,6-dihydro-4*H*-cyclopenta[*b*]thiophene-5-one (**3**) system would involve the use of an intramolecular cyclization of the α -diazoketone (**6**, shown in Scheme 2) derived from 2-thiophene acetic acid (~\$0.93/g from Aldrich). Given the chemistry developed by Padwa⁵⁷ involving other systems containing an α -diazoketone tethered to a thienyl moiety, we believed that **6** would allow access to the ring system **3**.

Preparation of **6** from commercially available 2-thiophene acetic acid involves the standard protocol for synthesis of α -diazoketones wherein the appropriate acid is treated with oxalyl chloride or thionyl chloride in the presence of catalytic amounts of *N,N*-dimethylformamide (DMF). The resultant acid chloride was subsequently added to 4-5 equivalents of ethereal diazomethane to give the desired α -diazoketone. In the case of **6**, this transformation was achieved in 73% yield.

A few practical points regarding the preparation of α -diazoketones using this methodology are worth noting. It is important to ensure that only 1.1 equivalents of the corresponding chlorinating agent is used and that most of the excess chlorinating agent is removed before adding the acid chloride to the diazomethane solution, since the chlorinating agent will compete with the acid chloride for the diazomethane (See Scheme

V in the introduction). Additionally, the preparation of diazomethane from DiazaldTM⁶² involves the use of carbitol (di(ethyleneglycol) ethyl ether) instead of the more commonly used ethanol. The high boiling carbitol will ensure that an alcohol free diazomethane solution is prepared, as the presence of any alcohol will result in ester formation.

Exposure of 1-diazo-3-(2-thienyl)-2-propanone (**6**) to rhodium (II) acetate in



Scheme 2

dichloromethane at 25°C for 3h afforded the desired **3** in 70% yield. Compound **3** has been characterized completely using NMR and MS. Additionally, crystals of the cyclopentanone-thiophene **3** were grown from benzene, allowing its structure to be determined *via* x-ray diffraction (see Figure 2).

As with the homologous members of this series, carbenoid insertion into the adjacent π -bond of the thienyl fragment allows for cyclopropanation to yield intermediate **7a** which was never isolated. The highly strained cyclopropane intermediate **7a** then undergoes an acid catalyzed ring opening to form the enol (**7b**) which can tautomerize to give the desired product 5,6-dihydro-4H-cyclopenta[*b*]thiophene-5-one (**3**) (Scheme 2). This route to **3** is a marked improvement over that described by Skramstad,⁶¹ in that we can arrive at the desired target, **3**, in 51% yield (compared to 48%) using a starting material that is ten times cheaper.

⁶² Vogel's Textbook of Practical Organic Chemistry, Fifth edition, Edited by: Furniss, B. S., Hannaford, A. J., Smith, P. W. G., Tatchell, A. R., (Harlow : Longman Scientific & Technical, 1989) 432.

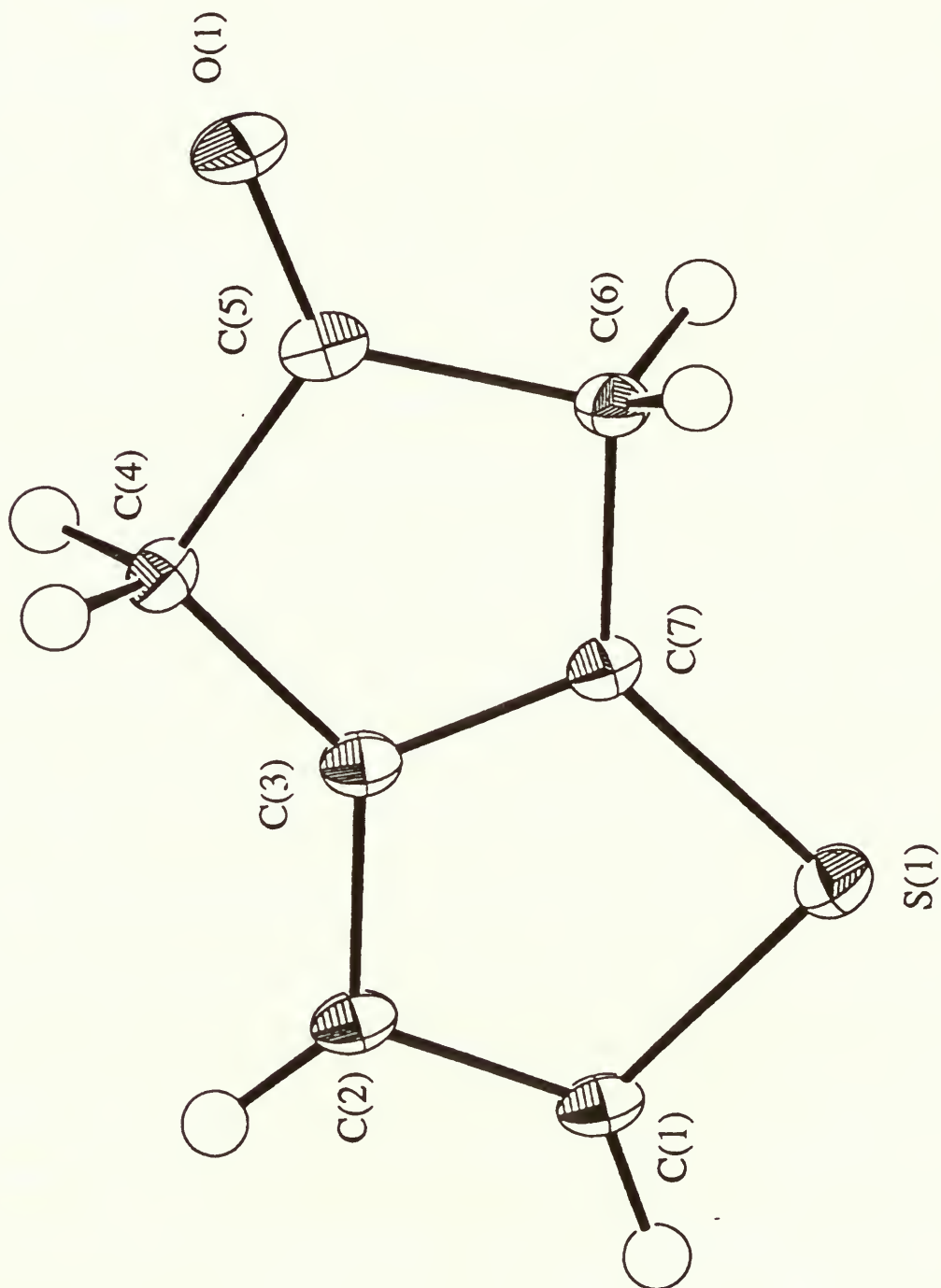
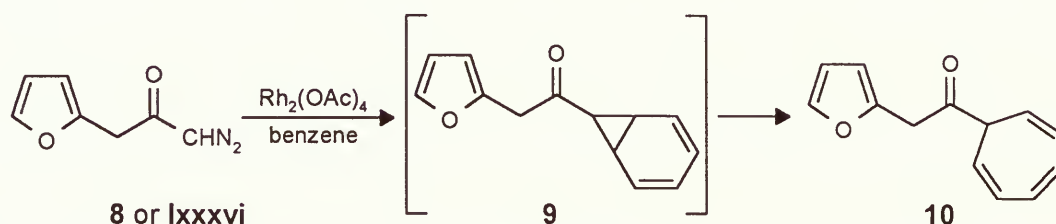


Figure 2. ORTEP view of 3

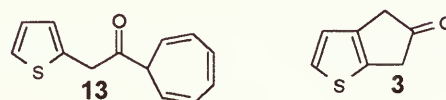
The transformation of **6** \rightarrow **3** is even more satisfying in light of the fact that Padwa's attempt to cyclize the analogous furanyl system, 1-diazo-3-(2-furanyl)-2-propanone (**8** Scheme 3 or **lxxxvi** Scheme XXVI), gave a "complex mixture of products".⁵⁷ When Padwa carried out the reaction using benzene as the solvent, a Buchner



Scheme 3

reaction was observed. The carbenoid inserts into a π -bond of the benzene to form a norcaradiene intermediate (**9**), which then undergoes an electrocyclic ring opening reaction to form the observed cycloheptatriene (**10**) in 68% yield. Padwa reasoned a single methylene spacer between the furan and the diazoketone (**8**) precluded intramolecular carbenoid insertion and only allowed for the intermolecular insertion into the solvent. While, at first glance, it could be reasoned that Durst's similar system (**lxxxvii**, Scheme XXVI) undergoes intramolecular insertion since the inclusion of a sulfur into the tether allows for a greater reach, it will be shown below that this is in fact not the case.

Carrying out the rhodium acetate catalyzed chemistry of **6** in benzene allowed for an examination of the competition between

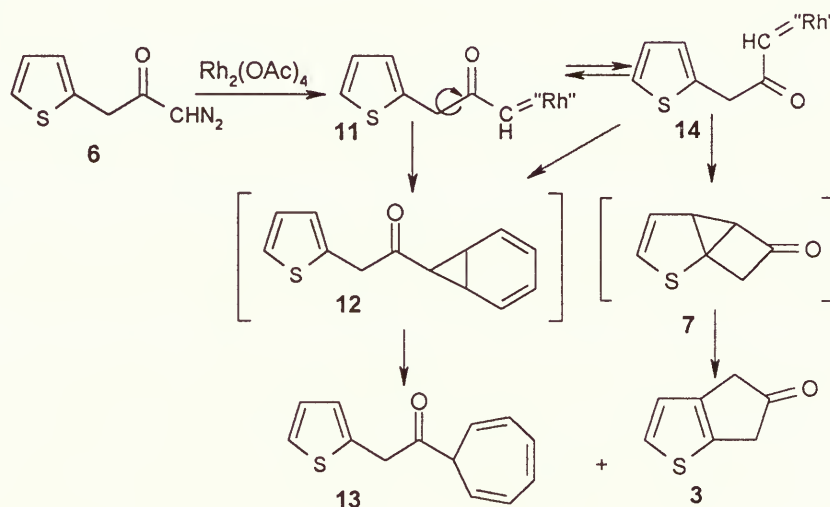


| Rxn Condition | Product Ratio | |
|------------------|---------------|----------|
| | 6 | 3 |
| Cold room (4 °C) | 75% | 25% |
| Room temperature | 66% | 33% |
| Reflux (80°C) | 33% | 66% |

Table 1

inter- and intramolecular carbenoid insertion. As expected, the reaction resulted in a mixture of both **3** and the cycloheptatriene **13**. More importantly, it was found that the ratio of the two products varied according to the reaction temperature (Table 1). When the reaction was carried out at 4 °C, the ratio of the cycloheptatriene **13** and the cyclic ketone **3** was determined to be 3 : 1, respectively. However, when the reaction was repeated at room temperature, the ratio of **13** and **3** decreased to 2 : 1. The ratio was completely reversed when the reaction was repeated in refluxing benzene (80 °C), yielding a 1 : 2 ratio of **13** and **3**.

The results of the competition experiment may be explained as arising from the conformational requirements of the attacking carbenoid.



Scheme 4

Treatment of **6** with

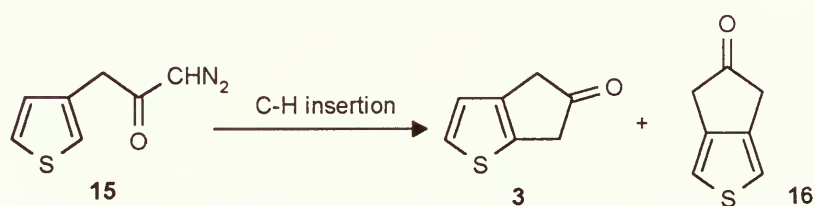
rhodium acetate gives rise to a carbenoid which can adopt either geometry **11** or **14**. Previous studies on the stability of conformational isomers of ketones by Romer⁶³ would assign **11** as the lower energy isomer since the more extended conformation effectively minimizes the steric interactions. However, in order for intramolecular cyclopropanation

⁶³ Romer, C., Creutzberg, J. E. G., *Rec.Trav.Chim.*, 1956, 75, 331.

to take place, the carbenoid must adopt conformation **14**. At low temperatures (4°C), the interconversion between **11** and **14** is slow with the equilibrium favoring the more stable conformer **11**. In other words, a smaller percentage of the population of **11** will have enough energy to overcome the energy barrier for interconversion to **14**. Assuming both intramolecular and intermolecular reactions occurs at the same rate, at lower temperatures, therefore, the predominance of conformer **11** results in a greater amount of intermolecular insertion product **13**. At higher temperatures (80°C), however, there will be enough energy to overcome the energy barrier for rotation from **11** to **14** and in this conformation (*i.e.* **14**) the carbenoid can insert intramolecularly. This conformational argument must be superimposed on the fact that, for the tether of this size, the intramolecular reaction is likely more favorable than the competing intermolecular one.

(ii) *Rhodium Acetate Catalyzed Decomposition of 1-Diazo-3-(3-Thienyl)-2-Propanone (15)*

In an attempt to explain the disparate behavior of the analogous furanyl (**8**)

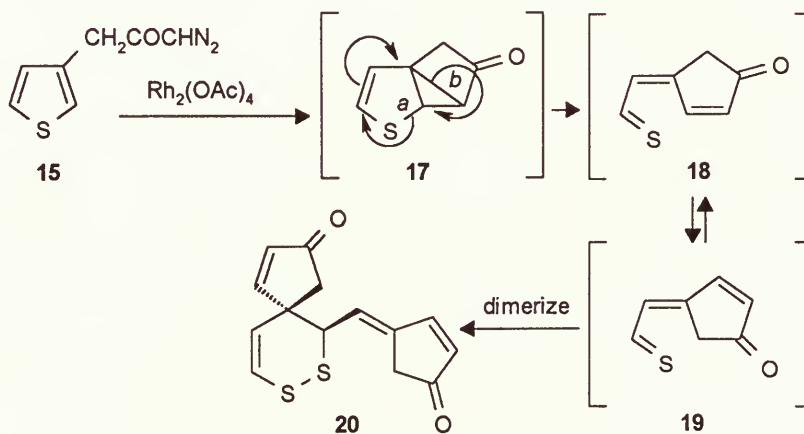


Scheme 5

and thienyl (**6**) systems, we investigated the rhodium acetate catalyzed chemistry of the isomeric thienyl system, 1-diazo-3-(3-thienyl)-2-propanone (**15**). While **3** is likely the result of ring opening of the intermediate cyclopropane **7**, another possible mechanism would involve an insertion by the carbenoid generated from **6** into the C-H bond at the 3-

position of the thiophene. If a C-H insertion were operating, then treatment of **15** with rhodium acetate should allow for the production of both **3** and the isomeric 5,6-dihydro-4*H*-cyclopenta[*c*]thiophen-5-one (**16**). Much to our surprise, however, catalytic decomposition of **15** allowed for isolation of a single product in 85% yield, with none of the expected products detected. MS of this product showed a molecular ion at $m/z = 276$ and revealed that a dimer had been produced. The distinctive ^1H - and ^{13}C -NMR spectra, in conjunction with COSY and NOE experiments, led us to assign the structure of the product as the complex spiro-disulfide (**20**) shown in Scheme 6. This structure has been confirmed *via* x-ray crystallography (see Figure 3).

One possible mechanism that would explain the production of the spiro-disulfide is illustrated in Scheme 6 below. In the presence of rhodium (II) acetate, α -diazoketone (**15**) undergoes the expected cyclopropanation reaction to **17**. But then, unlike the other thienyl systems, opening of this cyclopropane intermediate (**17**) gives a thioaldehyde (**18**) *via* a [4+2]-cycloreversion seen previously only in the furanyl systems. *This marks the first example of the retro-cycloaddition mechanism in the thienyl system.* Isomerization



Scheme 6

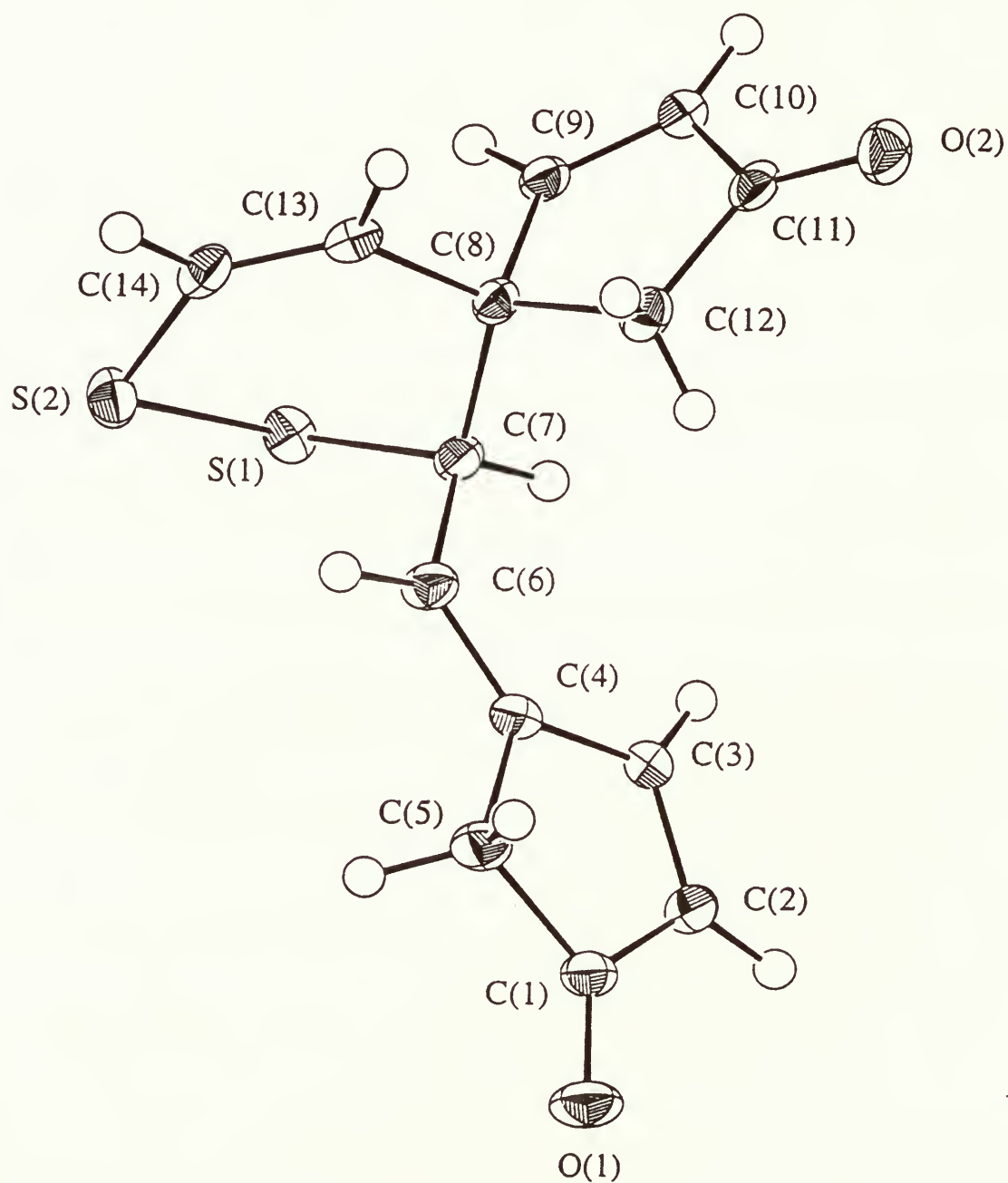


Figure 3. ORTEP view of **20**

(to **19**) is then followed by a Diels-Alder dimerization to give **20**.

A few key features of this mechanism deserve further comment. The isomerization of **18** to **19** must take place since dimerization of the initial [4+2]-cycloreversion product **18** does not lead to **20**. This interconversion of **18** to **19** likely involves the tautomerism

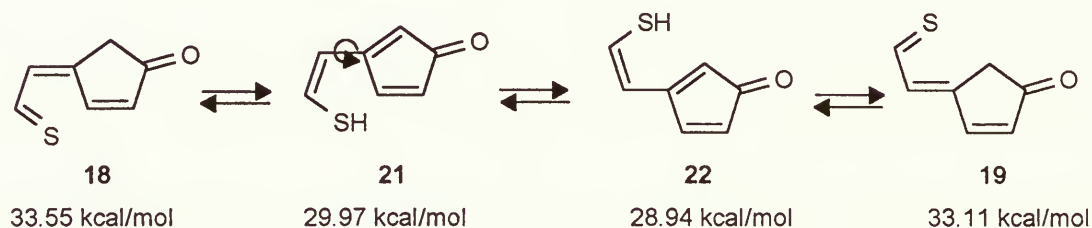
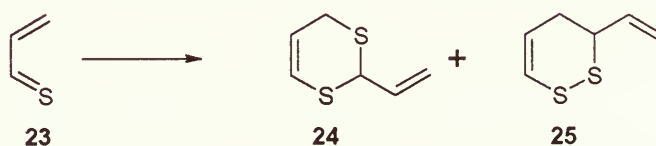


Figure 4

of thioaldehyde **18** to the conjugated thiol **21**. Tautomerization of these strongly polarized C-S bonds have been reported by McKenzie.⁶⁴ Semi-empirical modeling using the PM3 Hamiltonian in the Spartan⁶⁵ program (the calculated heats of formation (ΔH_f) appear in Figure 4) show that the enethiol tautomers are energetically more-stable than the thio-keto forms by about 3 kcal/mol. Rotation about the bond indicated in Figure 4 would lead to **22** which tautomerizes to **19** and is trapped in the Diels-Alder reaction driving the equilibrium forward.

The head-to-head regiochemistry of dimerization to give **20** is unusual in that head-to-tail addition would be expected



Scheme 7

based on Frontier Molecular Orbital (FMO) considerations. This may indicate that the dimerization proceeds in an ionic and stepwise fashion rather than *via* a concerted Diels-

⁶⁴ McKenzie, S., Reid, D. H., *J. Chem. Soc.*, **1970**, *1*, 145.

⁶⁵ Spartan, v. 4.0 (Irvine, California: Wavefunction, 1995).

Alder reaction. It is worthwhile to point out, however, that the head-to-head addition of α,β -unsaturated thioaldehyde is not uncommon as thioacrolein (**23**) is known to dimerize very quickly to a 9 : 1 mixture of the head-to-tail (**24**) and head-to-head (**25**) dimers (Scheme 7).⁶⁶ In addition, the exclusive production of the head-to-head dimer **20**, in the decomposition of **15** may be attributed to the added stability offered by greater overlap of the conjugated π systems in the transition state going from **19** to **20**. This secondary molecular orbital overlap could account, at least in part, for the observed regiochemistry.

Finally, one would expect monomeric species such as **18** or **19** to be rather unstable given their highly reactive thiocarbonyl moieties, which frequently participate in polymerization. The absence of any side product seems to imply that the rhodium either aids in the stabilization of these thioacyl species and/or participates in the dimerization reaction. Other methods for carbene generation were also investigated. Decomposition of **15** in the presence of Cu metal gives a complex mixture of products while photolysis of **15** results in Arndt-Eistert type chemistry⁶⁷ to give the homologous acid, 3-(3-thienyl)propanoic acid. These results indicate that the rhodium catalyst is essential for the transformation of **15**→**20** although its exact role (aside from carbenoid generation) has yet to be determined.

The reaction of 1-diazo-3-(3-thienyl)-2-propanone (**15**) is in marked contrast to the result obtained by Durst with system **xlvi**, (Scheme XXVIII) which undergoes the typical unraveling of the cyclopropane *via* the enol mechanism preferred by the

⁶⁶ Bock, H., Mohmand, S., Hirabayashi, T., Semkow, A., *Chem. Ber.*, **1982**, *115*, 1339.

⁶⁷ Agosta, W.C., Smith, A. B., III, *J. Am. Chem. Soc.*, **1973**, *95*, 1961; Smith, A. B., III, Toder, B., Branca, S.J., *J. Am. Chem. Soc.*, **1984**, *106*, 3995; Hudlicky, T., Sheth, J. P., *Tetrahedron Lett.*, **1979**, *29*, 2667.

thiophenes. This can be rationalized if one considers the intermediate cyclopropanes **17** and **xlix**. Inspection of the molecular models reveals that with a sulfur atom as part of the cyclobutenone system, **xlix** is considerably less strained than the corresponding cyclopropane **17** due to the longer C-S bonds. It is reasonable to assume, therefore, that **xlix** has a longer lifetime than **17** and, as a result, the enol mechanism can operate.

In an effort to induce acid catalyzed ring opening of the cyclopropane **17** to **3**, the reaction was repeated in the presence of catalytic amounts of trifluoroacetic acid. However, the spiro-disulfide (**20**) was once again the only product isolated.

(iii) *Molecular Modeling Studies*

The conversion of **15** \rightarrow **20** prompts a number of interesting questions. Why does the intermediate cyclopropane of the 2-substituted thienyl system (**7**) undergo the “normal” acid-catalyzed ring opening *via* an enol pathway, while the isomeric cyclopropane of the 3-substituted system (**17**) undergoes the [4+2] cycloreversion? Semi-empirical modeling studies have revealed some interesting trends.

Figure 5 shows a series of furanyl- and thienyl-based α -diazoketones, the intermediate cyclopropanes derived from intramolecular carbenoid insertion and their respective [4+2]-cycloreversion products. Geometry optimizations were carried out on the intermediate cyclopropanes and the [4+2]-cycloreversion using the PM3 Hamiltonian in the Spartan program. The heats of formation for these optimized structures compounds were then calculated and appear in Table 2. The thermodynamics of the reaction were then calculated by subtracting the heat of formation of the [4+2]-cycloreversion product

from the heat of formation of the starting cyclopropane to give the Δ heat of formation (ΔH_f) for the [4+2] cycloreversion (Shown in Figure 5).

Table 2: Calculated Heats of Formation. Values in kcal/mol.

| Cyclopropane | | | Transition State | | | Cycloreversion Product | | |
|--------------|--------|-------|-----------------------------------|-------|-------|------------------------|--------|-------|
| | X = O | X = S | | X = O | X = S | | X = O | X = S |
| 26 | -24.68 | 11.06 | 26 \rightarrow 30 | 40.96 | 43.71 | 30 | -46.19 | 23.06 |
| 27 | -23.76 | 12.39 | 27 \rightarrow 31 | 40.42 | 45.92 | 31 | -42.54 | 25.91 |
| 28 | 11.25 | 44.77 | 28 \rightarrow 32 | 36.35 | 42.99 | 32 | -6.62 | 66.11 |
| 29 | 9.72 | 44.09 | 29 \rightarrow 33 | 18.49 | 21.47 | 33 | -37.22 | 33.55 |

Let us first consider the thienyl series (Figure 5, X=S). The thermodynamics of the reactions revealed that cycloreversion of **26**, **27** and **28** are endothermic by 12.0, 13.5 and 21.3 kcal/mol respectively, while cycloreversion of **29** is exothermic by 10.5 kcal/mol. The relief of substantial strain energy associated with the fused tricyclic system, makes the cycloreversion of **29** thermodynamically favorable. On the other hand, similarly strained isomer **28** would be unaided by retro-[4+2] ring opening since cycloreversion leads to a highly strained cyclobutenone system **32**. [4+2] Cycloreversion of the four analogous furan-based systems followed the same trend but were all found to be exothermic (-21.5, -18.8, -17.9, and -21.5 kcal/mol for the oxy analogous of **26**, **27**, **28** and **29** respectively). This observation is in keeping with the greater bond strength of the aldehyde C=O bond compared to the thioaldehyde C=S bond.

The transition state structures for the cycloreversion of **26**, **27**, **28** and **29** were also explored computationally. Each transition structure gave only one imaginary harmonic vibrational frequency corresponding in motion to the desired reaction coordinate (*i.e.* stretching of bonds *a* and *b*, as in **17**, Scheme 6). As seen in Figure 6, the transition state associated with the conversion **29** \rightarrow **33** was calculated to lie 21.5 kcal/mol above the ground state energy of **29** while the energy of the transition states associated with the cycloreversions of **26**, **27**, and **28** were found to be 43.7, 45.9 and 43.0 kcal/mol above **30**, **31**, and **32** respectively. Clearly, the relief of strain in intermediate **29** facilitates cycloreversion despite the generation of a reactive C=S bond.

Turning our attention to the furanyl series, the modeling studies show that the transition state associated with the conversion of **29** \rightarrow **33** (X=O) was calculated to lie 18.5 kcal/mol above the ground state energy of **29** corresponding to half the value calculated for the other homologous members of the series. Given both the ΔH_f and the transition state energy associated with the conversion of **29** \rightarrow **33** (X=O), the modeling would seem to favor a [4+2]-cycloreversion for the cyclopropane derived from the rhodium acetate decomposition of 1-diazo-3-(3-furanyl)-2-propanone (*vide infra*).

Looking at the overall results from the molecular modeling at the PM3 level, one cannot make consistent comparisons between thienyl and furanyl systems. In an effort to reproduce computationally the differences between the heterocyclic series, the calculations should be repeated at an *ab initio* level.

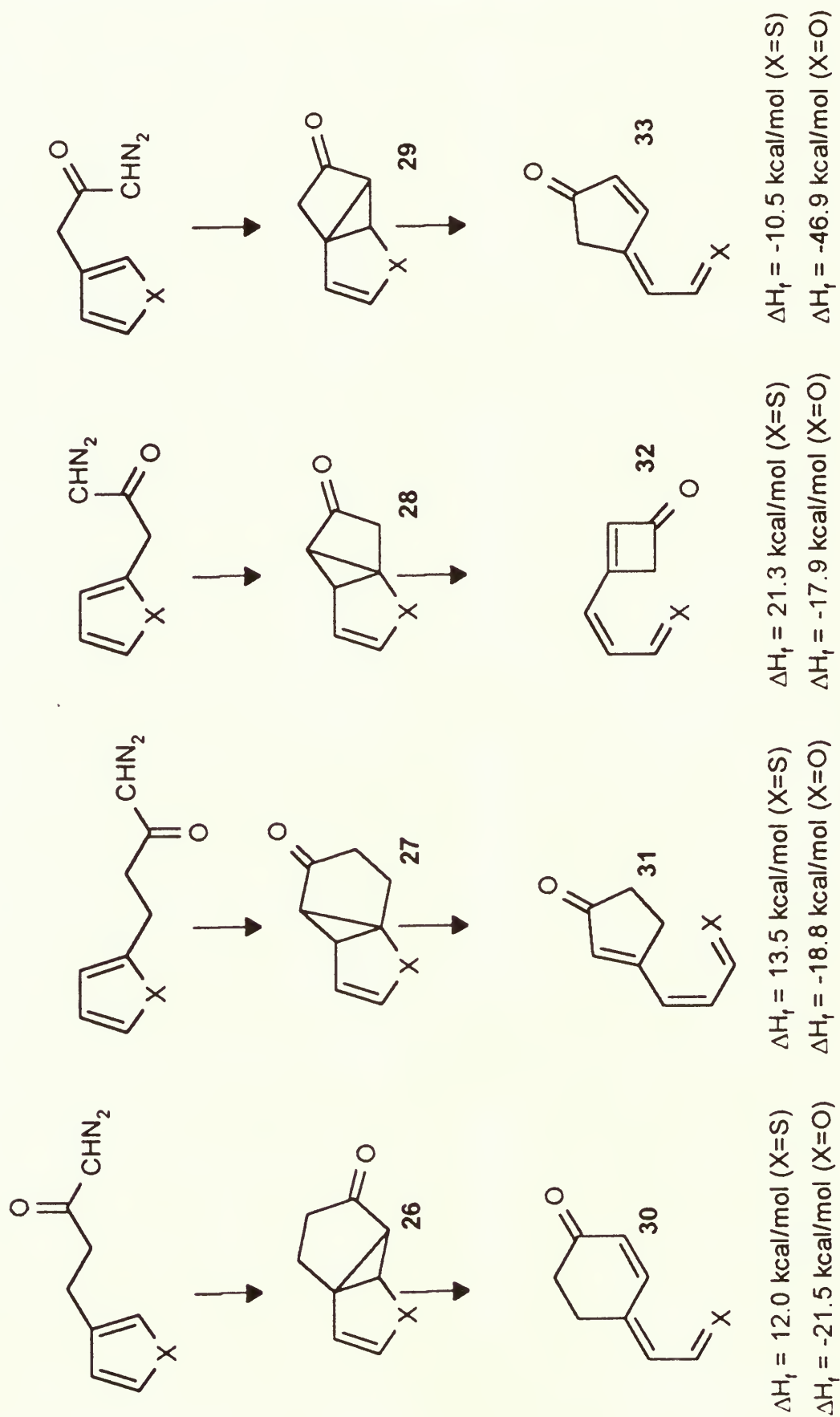


Figure 5

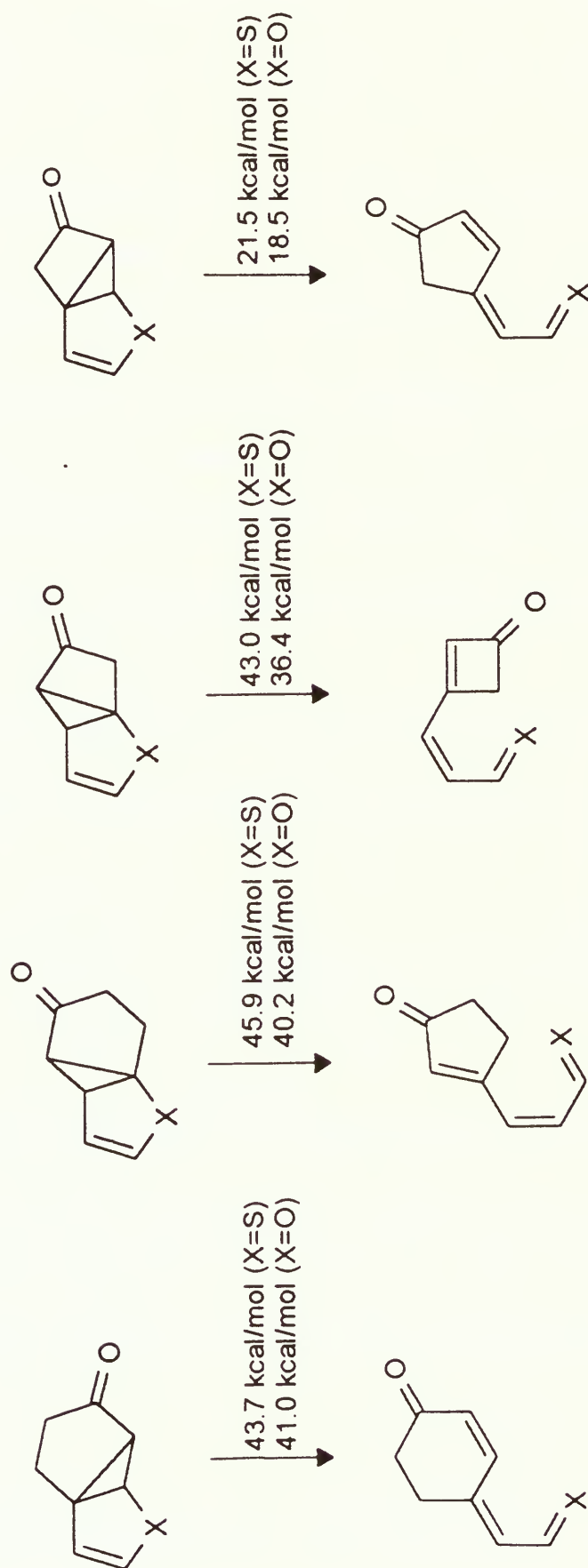
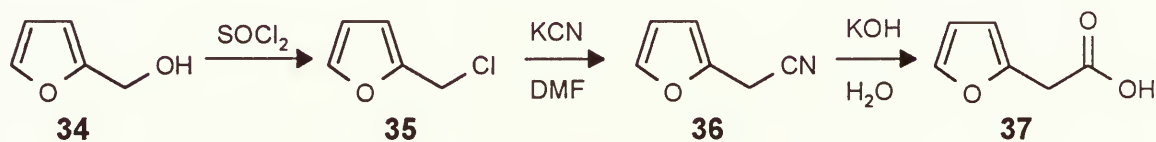


Figure 6

(iv) *Rhodium Acetate Catalyzed Decomposition of 1-Diazo-3-(2-Furanyl)-2-Propanone (8)*

While it is clear that the cyclopropane derived from the rhodium acetate catalyzed decomposition of 1-diazo-3-(2-furanyl)-2-propanone (**8**) avoids a [4+2]-cylcoreversion to a cyclobutenone product (**32**, X=O), we became intrigued with the possibility that we could affect some transformation of this intermediate cyclopropane by altering the reaction conditions. Recall that this was the α -diazoketone system which gave Padwa a “complex mixture of products”⁵⁷ while the comparable system **lxxxvii** gave Durst the sulfonylcyclobutenone **lxxxix**.⁵⁹ Given the success we had with the analogous thienyl system (**6**), we decided to revisit this system.

The requisite carboxylic acid precursor to the 1-diazo-3-(2-furanyl)-2-propanone (**8**) can be prepared according to the procedure outlined by Janda *et al.*⁶⁸ from 2-furfuryl alcohol.



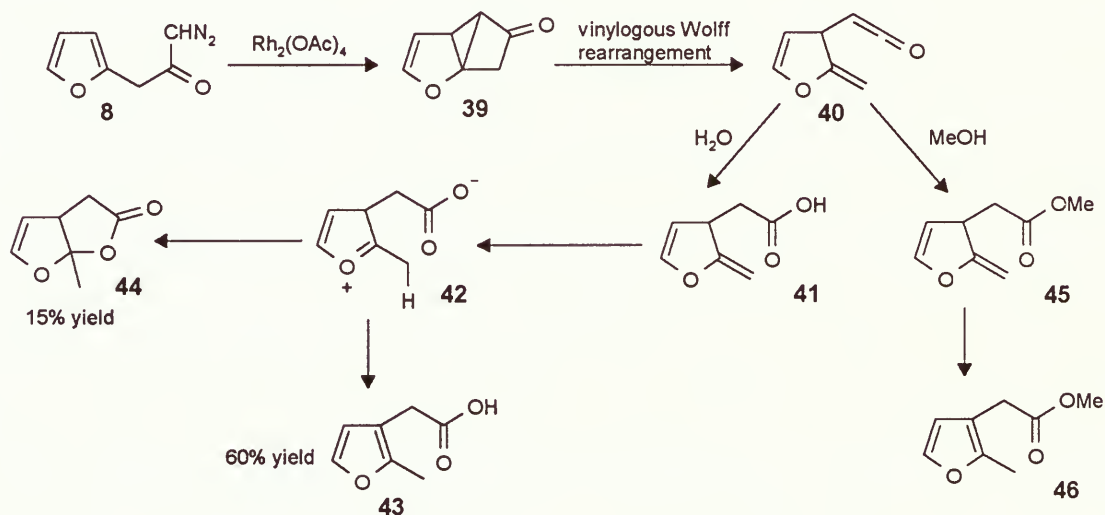
Scheme 8

As seen in Scheme 8, chlorination of the alcohol **34** allowed for formation of the unstable α -furfuryl chloride (**35**)⁶⁹, which was then immediately treated with potassium cyanide to generate 2-furfurylacetonitrile (**36**). Subsequent hydrolysis of the nitrile (**36**) under basic condition gave the required 2-furan acetic acid in an overall yield of 25%.

⁶⁸ Janda, W., Srogl, J., Körblóvá, E., Stibor I., *Coll. Czech. Chem. Commun.*, **1980**, *45*, 1361.

⁶⁹ Kirner, W.R., *J. Am. Chem. Soc.*, **1928**, *50*, 1955.

Conversion of 2-furan acetic acid to 1-diazo-3-(2-furanyl)-2-propanone (**8**) was achieved using the protocol developed previously wherein the acid was converted to the acid chloride, then reacted with ethereal diazomethane. Initial experiments with this α -diazoketone and rhodium (II) acetate in dry dichloromethane under an argon atmosphere at room temperature gave the mixture of products reported by Padwa.⁵⁷ However, when a few drops of water were added to the reaction mixture before the introduction of the rhodium catalyst, the reaction proceeded so as to allow for the production of only two products. Isolation *via* silica gel chromatography and characterization *via* MS and NMR identified the products to be 2-methyl-3-furan acetic acid (**43**)⁷⁰ and the bicyclic lactone (**44**) as shown in Scheme 9.



Scheme 9

It would appear that neither the [4+2]-cycloreversion nor the enol mechanism are operating in this system, but rather the cyclopropane generated (**39**) opens *via* a Vinylogous Wolff rearrangement (VWR).⁷¹ Although such rearrangement on a furanyl

⁷⁰ Nemoto, H., Shitara, E., Fukumoto, K., *Heterocycles*, **1985**, 23, 549.

⁷¹ Smith, A.B., III, Toder, B.H., Richmond, R.E., Branca, S.J., *J. Am. Chem. Soc.*, **1984**, 106, 4001; Smith, A.B., III, Dieter, R.K., *Tetrahedron*, **1981**, 37, 2407.

system has not been observed before, Amos B. Smith III has demonstrated the operation of VWR mechanism on a number of β,γ -unsaturated- α -diazoketones.⁷¹ As illustrated in Scheme 9, treatment of 1-diazo-3-(2-furanyl)-2-propanone (**8**) with rhodium acetate allows for cyclopropanation. The highly strained cyclopropane intermediate (**39**) then undergoes the VWR either by a concerted [2+2]-cycloreversion or *via* a stepwise process to give the vinyl ketene intermediate (**40**). In the absence of water or other nucleophiles, a complex mixture of products arises due to the high reactivity of the intermediate ketene (**40**). However, in the presence of water the ketene (**40**) was trapped to yield compound **41**. Protonation of the exocyclic double bond then gives the oxonium ion (**42**) which can either lose a proton to rearomatize to give **43** in 60% yield or cyclize to **44** in 15% yield.

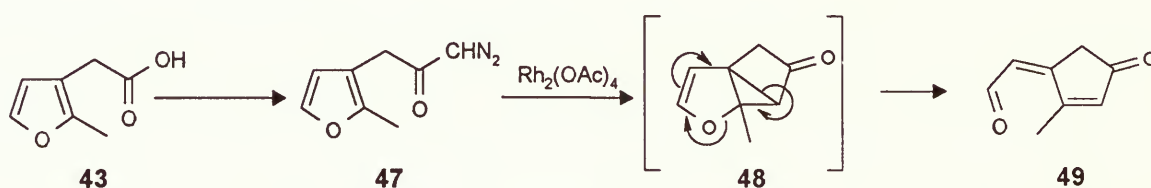
Further evidence for the intermediary of ketene (**40**) was obtained by carrying out the rhodium acetate catalyzed decomposition of 1-diazo-3-(2-furanyl)-2-propanone (**8**) in the presence of methanol. As shown in Scheme 9, trapping of the ketene with methanol results in the formation of the methyl ester **45** which can then rearomatize to methyl-(2-methyl-3-furanyl)acetate (**46**) in 80% overall yield.

(v) *Rhodium Acetate Catalyzed Decomposition of 1-Diazo-3-(3-Furanyl)-2-Propanone (52)*

As discussed above, the modeling would seem to indicate that this cycloreversion of **29** \rightarrow **33** (X=O, Figure 5) is a favorable transformation. This is further supported by Durst's ability to cyclize the comparable diazo compound **xc** to **xcii** (Scheme XXVI).⁵⁹ Preparation and rhodium acetate catalyzed reaction of 1-diazo-3-(3-furanyl)-2-propanone

provided not only a test for our modeling predictions but also access to a novel ring system **54**.

Although a preparative route to the precursor of **51**, 2-(3-furan)acetic acid, has been described by Janda *et al.*,⁷² the rather lengthy procedure results in a low overall yield (<30%). Our initial investigation into the 3-substituted furanyl system, therefore, took advantage of the some of the chemistry developed above. The 2-methyl-3-furan acetic acid prepared from 1-diazo-3-(2-furanyl)-2-propanone (see Scheme 9) differs from the



Scheme 10

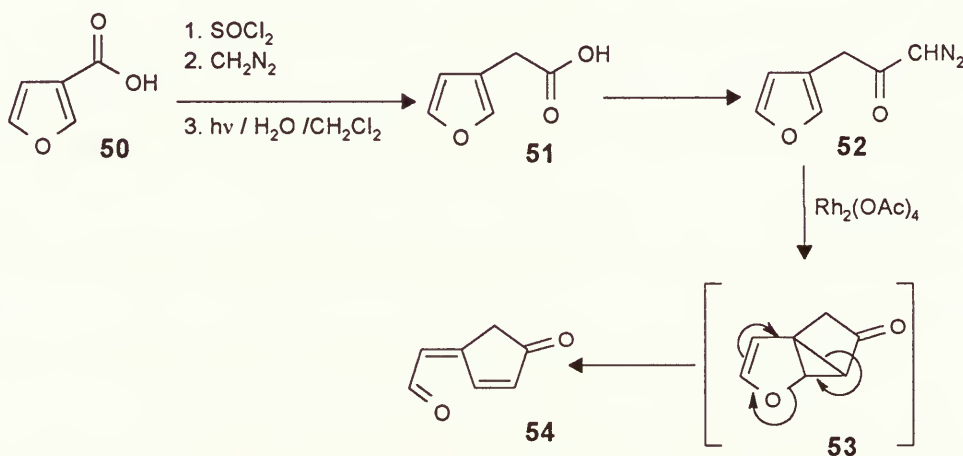
desired **51** in that a methyl group is present at the 2-position of **43**. Conversion of **43** to the corresponding acid chloride followed by treatment with ethereal diazomethane allowed for the production of **47**. As expected, treatment of this α -diazoketone with rhodium acetate allowed for a virtually quantitative conversion to **49** as evidenced by NMR. (Scheme 10)

Motivated by this result, we set about preparing the 1-diazo-3-(3-furanyl)-2-propanone systems *via* a route involving a modified Arndt-Eistert type reaction. Despite Janda's previously published synthesis, we envisioned preparing the requisite 3-furan acetic acid by homologating 3-furoic acid. As reported by Smith,⁷¹ the complications incurred when using the standard Arndt-Eistert reagents and conditions (silver (I) oxide in methanol under reflux) can be avoided using a photochemical protocol. Thus,

⁷² Janda, M., Srogl, J., Korblova, E., Stibor, I., *Coll. Czech. Chem. Commun.*, **1980**, *45*, 1361.

homologation of 3-furoic acid was achieved by conversion to the acid chloride, treatment with ethereal diazomethane and photolysis of the resultant diazoketone in the presence of water. The 3-furan acetic acid (**51**) could then be converted to the desired α -diazoketone by the standard protocol.

Treatment of 1-diazo-3-(3-furanyl)-2-propanone (**52**) with rhodium (II) acetate resulted in the formation of the expected keto-aldehyde (**54**) in >90% yield as determined by ^1H -NMR spectroscopy of the crude product. Attempts to purify the product by column chromatography on silica gel resulted in decomposition.



Scheme 11

2-(4-Oxo-2-cyclopentenylidene)acetaldehyde (**54**) was completely characterized by ^1H - and ^{13}C -NMR, MS[EI] and HRMS. Structurally, the keto-aldehyde product itself is interesting, being highly conjugated, including 2 α - β unsaturated carbonyl systems in a 7 carbon backbone. Yet, the functional groups may be distinguished from each other either by being chemically different (aldehyde vs ketone), or sterically different (mono- vs di-substituted) at the β -position of the α - β -unsaturated carbonyl. The *Z*-configuration of the α - β -unsaturated aldehyde also offers an opportunity for hetero-Diels-Alder reactions. All

of the above properties makes the keto-aldehyde (**54**) a promising synthon for organic synthesis.

(vi) *Rhodium Acetate Catalyzed Decomposition of 1-Diazo-3-(2-Benzofuranyl)-2-Propanone (69)*

Padwa has reported an extension of this intramolecular carbenoid insertion work involving benzofuran as the aromatic fragment. In contrast to the analogous furanyl systems, carbenoid insertion allows for an isolable cyclopropane intermediate. For example, when 1-diazo-4-(2-benzofuran)-2-butanone (**58**, Scheme 12) was exposed to a solution containing rhodium acetate, the cyclopropane **59** was isolated. Treatment with 1% sulfuric acid solution converted the cyclopropane to compound **60** *via* the enol pathway discussed previously. [4+2]-Cycloreversion can be induced at 180°C to give the ortho-quinoidal system **61**. The forcing conditions are required since the cycloreversion effectively destroys the aromaticity of the system. **61** Rapidly undergoes electrocyclic ring

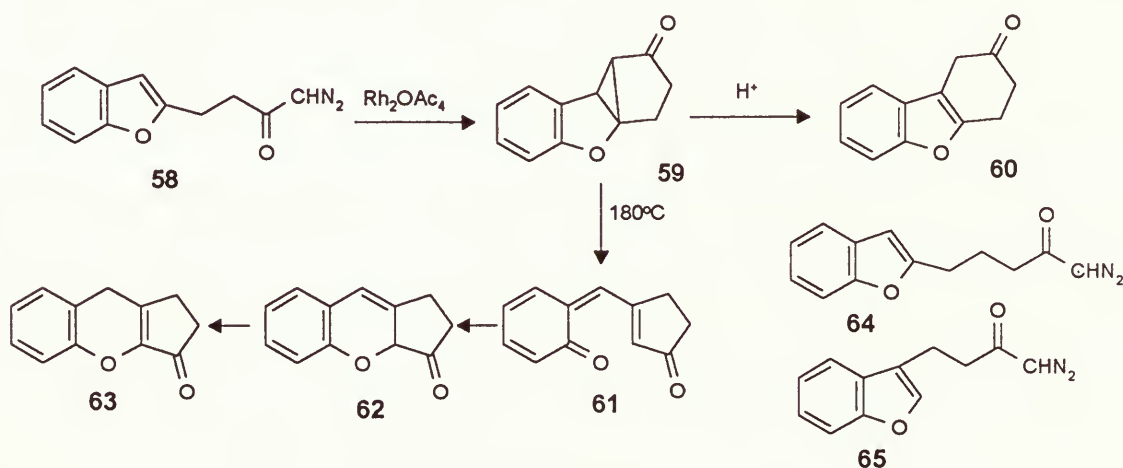
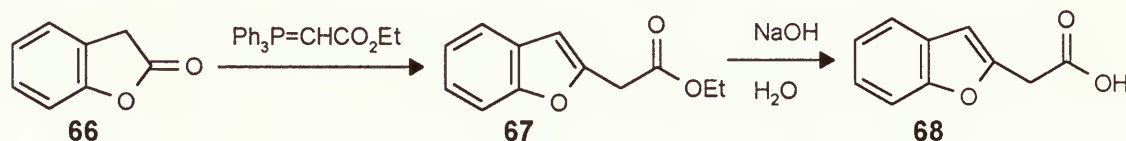


Figure 12

closure to **62** which, in turn, isomerizes to the more conjugated **63**. Benzofuranyl systems with longer tethers (for example, 1-diazo-5-(2-benzofuran)-2-pentanone, **64**) or with 3-substituted tethers (for example, 1-diazo-4-(3-benzofuran)-2-butanone, **65**) exhibit the same type of chemistry.

As we have demonstrated above, the high degree of strain imparted to intermediate cyclopropanes by short methylene tethers has allowed for some rather novel chemistry in the furanyl and thienyl series. Hence, we became interested in determining the effect of these short tethers on the α -diazoketones containing benzofuranyl moieties. The first target for this series was 1-diazo-3-(2-benzofuran)-2-propanone (**69**) which was prepared from the corresponding carboxylic acid, 2-benzofuran acetic acid (**68**).



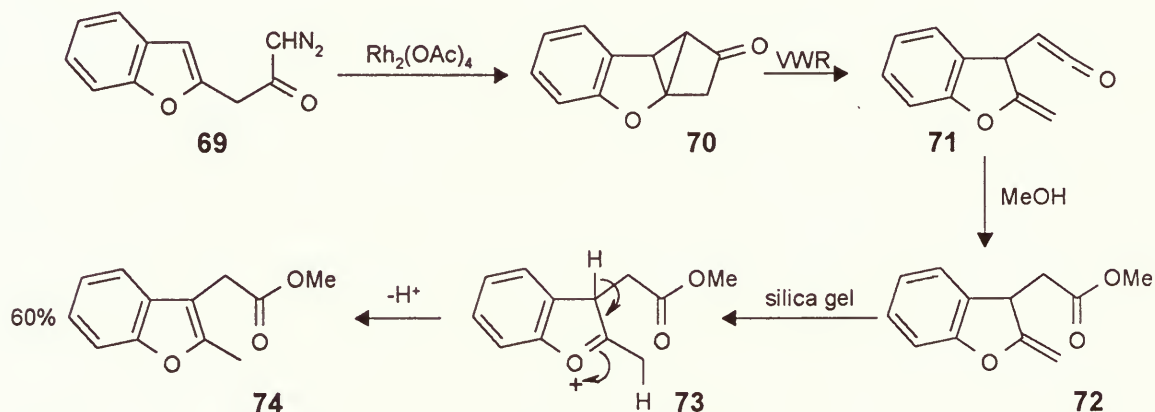
Scheme 13

A number of the syntheses of 2-benzofuran acetic acid have been reported previously.⁷³ In addition to being rather lengthy, the procedure yields of ~20% (in the best cases) made them less than desirable. Instead, the synthesis of 2-benzofuran acetic acid was carried out as illustrated in Scheme 13. Using commercially available 2-coumaranone (**66**), a Wittig reaction was carried out using carbethoxymethylene triphenylphosphorane

⁷³ Degenhardt, C.R., *Synth. Commun.*, **1982**, *12*, 415; Kasahara, A., Izumi, T., Suzuki, A., Takeda, T., *Bull. Chem. Soc. Jpn.*, **1976**, *49*, 5711.

in xylenes to give **67** in over 80% yield.⁷⁴ Base hydrolysis of the ester affords the 2-benzofuran acetic acid (**68**) in 60% yield. (Scheme 13)

With 2-benzofuran acetic acid in hand, conversion to the acid chloride followed by treatment with ethereal diazomethane allowed for the preparation of the desired 1-diazo-3-(2-benzofuranyl)-2-propanone (**69**). Exploratory experiments involving the treatment of the α -diazoketone (**69**) with rhodium acetate in dichloromethane resulted in a mixture of products and an inability to isolate any carbenoid insertion product. This led us to believe that, unlike the other homologous members of the benzofuranyl series, 1-diazo-3-(2-



Scheme 14

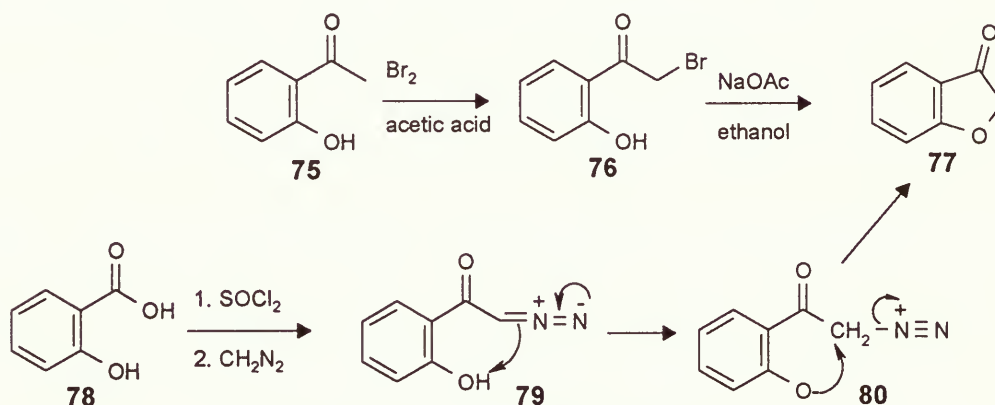
benzofuranyl)-2-propanone (**69**) behaved very much like 1-diazo-3-(2-furanyl)-2-propanone (**8**) in that the intermediate cyclopropane unraveled *via* a vinylogous Wolff rearrangement. This was confirmed when the rhodium acetate decomposition of **69** was repeated in the presence of 2 equivalents of methanol. The reaction was monitored *via* ¹H-NMR and clearly showed the formation of 1 major product which we assigned as **72**. When a preparative scale reaction was carried out and the product purified by silica gel

⁷⁴ Chan, J. H.-T., Elix, J. A., Ferguson, B. A., *Aust. J. Chem.*, **1975**, 28, 1097; Chan, J. H.-T., Elix, J. A., Ferguson, B. A., *Synth. Commun.*, **1972**, 2, 409.

chromatography, $^1\text{H-NMR}$ revealed that the product had isomerized to methyl-(2-methyl-3-benzofuranyl) acetate (**74**). Isomerization of **72** to **74** likely takes place *via* protonation of the exo-cyclic double bond to yield oxonium ion **73** which can then rearomatize to **74** by losing a proton.

Clearly the VWR is the lower energy pathway given that [4+2]-cycloreversion of **70** would not only lead to disruption of aromaticity in the benzo moiety but also produce a high-strained cyclobutenone.

(vii) *Rhodium Acetate Catalyzed Decomposition of 1-Diazo-3-(3-Benzofuranyl)-2-Propanone (**84**)*



Scheme 15

In an effort to examine the effect of the location of substitution on the insertion chemistry, we developed a synthesis for the isomeric, 3-substituted benzofuran system, 1-diazo-3-(3-benzofuranyl)-2-propanone (**84**). Once again, the desired α -diazoketone was to be derived from the corresponding carboxylic acid precursor, 3-benzofuran acetic acid (**83**), which, in turn could be prepared using a Wittig approach on 3-coumaranone (**77**), a method developed by Chan.⁷⁴

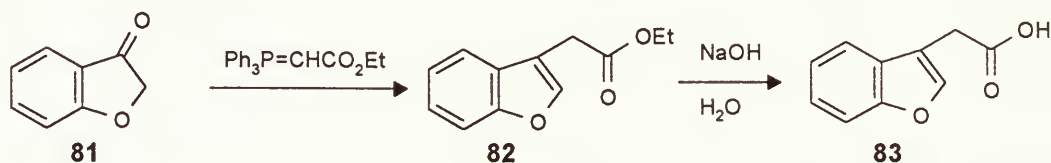
3-Coumaranone was prepared using variations of two literature preparations. The first protocol is a modification of that reported by Ghosh⁷⁵ and involves the conversion of salicylic acid (**78**, Scheme 15) to its acid chloride and subsequent treatment with ethereal diazomethane. The resultant α -diazoketone **79** is not isolated but rather is converted rapidly to the desired 3-coumaranone (**77**) in 80% overall yield. This last transformation likely takes place as illustrated in Scheme 15, wherein the carbon α to the diazo fragment is protonated by the phenolic moiety, and then undergoes cyclization when the phenolate displaces the nitrogen. Whilst the yields were good, this approach to 3-coumaranone was not amenable to scale-up due to the large quantities of diazomethane required. Preparative scale synthesis of **77** used a modification of the method reported by Paradkar⁷⁶ involving the cyclization of 2-bromo-2'-hydroxyacetophenone. The modified cyclization using sodium acetate and DMF as the authors suggested was less effective than the initial cyclization reported by Fries⁷⁷ using ethanol. Yields of 90% for the cyclization were common. Despite the differences in the precursor for the cyclization, the reaction mechanisms are actually very similar, a base, (sodium acetate for **76** and the diazoketone itself in **79**) abstracting the phenolic proton to form a phenolate ion, which then attacks the α -carbonyl carbon which has a good leaving group to form 3-coumaranone (**77**).

In a similar fashion to the preparation of 2-benzofuran acetic acid, a Wittig reaction involving 3-coumaranone (**81**) and carbethoxymethylene triphenylphosphorane

⁷⁵ Ghosh, S., Datta, I., Chakraborty, R., Kumar Das, T., Sengupta, J., Sarkar, D. C., *Tetrahedron*, **1989**, *45*, 1441.

⁷⁶ Deshpande, A.R., Paradkar, M.V., *Synth. Commun.*, **1990**, *20*, 809.

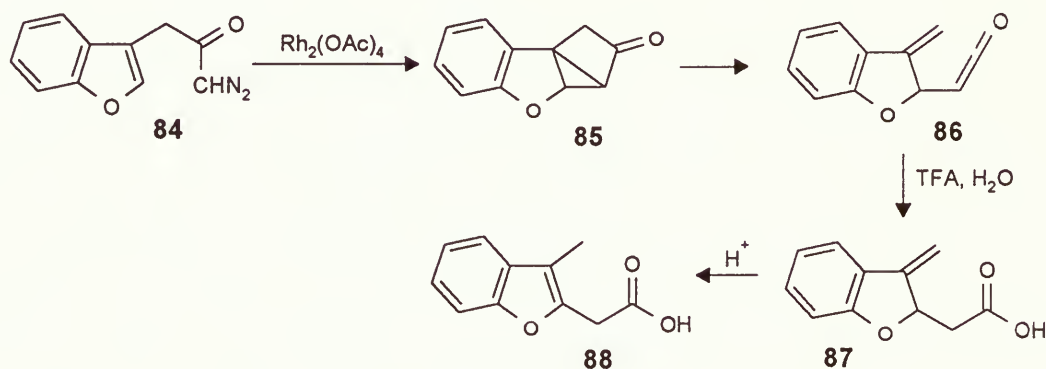
⁷⁷ Fries, K., Pfaffendorf, W., *Ber.*, **1910**, *43*, 212.



Scheme 16

gave **82** with subsequent base hydrolysis yielding the desired acid **83**.⁷⁶ Synthesis of the target α -diazoketone **84** was achieved using the standard protocol described above.

Exploratory reactions involving the treatment of 1-diazo-3-(3-benzofuranyl)-2-propanone with rhodium acetate quickly revealed that, once again, the vinylogous Wolff

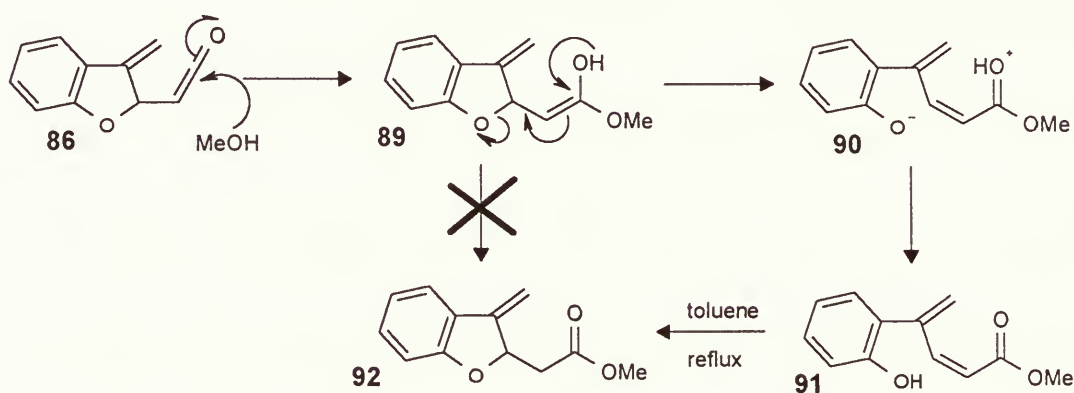


Scheme 17

rearrangement was at work. Cyclopropanation of **84** takes place to give **85**, but unlike the [4+2]-cycloreversion of the cyclopropane intermediate **53** in the 1-diazo-3-(3-furanyl)-2-propanone system, **85** undergoes a VWR in order to avoid disruption of the aromaticity. When the reaction is carried out in the presence of trifluoroacetic acid and water, the intermediate ketene is trapped to yield only one major product, which has been identified as 3-methyl-2-benzofuran acetic acid (**88**).

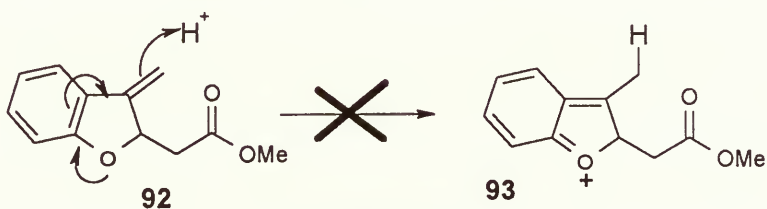
However, when methanol was used as the nucleophilic trap, we obtained an unexpected product. Using MS, ¹H- and ¹³C-NMR and the 2D-COSY experiment, we assigned the structure to be that of the poly-unsaturated ester **91** shown in Scheme 18.

The product can be shown to have arisen from nucleophilic attack of methanol onto the ketene to result in the enol shown. Rather than tautomerize to the ester (**92**), the enol collapses to give the ring opened product **90** and then to **91**. The preference for the formation of **91** over **92** may lie in part with the additional conjugation of **91** which imparts greater thermodynamic stability than **92**.



Scheme 18

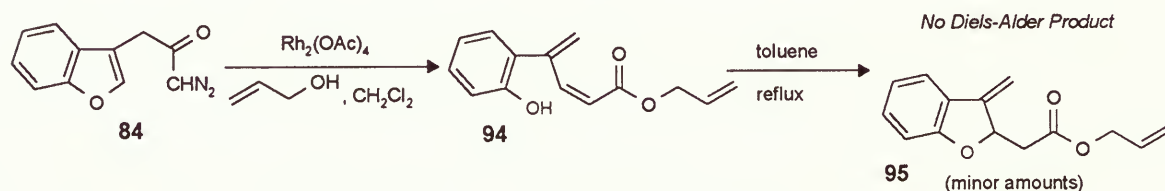
An intramolecular Michael addition was induced by refluxing a sample of the unsaturated ester **91** in toluene for 24 hours. Under these conditions, **92** was produced in 18% isolated yield after silica gel chromatography. It is worthwhile to point out that rearomatization of **92** to a benzofuranyl system does not take place *via* protonation of the exocyclic double bond, presumably since the oxonium cation resonance contributor effectively removes the aromaticity of the benzo fragment as illustrated in Scheme 19.⁷⁴



Scheme 19

The diene moiety of **91** makes it an attractive candidate for Diels-Alder chemistry. Attempts to trap the *Z*-diene using dienophiles such as maleic anhydride and dimethyl acetylenedicarboxylate (DMAD) were carried out under various conditions but no Diels-Alder product was isolated. It may be that more vigorous conditions (higher temperatures and/or pressure) or the use of catalysts may be required to affect this transformation and such studies should be undertaken.

Treatment of 1-diazo-3-(3-benzofuranyl)-2-propanone with rhodium acetate in the presence of allyl alcohol generated **94** in 77% yield. It is believed this compound would be an ideal candidate for an intramolecular Diels-Alder reaction and towards this end, the allylic ester (**94**) was refluxed in toluene for 2 days. No Diels-Alder product was obtained but rather the reaction mixture was shown to consist only of minor amounts of the intramolecular Michael product **95**, with the majority being the starting alkene **94**.



Scheme 20

(viii) *Rhodium Acetate Catalyzed Decomposition of 1-Diazo-3-(3-Benzothieryl)-2-Propanone (100)*

To date, there have not been any attempts to extend this intramolecular carbenoid insertion strategy to benzothiophene substrates. Therefore we first turned our attention to the chemistry carried out by the benzothieryl α -diazoketones containing a single

methylene tether. Once again the diazoketones were derived from the corresponding carboxylic acids.

3-Benzothiophene acetic acid was prepared by a procedure outlined by Blicke⁷⁸ and is shown in Scheme 21. Benzothiophene is treated with formalin saturated with hydrogen chloride to allow

for chloromethylation at C3. The resultant

chloromethylene compound

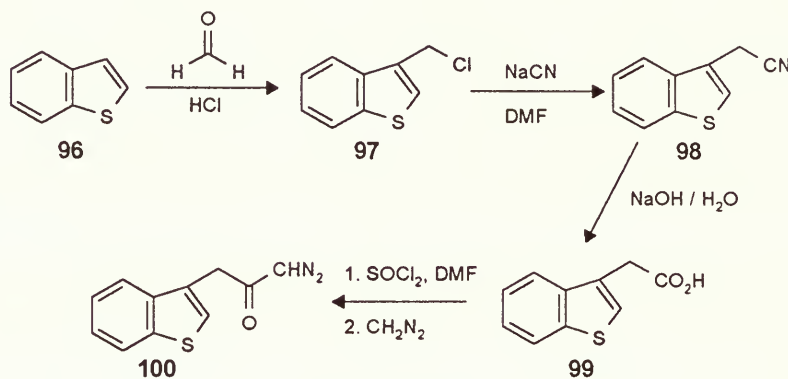
97 is then treated with sodium cyanide in DMF to

give **98** which then

hydrolyzed under basic conditions to give the desired 3-benzothiophene acetic acid (**99**).

The standard chlorination-diazomethane protocol was applied once again to give α -diazoketone **100**.

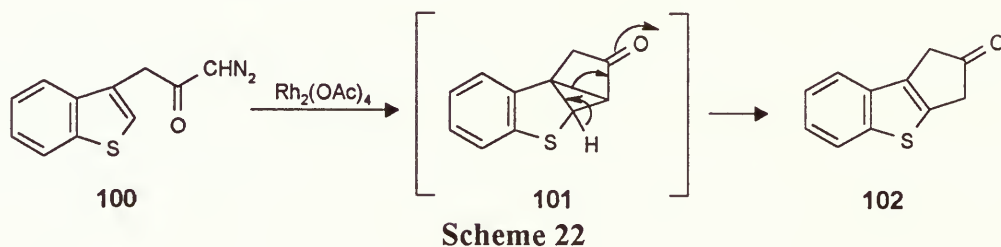
1-Diazo-3-(3-benzothiienyl)-2-propanone (**100**) was then decomposed in the presence of rhodium acetate to give 2,3-dihydro-1*H*-benzo[*b*]cyclopenta[*d*] thiophen-2-one **102** in 77% yield. It would appear that the intermediate cyclopropane **101** was unraveling *via* the enol mechanism seen previously in the thiophene series (for example, see the section on 1-diazo-3-(2-thienyl)-2-propanone **6**). Contrasting this behaviour to that exhibited by the analogous 1-diazo-3-(3-thienyl)-2-propanone **15**, one can rationalize



Scheme 21

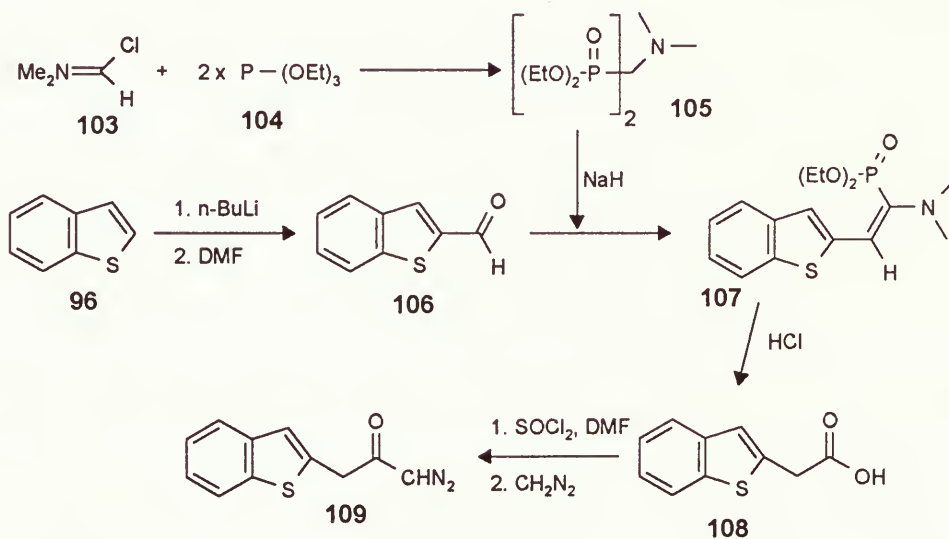
⁷⁸ Blicke, F. F., Sheets, D. G., *J. Am. Chem. Soc.*, **1948**, *70*, 3768.

that the [4+2]-cycloreversion seen for **15** is avoided since a similar unraveling for **101** would lead to the destruction of the aromaticity.



(ix) *Rhodium Acetate Catalyzed Decomposition of 1-Diazo-3-(3-Benzothiophenyl)-2-Propanone (109)*

The 2-benzothiophene acetic acid required for the preparation of 1-diazo-3-(2-benzothiophenyl)-2-propanone was prepared according to the protocol described by Degenhardt⁷⁹ as shown in Scheme 23.



Scheme 23

⁷⁹ Janda, M., Srogl, J., Korblova, E., Stibor, I., *Coll. Czech. Chem. Commun.*, 1980, 45, 1361; Degenhardt, C.R., *Synth. Commun.*, 1982, 12, 415.

Knowing that metallation of benzothiophene occurs exclusively at the 2-position, benzothiophene treated with *n*-butyllithium and trapped with DMF to allow for the formation of 2-thianaphthaldehyde (**106**). The one carbon chain extension of **106** was achieved using the modified Wittig reagent, dimethyl aminomethylene diphosphonate, to generate the phosphonate **107**, which was then hydrolyzed to give the desired 2-benzofuran acetic acid (**108**). 1-Diazo-3-(2-benzothieryl)-2-propanone (**109**) was prepared using standard procedure from its corresponding acid.

From the previous experience with the 2-thiophene system, we were expecting the intermediate cyclopropane to unravel *via* the enol pathway to give the cyclic ketone product **102**. However, catalytic decomposition of 1-diazo-3-(2-benzothiophene)-2-propanone gave not only the expected cyclic ketone **102** but also another crystalline product. Mass spectroscopy has shown this product to be a dimer with a molecular ion at $m/z = 376$.

Crystals grown from ethyl acetate were sent for x-ray crystallography to determine the structure. Unfortunately, the exact structure of this dimer has not been determined at this time. While the ^1H -NMR clearly shows two different benzothieryl moieties, preliminary x-ray crystallography work with crystals grown from ethyl acetate shows a symmetric structure with equivalent benzothiophene fragments (see Appendix III for a preliminary structure). At present, the structure refinement sits at about 15%. Clearly, either the x-ray structure is completely wrong or the crystals sent for analysis are of a minor reaction product. Work on this structure continues.

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CONCLUSION

The results from our study of intramolecular carbenoid insertion into 5-membered heteroaromatic systems shows that the resultant chemistry is dependent on the nature of the heteroatom, position of substitution, the length of the aliphatic tether and the substitution on the aromatic moiety. While others have shown that the rhodium acetate catalyzed chemistry of furan, thiophene and benzofuran tethered to an α -diazoketone by 2 or more methylenes is relatively consistent, the reactions of α -diazoketones derived from furanyl, thienyl, benzofuranyl and benzothienyl acetic acids varies from system to system.

Clearly the high degree of strain imparted to intermediate cyclopropanes by short methylene tethers allows for some rather atypical chemistry and access to a number of novel ring systems. We have shown that unraveling of these intermediate cyclopropanes can proceed *via* one of three distinct pathways: the [4+2]-cycloreversion, the “enol” mechanism or the vinylogous Wolff rearrangement.

Future Work:

The intramolecular attack of α -keto carbenoids into pyrrole systems has been reported previously by Galeazzi⁸⁰ and by Jefford.⁵² In these cases, however, the tethered diazoketone is connected to the pyrrole through the nitrogen. Treatment with copper catalysts has generally promoted C-H insertion at the α -position of the pyrrole. Introduction of a tethered diazoketone at either the 2- or 3-position of pyrrole and use of a rhodium catalyst should allow for cyclopropanation and, hence, access to different ring

⁸⁰ Galeazzi, E., Guzman, A., Pinedo, A., Saldana, A., Torre, D., Muchowski, J.M., *Can. J. Chem.* **1983**, *61*, 454.

systems. Work with these systems and analogous indole systems are currently being conducted in the Capretta lab.

A natural extension of the intramolecular carbenoid insertion work involves the use of such carbocycles as cyclopentadiene and dimethylfulvene in place of the heteroaromatic moiety. Work by Smith⁷¹ on analogous cyclopentenyl diazoketones has shown these systems to undergo cyclopropanation followed by vinylogous Wolff rearrangements. Introduction of conjugated double bonds may alter the electronics of the intermediate cyclopropane and allow for access to different ring systems *via* Hudlicky-type chemistry.⁸¹

Preliminary calculations performed have revealed some interesting trends and have, for the most part, been able to mirror what is observed experimentally. Unfortunately, comparisons between thienyl and furanyl systems have been inconsistent. In an effort to reproduce computationally the differences between the heterocyclic series, the calculations should be repeated at an *ab initio* level.

⁸¹ Hudlicky, T., Sheth, J. P., Gee, V., Barnvos, D., *Tetrahedron Lett.*, **1979**, 4889; Hudlicky, T., Kwart, L. D., Tiedje, M. H., Ranu, B. C., Short, R. P., Frazier, J. O., Rigby, H. L., *Synthesis*, **1986**, 716.

EXPERIMENTAL

APPARATUS AND MATERIALS

Proton magnetic resonance (^1H -NMR) spectra were recorded on either a Bruker AC-200 FT spectrometer (at 200.13 MHz) or a Bruker Avance DPX-300 Digital FT spectrometer (at 300.13 MHz) with chloroform- d as the solvent unless otherwise noted. Unless specified, the usual internal references were tetramethylsilane (TMS) or chloroform. The abbreviations (s)=singlet, (d)=doublet, (t)=triplet, (q)=quartet, (m)=multiplet and (br)=broad are used in the description of the spin-spin splitting pattern present in the spectra.

The natural abundance carbon-13 magnetic resonances (^{13}C -NMR) were recorded on a Bruker Avance DPX-300 Digital FT spectrometer (at 75.03 MHz) using chloroform- d as the solvent and internal reference unless otherwise noted. All ^{13}C spectra were broad band decoupled.

Low resolution mass spectra (MS) and high resolution mass spectra (HRMS) were obtained on Carlo Erba/Kratos HRGS/MS Concept 1S double focusing mass spectrometer interfaced to a Kratos DART acquisition system and a SUN SPARC workstation. Samples were introduced through a direct inlet system. Ions were generated using electron impact (EI).

Crystallographic structure determinations were carried out on a Rigaku AFC7R diffractometer with graphite-monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$). The crystals were cooled with an Oxford Cryosystem Cooler.⁸² The structures were solved

⁸² Cosier, J, Glazer A.M. *J. Appl. Crystallogr.* **1986**, *19*, 105.

with direct methods, SHELXS-90⁸³ and refined with full-matrix least-squares refinement on F^2 with SHELXL-93.⁸⁴ R -values; $R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$, and $wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$. Further details of the crystal structure investigation can be obtained from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Cambridge CB2 1EW, U.K.

Energy-minimized structures were generated using MMX force field calculations derived from MM2. The calculations were carried out using the program Hyperchem.⁸⁵ Restricted Hartree-Fock (RHF) calculations were carried out with the PM3 Hamiltonian of the general purpose molecular orbital computational package Spartan.⁶⁵ Optimizations were carried out with the PM3 default parameters.

Melting points were recorded on a Kofler Hot Stage melting point apparatus and are uncorrected.

Starting materials were purchased from Aldrich Chemical Co. and used without further purification.

Tetrahydrofuran (THF) was dried by refluxing and distilling from sodium and benzophenone under dry nitrogen. THF was collected from the distillation apparatus as required. *N,N*-Dimethylformamide (DMF) was refluxed and subsequently distilled from BaO. All other solvents employed were reagent grade, purchased from Caledon Laboratory Ltd.

⁸³ Sheldrick, G.M. *Acta Crystallogr. Sect. A* **1990**, *46*, 467.

⁸⁴ Sheldrick, G.M. SHELXL-93; Program for crystal structure refinement, Gottingen, 1993.

⁸⁵ HyperChem, v. 3.0, Hypercube Inc., 1993.

NMR solvents chloroform-d, methylene chloride-d₂, dimethylsulfoxide-d₆ and benzene-d₆ were purchased from Isotec Inc. and stored over molecular sieves (4Å) prior to use.

Column chromatography was performed by the "flash" method of Still, Kahn, and Mitra.⁸⁶ The silica gel used for column chromatography (5.0% of 100 mesh up; 47.6% of 100-200 mesh and 47.4% of 200 mesh down) was purchased from Aldrich Chemical Co.. Silica gel 60 F₂₅₄ (E. Merck Co.) plates of 0.2 mm thickness were used for analytical thin layer chromatography (TLC). Visualization was achieved using a UV lamp at 254 nm or *via* treatment of the TLC with either a molybdcic acid spray (20 g of molybdcic acid and 15 g of ceric sulphate dissolved in 1 litre of 10% sulphuric acid); a vanillin spray (5 g of vanillin dissolved in 200 ml of 95% ethanol followed by addition of 5 ml of sulfuric acid slowly); a potassium permanganate dip (12.5 g of potassium permanganate and 62.5 g of sodium carbonate added to 1.25 litre of water) or a ninhydrin spray (0.2% ninhydrin in ethanol) followed by heating.

SYNTHETIC PROTOCOLS

Preparation of alcohol free diazomethane solution⁶²

An ethereal solution of diazomethane free from ethanol is essential for the preparation of diazoketones. The following procedure was carried out in glassware with clear glass joints.

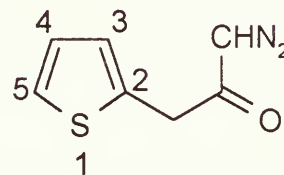
Potassium hydroxide (6g) was dissolved in 10 ml of water and 35 ml of carbitol (di(ethyleneglycol) ethyl ether) in a 250 ml round bottom flask. The basic solution was

⁸⁶ Still, W. C., Kahn, M., Mitra, A. J., *J. Org. Chem.*, 1978, 43, 2923.

stirred and heated to 70°C in an oil bath, with distillation apparatus connected to a 500 ml round bottom flask in an ice-salt bath. An ethereal solution (125 ml) of Diazald (*N*-methyl-*N*-nitrosotoluene-*p*-sulfonamide) was added slowly, over 20 minutes. Rinse the dropping with 2 x 20 ml portion of ether and added to the reaction flask. Ether was added to the reaction flask until the distillate was colourless. The bright yellow diazomethane solution is stored under potassium hydroxide pellets for one day to remove water. The anhydrous solution is decanted and stored in the freezer.

Synthesis of 1-Diazo-3-(2-Thienyl)-2-Propanone (6)

2-Thiophene acetic acid (600 mg, 4.22 mmol) was dissolved in 50 ml of dry CH₂Cl₂, and stirred in an ice-salt bath under an argon atmosphere. Oxalyl chloride (1.1 ml, 12.6 mmol) was added followed by two drops of



dimethylformamide (DMF). The reaction mixture was stirred for a further 30 minutes, then warmed up to room temperature slowly. The reaction mixture was evaporated under reduced pressure to give a brown residue. Residual oxalyl chloride was removed by redissolving the residue in 3 x 15 ml of dry benzene followed by evaporation under reduced pressure. The crude acid chloride was dissolved in 25 ml of benzene and added dropwise over 10 minutes to 25 ml of a dry ethereal diazomethane solution (about 38 mmol) cooled to 0°C. The reaction mixture was stirred under argon atmosphere and allowed to warm up to room temperature over a 2 hour period. The reaction mixture was then evaporated under a reduced pressure to give a brown oil. The diazoketone (6) was

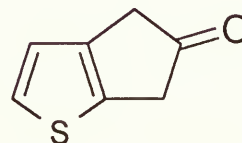
purified by column chromatography on silica gel using 50% dichloromethane in hexanes as eluent. The product was isolated as a yellow oil. TLC with dichloromethane as the eluent showed the product with an $R_f = 0.46$. The yield was 72.8% (511 mg, 3.08 mmol). The compound showed:

^1H NMR : (CDCl₃, 300 MHz); δ 3.78 (s, 2H, CH₂), 5.23 (s, 1H, CHN₂), 6.89 (d, 1H, $J=3.2$ Hz, C3H), 6.95 (dd, 1H, $J=5.0$ and 3.7 Hz, C4H), 7.20 (d, 1H, $J=5.3$ Hz, C5H).

^{13}C NMR : (CDCl₃, 75 MHz); δ 41.53 (CH₂), 54.62 (CHN₂), 125.38 (C_{Ar}), 127.11 (C_{Ar}), 127.16 (C_{Ar}), 135.63 (C_{Ar}), 191.37 (CO).

Synthesis of 5,6-Dihydro-4*H*-Cyclopenta[*b*]Thiophen-5-one (3)

1-Diazo-3-(2-thienyl)-2-propanone (6) (250 mg, 1.5 mmol) was dissolved in 50 ml of dry dichloromethane and stirred under an argon atmosphere at room temperature. A catalytic amount (approximately 1 mg) of rhodium (II) acetate was added and the resultant solution stirred for 4 hours. The solvent was then evaporated under reduced pressure to yield a brown oil which was purified by column chromatography on silica gel using 30% dichloromethane in hexanes. The product was isolated as a pale yellow crystalline solid which could be further purified by sublimation or recrystallized from benzene. TLC with 50% dichloromethane in hexanes as the eluent showed the product with an $R_f = 0.42$. The yield was 70% (145 mg, 1.1 mmol). The compound numbering appears in Figure 2. The compound showed:



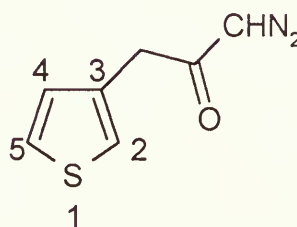
^1H NMR : (CDCl₃, 300 MHz) δ 3.40 (2H, s, C4H₂), 3.53 (2H, s, C6H₂), 6.96 (1H, d, $J=4.9$ Hz, C2H), 7.24 (1H, d, $J=5.2$ Hz, C1H).

^{13}C NMR : (CDCl₃, 75 MHz) δ 41.74 (C4), 41.80 (C6), 122.77 (C1), 126.60 (C2), 135.77 (C7), 139.54 (C3), 214.61 (C5).

MS [EI⁺]: m/z (RI%); 138 [M]⁺ (29), 110 [M-CO]⁺ (100).

HRMS: for C₇H₆OS: calculated 138.0139; observed 138.0142.

Synthesis of 1-Diazo-3-(3-thienyl)-2-propanone (15)



3-Thiophene acetic acid (600 mg, 4.22 mmol) was dissolved in 50 ml of dry CH₂Cl₂ and stirred in an ice-salt bath under an argon atmosphere. Oxalyl chloride (0.42 ml, 0.61 g, 4.8 mmol) was added followed by two drops of dimethylformamide (DMF). The reaction mixture was evaporated under reduced pressure to give a brown residue. Residual oxalyl chloride was removed by redissolving the residue in 3 x 15 ml of dry benzene followed by evaporation under reduced pressure. The crude acid chloride was dissolved in 25 ml of benzene and added dropwise over 10 minutes to 25 ml of a dry ethereal diazomethane solution (about 38 mmol) cooled to 0°C. The reaction mixture was stirred under argon atmosphere and allowed to warm up to room temperature over a 2 hour period. The reaction mixture was then evaporated under a reduced pressure to give a brown oil. The diazoketone (15) was purified by column chromatography on silica gel using 50% dichloromethane in hexanes as eluent and yielded a yellow oil. TLC of the product with dichloromethane gave an $R_f=0.36$. The yield was 78.3% (549 mg, 3.30 mmol). The compound showed:

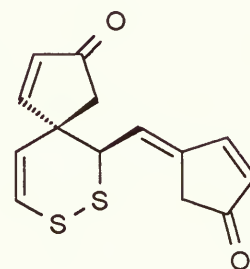
^1H NMR : (CDCl_3 , 300 MHz); δ 3.60 (2H, s, CH_2), 5.15 (1H, s, CHN_2), 6.95 (1H, d, $J=4.9$ Hz, C4H), 7.1 (1H, d, $J=2.1$ Hz, C2H), 7.27 (1H, d, $J=7.0$ Hz, C5H).

^{13}C NMR : (CDCl_3 , 75 MHz); δ 41.13 (CH_2), 54.56 (CHN_2), 123.07 (C_{Ar}), 126.18 (C_{Ar}), 128.30 (C_{Ar}), 134.17 (C_{Ar}), 191.43 (CO).

Synthesis of Spiro-Disulphide (20) via the Rhodium (II) Acetate

Catalyzed Decomposition of 1-Diazo-3-(3-Thienyl)-2-Propanone

(15)



1-Diazo-3-(3-thienyl)-2-propanone (15) (250 mg, 1.5

mmol) was dissolved in 50 ml of dry dichloromethane and stirred under an argon atmosphere at room temperature. A catalytic amount (approximately 1 mg) of rhodium (II) acetate was added to the reaction and the resultant solution was stirred for 4 hours. The solvent was evaporated under reduced pressure to yield a brown oil. The reaction mixture was then purified by column chromatography on silica gel using 30% dichloromethane in hexanes as eluent yielding (20) as a pale yellow crystalline solid. The product was recrystallized from benzene. TLC with 50% ethyl acetate in hexanes as the eluent showed the product with an $R_f = 0.41$. The yield was 85% (352 mg, 1.3 mmol). The compound numbering appears in Figure 3. The compound showed:

^1H NMR : (CDCl_3 , 300 MHz) δ 2.35 and 2.46 (each 1H, d, $J=19.2$ Hz, C_{12}H_2), 2.96 and 3.05 (each 1H, d, $J=21.1$ Hz, C_5H_2), 3.90 (1H, d, $J=9.8$ Hz, C7H), 5.66 (1H, d, $J=10.4$ Hz, C13H), 5.76 (1H, d, $J=9.9$ Hz, C6H), 6.18 (1H,

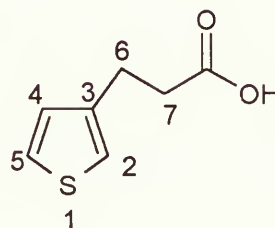
d, $J=5.4$ Hz, C10H), 6.41 (1H, d, $J=6.0$ Hz, C2H), 6.50 (1H, d, $J=10.4$ Hz, C14H), 7.59 (1H, d, $J=5.4$ Hz, C9H). 8.00 (d, 1H, $J=5.7$ Hz, C3H).

^{13}C NMR : (CDCl₃, 75 MHz) δ 39.82 (C5), 43.88 (C7), 47.00 (C12), 47.63 (C8), 121.95 (C14), 122.46 (C6), 128.38 (C13), 133.13 (C10), 137.01 (C2), 140.08 (C4), 152.41 (C9), 167.51 (C3), 204.75 (C11 or C1), 206.81 (C1 or C11).

MS [EI⁺]: m/z (RI%); 276 [M]⁺ (24), 244 [M-S]⁺ (24), 138 [monomer]⁺ (100), 110 [monomer - CO]⁺ (53), 84 (84).

HRMS: for C₁₄H₁₂O₂S₂; calculated 276.0279; observed 276.0266.

Photochemical decomposition of 1-Diazo-3-(3-thienyl)-2-propanone (15) to 3-(3-thienyl)Propanoic acid



1-Diazo-3-(3-thienyl)-2-propanone (**15**) (102 mg, 0.63 mmol) was dissolved in 100 ml of dry dichloromethane. The stirred solution was then photolyzed at room temperature using a low pressure mercury lamp for 3 hours. The solvent was evaporated under reduced pressure and the product was purified by column chromatography on silica gel using 20% ethyl acetate in hexanes as eluent. The product was isolated as a pale yellow solid. TLC with 50% ethyl acetate in hexanes as the eluent showed the product with an $R_f = 0.50$. The yield was 30% (32.6 mg, 0.19 mmol). The compound showed:

^1H NMR : (CDCl_3 , 300 MHz); δ 2.66 (2H, t, $J=7.5$ Hz, C7H), 2.95 (2H, t, $J=7.6$ Hz, C6H), 6.93 (1H, d, $J=4.6$ Hz, C5H), 6.97 (1H, broad s, C2H), 7.22 (1H, dd, $J=1.8, 2.8$ Hz, C4H).

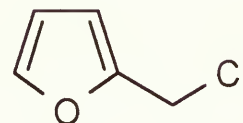
^{13}C NMR : (CDCl_3 , 75 MHz); δ 25.09 (C6), 34.81 (C7), 120.72 (C2), 125.73 (C5), 127.88 (C4), 140.40 (C3), 178.86 (COOH).

MS [EI $^+$]: m/z (RI%); 156 [M] $^+$ (63), 111 [$\text{M}-\text{COOH}$] $^+$ (58), 97 [$\text{M}-\text{CH}_2\text{COOH}$] $^+$ (100).

HRMS: for $\text{C}_7\text{H}_8\text{O}_2\text{S}$; calculated 156.0245; observed 156.0246

Synthesis of α -Furfuryl Chloride (35)⁶⁹

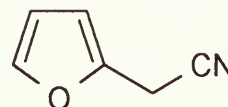
Freshly distilled furfuryl alcohol (23 ml, 26 g, 270 mmol) and pyridine (30 ml, 29.4 g, 300 mmol, 1.1 eq.) in 25 ml of dry ether was stirred in a salt-ice bath under argon atmosphere. To this solution was added thionyl chloride (20 ml, 32.6 g, 0.27 mole) in 20 ml of dry ether over 1.5 hours. The reaction mixture was stirred for an additional 0.5 hour after the complete addition of the thionyl chloride. The top ether layer was decanted and the greenish-black residue was extracted with 4 x 50 ml portions of cold ether while breaking up the solid with a glass rod. The ether extracts were combined and washed thoroughly with 50 ml of a cold 50% KOH solution. Note that ice was added periodically to maintain the temperature. The ether layer was then dried with Na_2SO_4 and concentrated under reduced pressure to about 50 ml. The remainder of the ether is removed by fractional distillation under reduced



pressure. The product (**35**) distilled about 43-44°C @ 21 mm Hg as a colourless oil. (lit.⁶⁹ 49.1°C @ 26 mm Hg) which decomposes rapidly on exposure to air and water. The yield was 51% (16.1 g, 139 mmol) and was used immediately in the next reaction.

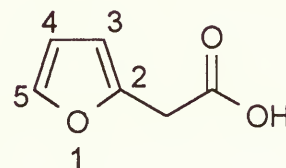
Synthesis of 2-Furfurylacetonitrile (**36**)⁶⁸

To a stirred solution of potassium cyanide (9.3 g, 190 mmol) in 50 ml of (DMF) heated to 50°C was added furfuryl chloride (**35**)(14 g, 120 mmol). The temperature was raised to 90°C slowly and stirred for 2 hours at which time the reaction mixture was cooled to room temperature and water added to dissolve inorganic salts. The aqueous layer was extracted with 4 x 40 ml ether and the combined ether extracts were washed with 3 x 30 ml of brine. The ether layer was dried with MgSO₄ and evaporated under a reduced pressure to yield a brown oil. The crude product was purified by vacuum distillation 43-45°C (~0.1 mm Hg) to give **36** as a colourless pungent oil and used immediately in the next step. The yield was 77% (10 g, 90 mmol).



Synthesis of 2-Furan acetic acid (**37**)

2-Furfurylacetonitrile (**36**)(9.6 g, 90 mmol) was added to an aqueous solution of NaOH (4M, 75 ml). Sufficient ethanol was



then added in order to give a homogenous solution. The reaction mixture was refluxed gently for 6 hours then cooled and the ethanol evaporated under a reduced pressure. The residue was acidified (hydrochloric acid) and extracted with ethyl acetate with 3 x 50 ml

portions. The combined ethyl acetate extracts were dried with Na_2SO_4 and evaporated under a reduced pressure to give the crude acid. The acid was then purified by recrystallization from CH_2Cl_2 /hexanes. The yield was 64.4% (7.3 g, 58 mmol). The compound showed:

^1H NMR: (CDCl_3 , 300 MHz); δ 3.72 (2H, s, CH_2), 6.24 (1H, d, $J=3.2$ Hz, C3H), 6.33 (1H, dd, $J=1.9$, 3.2 Hz, C4H), 7.36 (1H, d, $J=1.9$ Hz, C5H), 11.67 (1H, broad, COOH).

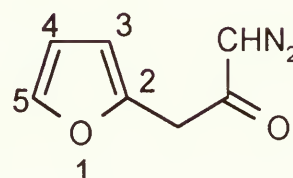
^{13}C NMR: (CDCl_3 , 75 MHz); δ 33.72 (CH_2), 108.48, 110.58 (C3 and C4), 142.33 (C5), 146.76 (C2), 175.66 (COOH).

MS [EI $^+$]: m/z (RI%); 126 [M] $^+$ (19), 81 [$\text{M}-\text{COOH}$] $^+$ (100).

HRMS: for $\text{C}_6\text{H}_6\text{O}_3$: calculated 126.0317; observed 126.0320

Synthesis of 1-Diazo-3-(2-Furanyl)-2-Propanone (8)

2-Furan acetic acid (37)(540 mg, 4 mmol) was dissolved in 50 ml of dry dichloromethane and stirred in an ice bath under



argon atmosphere. Oxalyl chloride (0.40 ml, 4.5 mmol) was added to the reaction mixture followed by a catalytic amount of DMF (2 drops). The reaction mixture was stirred for 30 minutes, then removed from the ice bath and stirred at room temperature for 2 hours. The reaction mixture was then evaporated under reduced pressure to give a brown residue. Residual oxalyl chloride was removed by redissolving the residue in 3 x 25 ml of dry benzene and evaporating under reduced pressure. The crude acid chloride was then redissolved in 25 ml of dichloromethane then added over 10 minutes to 50 ml of an ice-

cold solution of dry ethereal diazomethane (approximately 20 mmol) and stirred under an argon atmosphere for 2 hours. The reaction mixture was evaporated under reduced pressure to give crude diazoketone as a brown oil. The diazoketone was purified by column chromatography on silica gel using 20% ethyl acetate-hexanes as eluent yielding **8** as a yellow oil. TLC of the product with 33% ethyl acetate-hexanes mixture gave an $R_f=0.36$. The yield was 82% (493 mg, 3.29 mmol). The compound showed:

^1H NMR: (CDCl_3 , 300 MHz); δ 3.63 (2H, s, CH_2), 5.19 (1H, s, CHN_2), 6.20 (1H, d, $J=3.1$ Hz, C3H), 6.33 (1H, dd, $J=1.6$ Hz, 3.1 Hz, C4H), 7.36 (1H, d, $J=1.8$ Hz, C5H).

^{13}C NMR: (CDCl_3 , 75 MHz); δ 40.31 (CH_2), 54.55 (CHN_2), 108.56 (C3), 110.74 (C4), 142.35 (C5), 148.27(C2), 190.24 (C=O)

MS [EI $^+$]: m/z (RI%); 150 [M] $^+$ (30), 81 [M-COOH] $^+$ (100)

HRMS [EI $^+$]: for $\text{C}_7\text{H}_6\text{N}_2\text{O}_2$: calculated 150.0429, observed 150.0446

Rhodium(II) Acetate Catalyzed Decomposition of 1-Diazo-3-(2-Furanyl)-2-Propanone (**8**)

To a stirred solution containing 1-diazo-3-(2-furanyl)-2-propanone (**8**)(100 mg, 0.67 mmol) in 100 ml of dichloromethane and 0.5 ml of water is added rhodium(II) acetate (approximately 1 mg) and the reaction was stirred for 1 hour. The reaction solution was then concentrated to ~10 ml and filtered through a small plug of silica gel. The silica gel plug is then washed several times with ethyl acetate. The eluent was combined and evaporated under reduced pressure to give the crude products which were separated by gradient column chromatography using ethyl acetate-hexanes as eluent

yielding 6a-methyl-2,3,3a,6a-tetrahydrofuro[2,3-b]furan-2-one (**44**) in 15% (14.2 mg, 0.10 mmol) and 2-(2-methyl-3-furanyl)acetic acid (**43**) in 60% (56.3 mg, 0.40 mmol).

(**44**) showed:

TLC: $R_f=0.24$ (dichloromethane as the eluent)

^1H NMR: (CDCl_3 , 300 MHz): δ 1.74 (3H, s, CH_3), 2.58 (1H, dd, $J=1.6$ Hz, 18.1 Hz, CH_2), 2.86 (1H, dd, $J=9.1$ Hz, 18.1 Hz, CH_2), 3.40 (1H, dq, $J=1.6$ Hz, 9.1 Hz, C3H), 4.99 (1H, t, $J=2.4$ Hz, C4H), 6.33 (1H, t, $J=2.4$ Hz, C5H)

^{13}C NMR: (CDCl_3 , 75 MHz): δ 23.55 (CH_3), 34.79 (CH_2), 46.52 ($\text{CH}-\text{CH}_2-\text{CO}$), 104.67 ($\text{CH}=\text{CH}-\text{O}$), 116.43 ($\text{C}-\text{CH}_3$), 144.99 ($\text{CH}=\text{CH}-\text{O}$), 173.87 ($\text{C}=\text{O}$)

MS[EI $^+$]: m/z (RI%); 140 [M] $^+$ (100), 98 [$\text{M}-\text{CH}_2\text{C}=\text{O}$] $^+$ (90), 97 [$\text{M}+1-\text{CO}_2$] $^+$ (66), 81 [$\text{M}-\text{CH}_3-\text{CO}_2$] (69).

HRMS: for $\text{C}_6\text{H}_8\text{O}_3$: calculated 140.0473; observed 140.0475

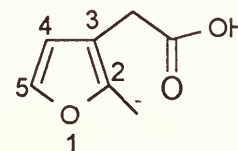
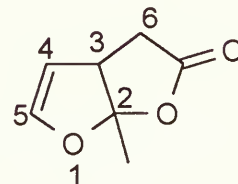
(**43**) showed:

TLC: $R_f=0.28$ (ethyl acetate as the eluent)

^1H NMR: (CDCl_3 , 300 MHz): δ 2.22 (3H, s, CH_3), 3.38 (2H, s, CH_2), 6.28 (1H, s, $\text{CH}=\text{CH}-\text{O}$), 7.24 (1H, s, $\text{CH}=\text{CH}-\text{O}$)

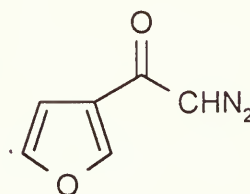
^{13}C NMR: (CDCl_3 , 75 MHz): δ 11.82 (CH_3), 31.05 (CH_2), 111.02, 111.92, 140.30, 149.24(C_{Ar}), 176.85 ($\text{C}=\text{O}$)

MS[EI $^+$]: m/z (RI%); 140 [M] $^+$ (55), 95 [$\text{M}-\text{COOH}$] $^+$ (100).



Synthesis of 1-(3-Furyl)-2-Diazo-1-Ethanone

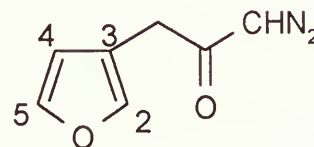
A stirred solution of 3-furoic acid (452 mg, 4 mmol) in 30 ml dichloromethane under argon atmosphere was cooled in an ice bath. The mixture was then treated with oxalyl chloride (0.42 ml, 0.61 g, 4.8 mmol) and a catalytic amount of dimethylformamide (2 drops). The resultant acid chloride was added to an ethereal diazomethane solution (25 ml, ~38 mmol). The reaction mixture was then warmed to room temperature and stirred for an additional 2 hours at which time the solvent evaporated under reduced pressure to give a yellow residue. The residue is re-dissolved in ether (50 ml). The solution is then filtered and the ether evaporated to give 500 mg of crude diazoketone. While the crude diazoketone can be purified *via* column chromatography on silica gel using 50% ether-hexanes mixture as eluent, the crude diazoketone may be used in the subsequent reaction. TLC of the product with 50% ether-hexanes mixture gave an $R_f=0.29$. The compound showed:



$^1\text{H NMR}$: (CDCl_3 , 300 MHz): δ 5.63 (1H, s, CHN_2), 6.61 (1H, d, $J=2.2$ Hz, C4H), 7.37 (1H, d, $J=1.9$ Hz, C5H), 7.87 (1H, s, C2H).
 $^{13}\text{C NMR}$: (CDCl_3 , 75 MHz): δ 54.58 (CHN_2), 108.05 (C4), 126.12 (C3), 144.08 (C5), 144.70 (C2), 180.38 (C=O)

Synthesis of 1-Diazo-3-(3-Furanyl)-2-Propanone (52)

A stirred solution of 1-(3-furyl)-2-diazo-1-ethanone (150 mg, 1.10 mmol) in 200 ml dichloromethane, 0.5 ml of water and 2.0 ml of triethyl amine was irradiated at room temperature with a low pressure



mercury lamp for 3 hours. Water (30 ml) was then added to the reaction solution. The aqueous layer is then collected and the organic layer extracted with 3 x 50 ml of water. The combined aqueous extracts were acidified with concentrated hydrochloric acid (congo red indicator). The product was then extracted with 4 x 50 ml ethyl acetate. The combined organic extracts were dried with magnesium sulfate and evaporated under reduced pressure to give 48 mg (0.38 mmol) of crude 3-furan acetic acid.

Crude 3-furan acetic acid (48 mg, ~0.4 mmol) was dissolved in 10 ml dichloromethane under argon atmosphere and 0.1 ml of thionyl chloride was added. The reaction was then refluxed for 0.5 hour at which time the solution is cooled to room temperature and added to 10 ml of an ethereal diazomethane solution (2 mmol). The mixture was stirred for 2 hours at which time the solvent was evaporated under a reduced pressure. The resultant diazoketone was purified by column chromatography on silica gel using 33% hexanes in dichloromethane as eluent yielding a yellow oil. TLC of **52** with 33% hexanes in dichloromethane gave an $R_f=0.26$. The yield was 14.5% (24 mg, 0.16 mmol). The compound showed:

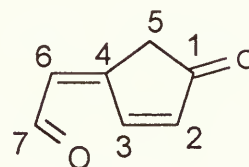
^1H NMR: (CDCl_3 , 300 MHz): δ 3.42 (2H, s, CH_2), 5.22 (1H, s, CHN_2), 6.31 (1H, d, $J=3.1$ Hz, C4H), 7.34 (1H, d, $J=3.1$ Hz, C5H), 7.38 (1H, s, C2H).

^{13}C NMR: (CDCl_3 , 75 MHz): δ 837.12 (CH_2), 54.49 (CHN_2), 111.25 (C4H), 117.85 (C3), 140.60 (C5), 143.43 (C2), 192.34 (C=O).

MS[EI $^+$]: m/z (RI%); 150 $[\text{M}]^+$ (4), 136 $[\text{M}-\text{N}_2]^+$ (80), 94 $[\text{M}-\text{C}(\text{O})\text{N}_2]^+$ (100), 81 $[\text{M}+1-\text{C}(\text{O})\text{CHN}_2]^+$ (99)

Synthesis of 2-(4-Oxo-2-cyclopentenyliden)acetaldehyde (54)

Rhodium (II) acetate (approximately 1 mg) is added to a stirred solution of 1-diazo-3-(3-furanyl)-2-propanone (**52**) (100 mg, 0.66 mmol) in 50 ml of dichloromethane under argon atmosphere.



The reaction is stirred for 1 hour at which time the solvent is evaporated under reduced pressure to give >90% yield of keto-aldehyde (**54**) as the only product (as evidenced by NMR). Attempts to purify **54** using silica gel were unsuccessful due to decomposition. The product showed:

^1H NMR: (CDCl_3 , 300 MHz): δ 3.14 (2H, s, C5H_2), 6.14 (1H, d, $J=7.0$ Hz, C6H), 6.70 (1H, d, $J=5.7$ Hz, C2H), 8.55 (1H, d, $J=5.7$ Hz, C3H), 10.14 (1H, d, $J=7.2$ Hz, C7H)

^{13}C NMR: (CDCl_3 , 75 MHz): δ 39.66 (C5), 124.49 (C2), 141.47 (C6), 151.68 (C3), 154.74 (C4), 188.51 (C7), 202.15 (C1).

MS[EI $^+$]: m/z (RI%); 122 [M] $^+$ (100), 94 [M-CO] $^+$ (37), 66 [M-2CO] $^+$ (37)

HRMS: for $\text{C}_7\text{H}_6\text{O}_2$: calculated 122.0368, observed 122.0372.

Synthesis of Carbethoxymethylene triphenylphosphorane⁸⁷



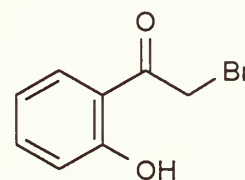
Triphenylphosphorane (13.6 g, 52 mmol) was suspended in 20 ml of benzene in a 250 ml Erlenmeyer flask and heated to solution. The solution was then cooled to $\sim 5^\circ\text{C}$ using an ice bath, treated with bromo ethyl acetate (7.75 ml, 70 mmol, 11.625 g) and allowed to stir over 18 hours gradually warming to room

⁸⁷ Isler, O., Gutmann, H., Montavon, M., Rüegg, R., Ryser, G., Zeller, P., *Helv. Chim. Acta*, 1957, 40, 1242.

temperature. The white precipitate formed was then filtered, washed with 3 x 30 ml ether, and dried under vacuum. The salt formed was dissolved in 100 ml water, treated with 3 drops of phenolphthalein and titrated with 3M sodium hydroxide solution until a pale pink colour persisted. The white precipitate collected by filtration and was washed with water until the filtrate was colourless. The crude product was dried under vacuum. Recrystallization from ethyl acetate/hexanes gave white crystals of carbethoxymethylene triphenylphosphine. The overall yield was 76% (13.8 g, 39.6 mmol).

Synthesis of ω -Bromo-2-hydroxyacetophenone (76)⁸⁸

To a stirred solution of *o*-hydroxyacetophenone (29 ml, 32.8 g, 240 mmol) in 100 ml glacial acetic acid, a solution of bromine (12 ml, 37.2 g, 230 mmol) in 30 ml glacial acetic acid was added slowly over 3 hours. The reaction solution was stirred for an hour after addition is completed. The reaction solution is then poured into 150 ml of water and extracted with 4 x 80 ml chloroform. The combined organic extracts are dried with sodium sulfate and evaporated under a reduced pressure. The crude product is then purified *via* vacuum distillation (b.p. 102°C @ approximately 0.4 mm Hg) and collected as a yellow solid. The product (76) can be purified further by dissolving in hexanes (10 ml per gram) and recrystallizing to obtain pale yellow crystals. The compound showed:



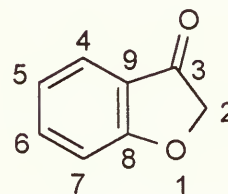
mp: 46°C

⁸⁸ Buu-Hoï, N.P., Lavit, D., *J. Chem. Soc.*, 1955, 18.

^1H NMR: (CDCl_3 , 300 MHz): δ 4.43 (2H, s, CH_2Br), 6.92 (1H, t, $J=7.6$ Hz, ArH), 7.00 (1H, d, $J=8.4$ Hz, ArH), 7.15 (1H, t, $J=7.8$ Hz, ArH), 7.73 (1H, d, $J=8.2$ Hz, ArH), 11.71 (1H, s, ArOH)

^{13}C NMR: (CDCl_3 , 75 MHz): δ 29.93 (CH_2Br), 117.02, 118.94, 119.27, 130.32, 137.43 (5 C_{Ar}), 163.19 (C_{ArOH}), 196.98 (C=O).

MS[EI $^+$]: m/z (RI%); 214 [M] $^+$ (11), 121 [$\text{M}-\text{CH}_2\text{Br}$] $^+$ (100)



Synthesis of 3-coumaranone (77)⁷⁷

ω -Bromo-2-hydroxyacetophenone (10 g, 46.5 mmol) and anhydrous sodium acetate (15 g, 183 mmol) are dissolved in 100 ml of dry ethanol and refluxed for 1 hour. The reaction mixture is then poured into 100 ml of 50% sodium chloride solution to give a fine precipitate of 3-coumaranone. The precipitate is filtered, washed with 2 x 20 ml of cold water and dried under vacuum to give 3-coumaranone (77) in 98% yield (6.20 g, 45 mmol). TLC of the product with dichloromethane gave $R_f=0.32$. The compound showed:

^1H NMR: (CDCl_3 , 300 MHz): δ 4.59 (2H, s, CH_2), 7.06 (1H, t, $J=7.5$ Hz, C5H), 7.11 (1H, d, $J=8.5$ Hz, C4H), 7.58 (1H, t, $J=7.5$ Hz, C6H), 7.64 (1H, d, $J=7.7$ Hz, C7H).

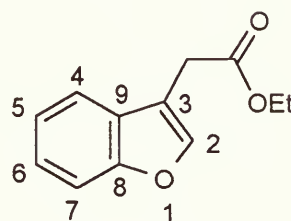
^{13}C NMR: (CDCl_3 , 75 MHz): δ 74.64 (CH_2), 113.62 (C4), 121.14 (C9), 121.94 (C5), 124.03 (C6), 137.81 (C7), 173.95 (C8), 199.81 (C=O)

MS[EI $^+$]: m/z (RI%); 134 [M] $^+$ (100), 105 [$\text{M}+1-\text{CH}_2\text{O}$] $^+$ (83), 76 [$\text{M}-\text{C}(\text{O})-\text{CH}_2$] $^+$ (63).

HRMS: for $\text{C}_8\text{H}_6\text{O}_2$: calculated 134.0368; observed 134.0371

Synthesis of Ethyl-3-Benzofuran acetate (**82**)⁷⁶

A solution of 3-coumaranone (**77**) (1.6 g, 11 mmol) and carbethoxymethylene triphenylphosphorane (4.5 g, 12 mmol) in 20 ml of xylenes was refluxed for 24 hours. The reaction was then cooled to room temperature, treated with more carbethoxymethylene triphenylphosphorane (2.25 g, 6 mmol) and refluxed for an additional 24 hours. The solvent was removed under reduced pressure to give a dark brown paste which was thoroughly extracted with hot hexanes (4 x 50 ml). The extracts were combined, concentrated to about 100 ml and filtered to give a yellow solution. Evaporation of the solvent under reduced pressure gave ethyl 3-benzofuran acetate (**82**) in a crude yield of 90% (2.02 g, 10 mmol). The compound showed:



¹H NMR: (CDCl₃, 300 MHz): δ1.29 (3H, t, *J*=7.1 Hz, CH₃), 3.72 (2H, s, Ar-CH₂), 4.22 (2H, q, *J*=7.1 Hz, CH₂CH₃), 7.27-7.33 (2H, m, 2ArH), 7.49-7.65 (3H, m, 3ArH).

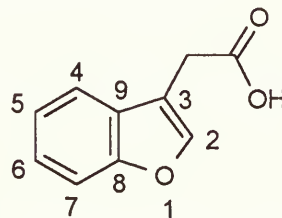
¹³C NMR: (CDCl₃, 75 MHz): δ14.59 (CH₂CH₃), 30.24 (CH₂CH₃), 61.48 (ArCH₂), 111.90 (C_{Ar}), 113.57 (C_{Ar}), 120.09 (C_{Ar}), 122.99 (C_{Ar}), 124.83 (C_{Ar}), 128.04 (C_{Ar}), 143.22 (C_{Ar}), 155.60 (C_{Ar}), 171.05 (C=O)

MS[EI⁺]: *m/z* (RI%); 204 [M]⁺ (41), 131 [M-COOEt]⁺ (100).

HRMS: for C₁₂H₁₂O₃: calculated 204.0786, observed 204.0790

Synthesis of 3-benzofuran acetic acid (**83**)

The crude ethyl-3-benzofuran acetate (**82**) (2.20 mg, 10.7 mmol) was suspended in 25 ml of 3M sodium hydroxide solution. A minimum amount of ethanol was added to allow for dissolution and the resultant solution stirred at room temperature overnight. The reaction mixture was then extracted with ether (2 x 25 ml). The aqueous layer was acidified with concentrated hydrochloric acid (congo red) and extracted with ethyl acetate (6 x 25 ml). The combined ethyl acetate extracts were then washed with brine (2 x 25 ml), dried with magnesium sulfate and evaporated to dryness under reduced pressure to give a pale yellow solid. The yield of 3-benzofuran acetic acid (**83**) is 58% (1.13 g, 6.4 mmol) and showed:



$^1\text{H NMR}$: (CDCl_3 , 300 MHz): δ 3.74 (2H, s, CH_2), 7.27 (2H, m, C5 and C6), 7.47 (1H, d, $J=7.8$ Hz, C4H), 7.56 (1H, d, $J=7.9$ Hz, C7H), 7.62 (1H, s, C2H), 11.81 (1H, broad, COOH).

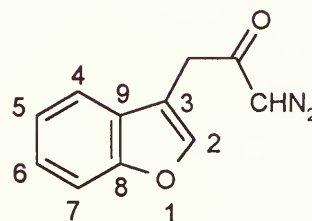
$^{13}\text{C NMR}$: (CDCl_3 , 75 MHz): δ 29.49 (CH_2), 111.56 (Ar-H), 112.34 (C9), 119.59 (ArH), 27.71 (ArH), 124.58 (ArH), 127.39 (C3), 143.04 (C2), 155.18 (C8), 177.13 (COOH).

MS[EI $^+$]: m/z (RI%); 176 [M] $^+$ (49), 131 [$\text{M}-\text{COOH}$] $^+$ (100).

HRMS: for $\text{C}_{10}\text{H}_8\text{O}_3$: calculated 176.0473, observed 176.0478.

Synthesis of 1-diazo-3-(3-benzofuran)-2-propanone (**84**)

3-Benzofuran acetic acid (**83**) (470 mg, 2.7 mmol) was dissolved in 50 ml of dry dichloromethane and stirred in an ice



bath under argon atmosphere. Oxalyl chloride (0.30 ml, 3.4 mmol) was added to the reaction mixture followed by a catalytic amount of *N,N*-dimethyl formamide (2 drops). The reaction mixture was stirred for 30 minutes, then removed from the ice bath and stirred at room temperature for 2 hours. The reaction mixture was then evaporated under reduced pressure to give a brown residue. Residual oxalyl chloride was removed by redissolving the residue in 3 x 25 ml of dry benzene and evaporating under reduced pressure. The crude acid chloride was then redissolved in 25 ml of dichloromethane and then added over 10 minutes to 50 ml of an ice-cold solution of dry ethereal diazomethane (approximately 20 mmol) and stirred under an argon atmosphere for 2 hours. The reaction mixture was evaporated under reduced pressure to give crude diazoketone as a brown oil which was purified by column chromatography using silica gel and 20% ethyl acetate-hexanes as eluent. TLC with 50% ethyl acetate showed the product (**84**) with an $R_f=0.48$. The yield was 74% (400 mg, 2.0 mmol). The compound showed:

^1H NMR: (CDCl_3 , 300 MHz): δ 3.65 (2H, s, CH_2), 5.23 (1H, s, CHN_2), 7.21-7.32 (2H, m, ArH), 7.46-7.54 (2H, m, ArH), 7.56 (1H, s, C2H).

^{13}C NMR: (CDCl_3 , 75 MHz): δ 35.68 (CH_2), 54.57 (CHN_2), 111.55 (C_{Ar}), 113.62 (C9 or C3), 119.55 (C_{Ar}), 122.81 (C_{Ar}), 124.67 (C_{Ar}), 127.32 (C3 or C9), 142.95 (C2), 155.24 (C8), 191.54 (C=O).

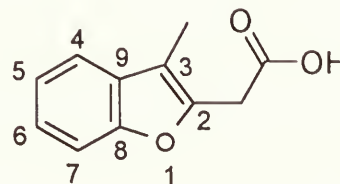
MS[EI $^+$]: m/z (RI%); 200 [M] $^+$ (7), 172 [$\text{M}-\text{N}_2$] $^+$ (100), 144 [$\text{M}-\text{CO}-\text{N}_2$] $^+$ (31), 131 [$\text{M}-\text{C}(\text{O})\text{CHN}_2$] $^+$ (69), 115 [$\text{M}-\text{O}-\text{C}(\text{O})\text{CHN}_2$] $^+$ (50).

HRMS: for $\text{C}_{11}\text{H}_8\text{O}_2\text{N}_2$: calculated 200.0588, observed 200.0575.

Rhodium (II) Acetate Catalyzed Decomposition of 1-Diazo-3-(3-Benzofuran)-2-Propanone (84).

In presence of TFA:

To a solution of diazoketone (84) (100 mg, 580 mmol) in dichloromethane (50 ml) rhodium(II) acetate (~1 mg) was added followed by 1 drop of trifluoroacetic acid.



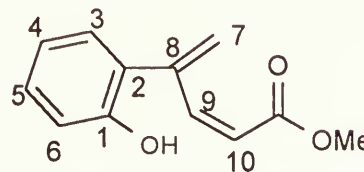
After 1 hour, the reaction mixture was concentrated under reduced pressure to about 10 ml and flushed through a small silica gel column eluted with 200 ml of ethyl acetate. Evaporation of the eluent gave 3-methyl-2-benzofuran acetic acid (88) in 62% yield (68 mg, 0.36 mmol). TLC with 33% ethyl acetate in hexanes the eluent showed the product (88) with an $R_f = 0.1$. The compound showed:

$^1\text{H NMR}$: (CDCl_3 , 300 MHz): δ 2.20 (3H, s, CH_3), 3.80 (2H, s, CH_2), 7.2-7.3 (2H, m, ArH), 7.41 (1H, d, $J = 7.8$ Hz, ArH), 7.45 (1H, d, $J = 7.2$ Hz, ArH).

MS[EI $^+$]: m/z (RI%); 190 [M] $^+$ (44), 145 [$\text{M}-\text{COOH}$] $^+$ (100).

In presence of methanol:

To a stirred solution of the diazoketone (84) (100 mg, 0.50 mmol), 0.1 ml methanol and 50 ml of



dichloromethane under argon atmosphere at room temperature was added 1 mg of rhodium (II) acetate. The reaction mixture was allowed to stir for 1 hour. Upon consumption of the diazoketone (as evidenced by TLC), the reaction mixture was concentrated under reduced pressure. The residue was purified by column

chromatography using silica gel with dichloromethane as eluent. The yield was 71% (72 mg, 0.35 mmol) of the phenolic diene (**91**). TLC with 33% ethyl acetate in hexanes the eluent showed the product (**91**) with an $R_f = 0.17$. The compound showed:

^1H NMR: (CDCl_3 , 300 MHz): δ 3.71 (3H, s, OCH_3), 4.91 (1H, s, ArOH), 5.59 and 5.88 (each 1H, d, $J=1.5$ Hz, $\text{C}7\text{H}_2$), 5.66 (1H, d, $J=15.7$ Hz, $\text{C}10\text{H}$), 6.90-6.94 (2H, m, 2ArH), 7.04 and 7.23 (each 1H, dd, $J=1.8, 7.8$ Hz, ArH), 7.53 (1H, d, $J=15.6$ Hz, $\text{C}9\text{H}$).

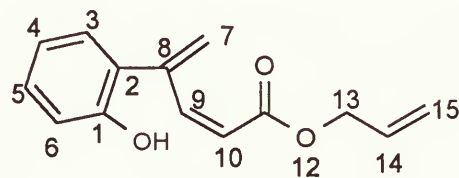
^{13}C NMR: (CDCl_3 , 75 MHz): δ 51.71 (CH_3), 115.87, 120.64, 122.15, 124.19, 127.53, 129.78, 130.01, 142.11, 145.03, 152.39 ($\text{C}_{\text{Ar-OH}}$), 167.15 (C=O)

MS[EI $^+$]: m/z ($\text{RI}\%$); 204 [M] $^+$ (73), 189 [M-CH_3] $^+$ (11), 172 [$\text{M-CH}_3\text{-OH}$] $^+$ (45), 145 [M-COOCH_3] $^+$ (100), 115 [M-OH-CH-COOCH_3] $^+$ (50)

HRMS: for $\text{C}_{12}\text{H}_{12}\text{O}_3$: calculated 204.0786, observed 204.0788

In the presence of allyl alcohol:

To a stirred solution of the diazoketone (**84**) (60 mg, 0.3 mmol) and allyl alcohol (0.5 ml, 7.4



mmol) in 30 ml of dichloromethane was added ~1 mg of rhodium (II) acetate. The resultant solution was stirred under an argon atmosphere for 1 day at room temperature. The solvent was subsequently evaporated under reduced pressure, and the residue purified by column chromatography using silica gel and dichloromethane as eluent. TLC in ethyl acetate showed the product (**94**) with an $R_f = 0.28$. The yield was 77% (532 mg, 0.23 mmol). The compound showed:

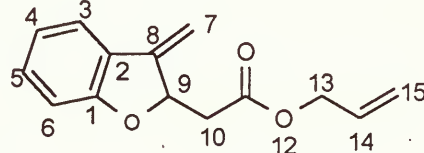
^1H NMR: (CDCl_3 , 300 MHz): δ 4.62 (2H, dt, $J=1.2$ and 5.8 Hz, C13H_2), 5.08 (1H, s, OH), 5.22 (1H, dd, $J=10.4$ Hz and 1.2 Hz, C15H), 5.30 (1H, dd, $J=1.5$ and 17.2 Hz, C15H), 5.60 (1H, d, $J=1.4$ Hz, C7H), 5.67 (1H, d, $J=15.7$ Hz, C10H), 5.89 (1H, br, C7H), 5.85-5.96 (1H, m, C14H), 6.90-6.94 (2H, m, Ar-H), 7.04 (1H, dd, $J=1.7$ and 7.8 Hz, Ar-H), 7.23-7.25 (1H, m, ArH), 7.55 (1H, d, $J=15.7$ Hz, C9H).

^{13}C NMR: (CDCl_3 , 75 MHz): δ 65.32 (CH_2), 115.88, 118.53, 120.64, 122.16, 124.21, 127.64, 129.78, 130.05, 132.03, 142.15, 145.27, 152.42, 166.39 ($\text{C}=\text{O}$).

MS[EI $^+$]: m/z (RI%); 230 $[\text{M}]^+$ (100), 189 $[\text{M}-\text{C}_3\text{H}_5]^+$ (79), 145 $[\text{M}-\text{CO}_2-\text{C}_3\text{H}_5]^+$ (71), 115 $[\text{M}-\text{OH}-\text{CO}_2-\text{C}_4\text{H}_6]^+$ (63)

HRMS: for $\text{C}_{14}\text{H}_{14}\text{O}_3$: calculated 230.0943, observed 230.0958

Synthesis of Allyl 2-(3-methylene-2,3-dihydrobenzo[*b*]furan-2-yl) acetate (**95**) via the Intramolecular Michael Addition of Allyl (2*Z*)-4-(2-hydroxyphenyl)-2,4-pentadienoate (**94**)



Reflux a solution of **94** (50 mg, 220 μmol) in

5 ml toluene for 2 days. The solvent was then evaporated under reduced pressure and the residue purified by column chromatography using silica gel and 10% to 25% ethyl acetate in hexanes as eluent. TLC with 20% ethyl acetate in hexanes as the eluent showed the product with an $R_f = 0.61$. The conversion to (**95**) was 18% (9.1 mg, 0.04 mmol) with 64% (32.5 mg, 0.14 mmol) being the recovered starting material (**94**).

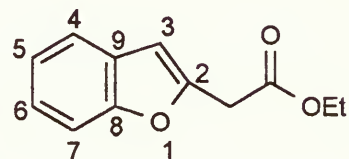
^1H NMR: (CDCl_3 , 300 MHz): δ 2.78 (1H, dd, $J=4.6$, 14.7 Hz, CH_2COO), 2.84 (1H, dd, $J=7.8$, 14.7 Hz, CH_2COO), 4.69 (2H, dd, $J=1.2$ Hz, 5.7 Hz, $\text{OCH}_2\text{CH}=\text{CH}$), 4.97 (1H, d, $J=2.4$ Hz, $\text{ArC}=\text{CH}_2$), 5.24 (1H, dt, $J=1.2$ Hz, 10.1 Hz, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.53 (1H, dt, $J=1.4$ Hz, 17.2 Hz, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.43 (1H, d, $J=2.9$ Hz, $\text{ArC}=\text{CH}_2$), 5.55-5.59 (1H, m, CHCH_2COO), 5.74-5.97 (1H, m, $\text{CH}_2\text{CH}=\text{CH}_2$), 6.83-6.92 (2H, m, ArH), 7.20 (1H, t, $J=7.7$ Hz, ArH), 7.37 (1H, d, $J=7.7$ Hz, ArH).

MS[EI $^+$]: m/z (RI%); 230 [M] $^+$ (67), 145 [$\text{M}-\text{COO}-\text{C}_3\text{H}_5$] $^+$ (100)

HRMS: for C_{14}O_4 : calculated 230.09429, observed 230.09358

Synthesis of Ethyl-2-benzofuran acetate (**67**)

Ethyl-2-benzofuran was prepared by a Wittig reaction of 2-coumaranone and carbethoxymethylene



triphenyl phosphorane following the similar procedure as for the preparation of ethyl-3-benzofuran acetate (**84**). The ethyl ester (**67**) can be purified by column chromatography using silica gel and 30% ether-hexanes as the eluent. TLC with 33% ethyl acetate in hexanes as the eluent showed that **67** has an $R_f = 0.50$. The yield was 73%.

^1H NMR: (CDCl_3 , 300 MHz): δ 1.28 (3H, t, $J=7.1$ Hz, CH_2-CH_3), 3.82 (2H, s, CH_2-Ar), 4.21 (2H, q, $J=7.1$ Hz, CH_2-CH_3), 6.62 (1H, s, C3H), 7.17-7.27 (2H, m, Ar-H), 7.44 (1H, d, $J=8.0$ Hz, Ar-H), 7.51 (1H, d, $J=7.1$ Hz, Ar-H).

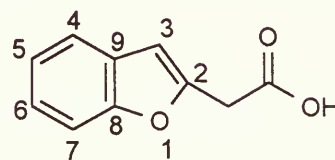
^{13}C NMR: (CDCl_3 , 75 MHz): δ 14.09 ($\text{CH}_2\text{-}\underline{\text{C}}\text{H}_3$), 34.64 ($\text{Ar-}\underline{\text{C}}\text{H}_2$), 61.33 ($\underline{\text{C}}\text{H}_2\text{-CH}_3$), 104.98, 110.98, 120.66, 122.64, 123.83, 128.67, 150.73, 154.85 (Ar), 168.79 (CO).

MS[EI $^+$]: m/z (RI%): 204 [M] $^+$ (45), 131 [M-COOEt] $^+$ (100)

HRMS: for $\text{C}_{12}\text{H}_{12}\text{O}_3$: calculated 204.0786, observed 204.0792

Synthesis of 2-benzofuran acetic acid (**68**)

2-Benzofuran acetic acid was prepared by the hydrolysis of its corresponding ester with 5% sodium hydroxide using the same procedure as that employed in the hydrolysis of ethyl-3-benzofuran acetate. The crude yield was 60% and was used for the preparation of diazoketone (**69**) without further purification.



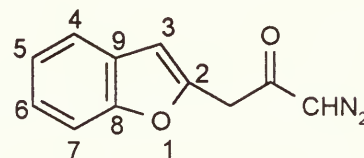
^1H NMR: (CDCl_3 , 300 MHz): δ 3.78 (2H, s, CH_2), 6.65(1H, s, C3H), 7.17-7.28 (2H, m, C5H and C6H), 7.44 (1H, d, $J=7.8$ Hz, C4H), 7.52 (1H, d, $J=7.8$ Hz, C7H), 9.43 (1H, broad, COOH).

^{13}C NMR: (CDCl_3 , 75 MHz): δ 34.29 (CH_2), 105.54, 111.08, 120.83, 122.81, 124.14 (5C_{Ar}), 128.31 (C8), 149.66, 154.93 (2O-C_{Ar}), 175.13 (CO).

MS[EI $^+$]: m/z (RI%): 176 [M] $^+$ (39), 131 [M-COOH] $^+$ (100).

HRMS: for $\text{C}_{10}\text{H}_8\text{O}_3$: calculated 176.0473, observed 176.0474.

Synthesis of 1-Diazo-3-(2-Benzofuran)-2-Propanone (**69**)



The diazoketone was prepared following the procedure employed for the synthesis of 1-diazo-3-(3-benzofuran)-2-propanone (**84**). The reaction mixture can be purified by column chromatography using silica gel with 50% dichloromethane-hexanes as eluent. TLC with dichloromethane as the eluent showed the product (**69**) with an $R_f = 0.28$. The yield was 66%.

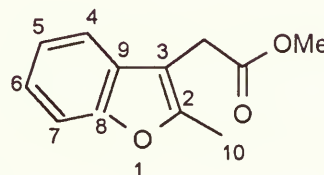
^1H NMR: (CDCl_3 , 300 MHz): δ 3.77 (2H, s, CH_2), 5.31 (1H, s, CHN_2), 6.60 (1H, s, C3H), 7.15-7.28 (2H, m, ArH), 7.43 (1H, d, $J=8.1$ Hz, ArH), 7.52 (1H, d, $J=8.0$ Hz, ArH).

^{13}C NMR: (CDCl_3 , 75 Hz): δ 40.76 (CH_2), 55.04 (CHN_2), 105.62, 111.06, 120.79, 122.92, 124.18, 128.40, 151.18, 155.01 (8 Ar-C), δ 184.55 ($\text{C}=\text{O}$).

MS[EI $^+$]: m/z (RI%): 200 [M] $^+$ (34), 172 [$\text{M}-\text{N}_2$] $^+$ (82), 144 [$\text{M}-\text{CO}-\text{N}_2$] $^+$ (62), 131 [$\text{M}-\text{CO}-\text{N}_2-\text{CH}$] $^+$ (100), 115 (56).

HRMS: for $\text{C}_{11}\text{H}_8\text{N}_2\text{O}_2$: calculated 200.0586, observed 200.0574.

Rhodium(II) Acetate Catalyzed Decomposition of 1-Diazo-3-(2-Benzofuran)-2-Propanone (**69**)



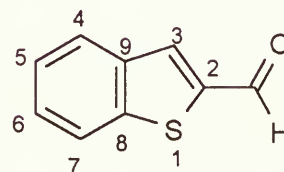
To a stirred solution of diazoketone **69** (100 mg, 0.5 mmol) in 50 ml of dichloromethane and 3 drops of methanol under argon atmosphere was added about 1 mg of rhodium(II) acetate. The reaction solution was stirred at room temperature for 2 hours. Then the solvent was evaporated under reduced pressure and the

residue was purified by column chromatography using silica gel and 30% dichloromethane-hexanes as eluent to yield methyl 2-(2-methylbenzo[*b*]furan-3-yl)acetate (**74**) as the only isolable product. TLC with dichloromethane as the eluent showed the product with an $R_f = 0.20$. The yield was 58% (42 mg, 0.29 mmol).

^1H NMR: (CDCl_3 , 300 MHz): δ 2.42 (3H, s, ArCH_3), 3.60 (2H, s, $\text{Ar-CH}_2\text{-C=O}$), 3.67 (3H, s, OCH_3), 7.13-7.26 (2H, m, ArH), 7.32-7.4 (1H, m, ArH), 7.41-7.47 (1H, m, ArH).

MS[EI $^+$]: m/z (RI%): 204 [M] $^+$ (52), 145 [M-COOMe] $^+$ (100).

Synthesis of 2-thianaphthaldehyde (**106**)⁸⁹



To a stirred solution of benzothiophene (10.0g, 75 mmol) in 60 ml of anhydrous ether under argon atmosphere at -78°C , was added *n*-butyllithium in hexanes solution (7.3 M, 11.0 ml, 80 mmol). The reaction solution was stirred and allowed to warm up to 0°C slowly. The lithiated benzothiophene was then added to a stirred solution of DMF (5.5 g, 5.8 ml, 75 mmol) in 50 ml of anhydrous ether *via* a cannular and the resultant mixture stirred overnight under argon atmosphere. The reaction mixture was then poured into 30 ml of 3M hydrochloric acid and extracted with 3 x 50 ml of ether. The organic extracts were combined, washed with 3 x 50 ml of 1M hydrochloric acid followed by 50 ml of saturated sodium bicarbonate solution. The ether layer was then dried over anhydrous magnesium sulfate and evaporated under a reduced pressure. The crude aldehyde (**106**) was then purified by

⁸⁹ Shirley, D. A., Danzig, M. J., *J. Am. Chem. Soc.*, **1952**, 74, 2935.

dissolving the residue in a small amount of ethanol and treating with 50 ml of saturated sodium bisulfite solution. The resultant mixture was mixed thoroughly and then allowed to stand for 20 minutes. The crystalline bisulfite compound was filtered off, washed with ether and dried under a vacuum. The aldehyde can be regenerated taking a cooled aqueous solution of the bisulfite addition compound and treating with excess saturated sodium carbonate solution. The precipitated aldehyde can then be filtered off and dried. TLC with 20% ethyl acetate in hexanes as the eluent showed the product (**106**) with an $R_f = 0.63$. The overall yield was 60% (7.1g, 0.44 mmol). The product showed:

^1H NMR: (CDCl_3 , 300 MHz): δ 7.39-7.51 (2H, m, Ar-H), 7.88 (1H, d, $J=7.8$ Hz, Ar-H), 7.92 (1H, d, $J=8.3$ Hz, Ar-H), 8.00 (1H, s, Ar-H), 10.09 (1H, s, CHO).

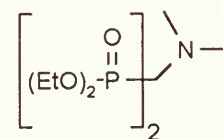
^{13}C NMR: (CDCl_3 , 75 MHz): δ 123.27, 125.22, 126.24, 128.13, 134.43, 138.51, 142.64, 143.32 (Ar), 184.63(CO).

MS [EI $^+$]: m/z (RI%): 162 [M] $^+$ (100), 133 [$\text{M}-\text{CHO}$] $^+$ (18.3), 89 [$\text{M}-\text{SCCHO}$] $^+$ (32).

HRMS: for $\text{C}_9\text{H}_6\text{OS}$: calculated 162.0139, observed 162.0146.

Synthesis of Tetraethyldimethylaminomethylenediphosphonate (**105**)⁷⁹

To a stirred solution of DMF (7.6 ml, 7.16 g, 97.9 mmol) in 150 ml of anhydrous ether in ice bath under an argon atmosphere, a solution of oxalyl chloride (8.6 ml, 12.51 g, 98.5 mmol) in 20 ml of anhydrous ether was added. The reaction mixture was allowed to warm to room temperature and stirred for an additional hour. Triethyl phosphite (37 ml, 35.85 g, 216



mmol) was then added dropwise and the reaction mixture stirred for another hour. The reaction mixture was concentrated under reduced pressure then vacuum distilled (135°C @ 0.15 mmHg) to give 88% yield (28.4 g, 85.8 mmol) of **105** as pale yellow oil. The compound showed:

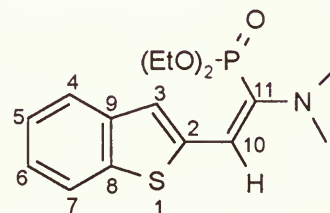
^1H NMR: (CDCl_3 , 300 MHz): δ 1.22 (12H, t, $J=6.9$, CH_2CH_3), 2.50 and 2.51 (each 3H, s, $\text{N}(\text{CH}_3)_2$), 3.21 (1H, broad t, $J\sim 24.9$ Hz, CH-P), 4.06 (8H, q, $J=6.8$ Hz, CH_2CH_3).

MS[EI $^+$]: m/z (RI%): 331 $[\text{M}]^+$ (5.2), 133 $[\text{M-PO}(\text{OEt})_2]^+$ (100).

HRMS: for $\text{C}_{11}\text{H}_{27}\text{NO}_6\text{P}_2$: calculated 331.0746, observed 331.1300.

Synthesis of the 2-Benzothiophene Phosphonate (**107**)⁷⁹

40% Sodium hydride dispersed in mineral oil (550 mg, 23 mmol) was washed 3 times with hexanes, then suspended in 20 ml of tetrahydrofuran (THF). A solution of tetraethyldimethylamino methylenediphosphonate (**105**) (5.52 g, 16.7 mmol) in 200 ml of THF was then added slowly while stirring. One hour after the addition, a solution of 2-thianaphthaldehyde (**106**) (2.7 g, 16.7 mmol) in 20 ml of THF was added, and the resultant mixture refluxed gently for one hour. The solvent was then evaporated and the residue was partitioned between ether and water. The aqueous layer was extracted with 3 x 50 ml of ether. The combined extracts were dried with magnesium sulfate and evaporated to dryness. The crude product was purified by column chromatography using silica gel with 20% ethyl acetate in hexanes as eluent to yield the desired phosphonate (3.53 g, 10.4 mmol, 61.5%



yield) together with a small amount of starting material and reduced product (2-thianaphthol). TLC of the product with 50% ethyl acetate in hexanes gave an $R_f = 0.29$.

The compound showed:

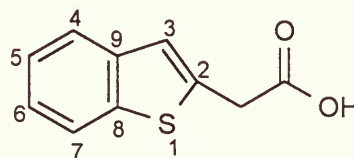
^1H NMR: (CDCl_3 , 300 MHz): δ 1.34 (6H, t, $J=6.9$ Hz, CH_2CH_3), 2.65 and 2.66 (each 3H, s, $\text{N}(\text{CH}_3)_2$), 4.12 (4H, q, $J=6.6$ Hz, CH_2CH_3), 7.24-7.36 (4H, m, ArH), 7.67-7.74 (2H, m, Ar-H).

^{13}C NMR: (CDCl_3 , 75 MHz): δ 16.19, 43.91, 61.56, 121.98, 123.66, 125.14, 127.24, 131.49, 131.99, 137.35, 137.92, 142.38 (Ar).

MS[EI+]: m/z (RI%): 339 $[\text{M}]^+$ (100), 295 $[\text{M}-\text{NMe}_2]^+$ (20), 202 $[\text{M}-\text{PO}(\text{OEt})_2]^+$ (84), 187 $[\text{M}-\text{PO}(\text{OEt})_2-\text{Me}]^+$ (48), 172 $[\text{M}-\text{PO}(\text{OEt})_2-\text{Me}_2]^+$ (70).

HRMS: for $\text{C}_{16}\text{H}_{22}\text{NO}_3\text{PS}$: calculated 339.0774359, observed 339.1044

Synthesis of 2-Benzothiophene acetic acid (**108**)⁷⁹



A solution of the phosphonate (**107**) (1.0 g, 2.95 mmol) in 50 ml of 12N hydrochloric acid was refluxed for 30 minutes. The mixture was then cooled, poured into 300 ml of ice-water, and extracted 4 times with 100 ml of ether. The combined organic layer was then dried with magnesium sulfate and treated with activated charcoal to give a pale yellow solution of **108**. Evaporation of the ether gave 500 mg of **108** as yellowish crystalline solid (2.60 mmol, 88% yield). The compound showed :

M.P.: 140-142°C.

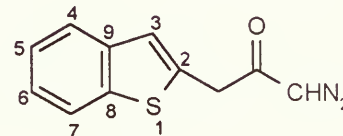
^1H NMR: (CDCl_3 , 300 MHz): δ 3.98(2H, s, CH_2), 7.18 (1H, s, C3H), 7.25-7.36 (2H, m, Ar-H), 7.73 (1H, d, $J=6.8$ Hz, ArH), 7.81 (1H, d, $J=7.5$ Hz, ArH), 9.40 (1H, broad, COOH).

MS[EI+]: m/z (RI%): 192 $[\text{M}]^+$ (39), 147 $[\text{M}-\text{COOH}]^+$ (100).

HRMS: for $\text{C}_{10}\text{H}_8\text{O}_2\text{S}$: calculated 192.0245, observed 192.0243.

Synthesis of 1-Diazo-3-(2-Benzothieryl)-2-Propanone (109)

The diazoketone was prepared following the procedure employed for the synthesis of 1-diazo-3-(3-benzofuran)-2-propanone (**84**). The reaction mixture was purified by column chromatography using silica gel with 33% hexanes in dichloromethane as eluent. TLC of the product (**109**) with 50% ethyl acetate in hexanes gave an $R_f = 0.64$. The yield was 76%.



^1H NMR: (CDCl_3 , 300 MHz): δ 3.85 (2H, s, CH_2), 5.31 (1H, s, CHN_2), 7.14 (1H, s, C3H), 7.26-7.35 (2H, m, Ar-H), 7.70 (1H, d, $J=6.8$ Hz, Ar-H), 7.77 (1H, d, $J=7.1$ Hz, Ar-H).

^{13}C NMR: (CDCl_3 , 75 Hz): δ 42.44 (CH_2), 54.97 (CHN_2), 122.15, 123.23, 123.87, 124.27, 124.43, 136.69, 139.74, 140.05 (8 C_{Ar}), 190.71 ($\text{C}=\text{O}$)

MS[EI+]: m/z (RI%): 216 $[\text{M}]^+$ (13), 188 $[\text{M}-\text{N}_2]^+$ (69), 160 $[\text{M}-\text{CO}-\text{N}_2]^+$ (100), 147 $[\text{M}-\text{CO}-\text{N}_2-\text{CH}]^+$ (90), 115 (57).

HRMS: for $\text{C}_{11}\text{H}_8\text{N}_2\text{OS}$: calculated 216.0357, observed 216.0368.

Rhodium(II) Acetate Catalyzed Decomposition of 1-Diazo-3-(2-Benzothienyl)-2-Propanone (109)

To a stirred solution of diazoketone (109) (140 mg, 0.66 mmol) in 50 ml dichloromethane under an argon atmosphere, 1 mg of rhodium (II) acetate was added. The reaction was stirred for 1 hour at which time the solvent was evaporated under reduced pressure and the products separated by column chromatography on silica gel using 50% dichloromethane in hexanes as the eluent. Two major products were obtained. 2,3-Dihydro-1*H*-benzo[*b*]cyclopenta[*d*]thiophen-2-one (102) (26.1 mg, 0.14 mmol, 21% yield) showed:

TLC: R_f = 0.20 (using 50% dichloromethane in hexanes as the eluent)

^1H NMR: (CDCl_3 , 300 MHz): δ 3.53 (2H, s, C5H), 3.64 (2H, s, C3H), 7.30-7.41 (2H, m, C9H and C10H), 7.60 (1H, d, $J=7.4$ Hz, C8H), 7.85 (1H, d, $J=7.8$ Hz, C11H).

^{13}C NMR: (CDCl_3 , 75 Hz): δ 40.78 (C5), 42.44 (C3), 121.84, 123.25, 124.45, 124.72, 134.75, 135.19, 136.89, 141.95 (8 C_{Ar}), 213.16 (CO).

MS [EI $^+$]: m/z (RI%): 188 [M] $^+$ (38), 160 [$\text{M}-\text{CO}$] $^+$ (100), 115 (29).

HRMS: for $\text{C}_{10}\text{H}_8\text{O}_2\text{S}$: calculated 188.0296, observed 188.0292.

Dimeric product (71.0 mg, 0.19 mmol, 28% yield (from 56% of S.M.)) showed:

TLC: R_f = 0.76 (using 50% ethyl acetate in hexanes as the eluent)

^1H NMR: (CDCl_3 , 300 MHz): δ 3.32, 3.41 (1H each, dd, $J=5.0, 15.1$ Hz), 4.87, 4.93 (1H each, t, $J=2.0$ Hz), 4.97 (1H, br), 5.25 (1H, t(br), $J=5.2$ Hz), 6.85

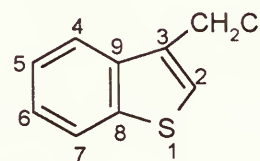
(2H, m), 6.97, 7.04 (1H each, s), 7.12 (2H, d, $J=3.3$ Hz), 7.30 (2H, m),
7.67, 7.74 (1H each, dd, $J=2.2, 6.8$ Hz)

MS[EI⁺]: m/z (RI%): 376 [M]⁺ (18), 147 (100).

HRMS: for C₂₂H₁₆O₂S₂ : calculated 376.0592, observed 376.0570.

Synthesis of 3-Chloromethyl Benzothiophene (97) ⁷⁸

A rapid stream of hydrogen chloride gas was bubbled for one hour through a stirred solution of benzothiophene (6.55 g, 53.5 mmol) and 37% aqueous formaldehyde (5.0 ml, 60 mmol) in 12N hydrochloric acid (5 ml) . The rate of the hydrogen gas bubbling was then decreased and the mixture stirred for another 6 hours. The reaction mixture was poured into 20 ml of ice water, and the organic layer separated. The aqueous layer was then extracted with 3 x 50 ml portions of ether. The combined organic layers were then washed successively with water, sodium bicarbonate, and water respectively. The ether layer was then dried with magnesium sulfate and evaporated under a reduced pressure. The crude product was then purified by vacuum distillation (0.15 mm Hg) to obtain benzothiophene (1.2 g) and the desired 3-chloromethyl benzothiophene (97) (5.2 g, 28.5 mmol, 65% yield). The product showed :



¹H NMR: (CDCl₃, 300 MHz); δ 4.90 (2H, s, CH₂), 7.49 (1H, s, Ar-H), 7.51-7.60 (2H, m, 2 x Ar-H), 8.00 (t, 2H, $J=8.9$ Hz, 2 x Ar-H)

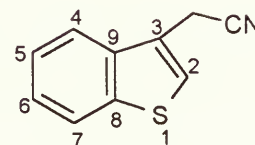
¹³C NMR: (CDCl₃, 75 MHz); δ 39.35 (CH₂), 121.67, 122.69, 124.20, 124.57, 126.09, 131.62, 136.96, 140.24 (Ar).

MS[EI⁺]: m/z (RI%); 182 [M]⁺ (26), 147 [M-Cl]⁺ (100).

HRMS: for C₉H₇ClS: Calculated 181.9957, observed 181.9953.

Synthesis of 3-Cyanomethylthianaphthene (**98**)⁶⁸

To a stirred solution of potassium cyanide (4.5 g, 69 mmol) in 25 ml of DMF at 50°C was added 3-chloromethyl benzothiophene (**97**) (7.8 g, 43 mmol). The reaction temperature was raised to 80°C and the mixture stirred for 3 hours. The reaction mixture was then allowed to cool to room temperature. Ether (50 ml) and sufficient water to dissolve all inorganic salts were added. The ether layer was separated and the aqueous layer extracted with a further 4 x 40 ml of ether. The combined ether extracts were washed with 3 x 30 ml of brine, dried with magnesium sulfate and evaporated to dryness under a reduced pressure. The crude **98** was purified by vacuum distillation at 125-127°C @ 0.15 mmHg (lit. 138-140°C @ 2 mmHg⁷⁸). The yield was 70% (5.21 g, 30 mmol). The product shows :



¹H NMR: (CDCl₃, 300 MHz); δ 3.87 (s, 2H, CH₂), 7.37-7.46 (m, 3H, 3 x ArH), 7.68 (dd, 1H, J=6.5, 2.3 Hz, ArH), 7.87 (dd, 1H, J=6.5, 2.2 Hz, ArH)

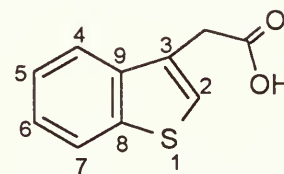
¹³C NMR: (CDCl₃, 75 MHz); δ 17.66 (CH₂), 116.92 (CN), 120.76, 123.09, 123.81, 124.60, 124.89, 124.99, 136.91, 140.38 (Ar).

MS[EI⁺]: m/z (RI%); 173 [M]⁺ (100), 147 [M-CN]⁺ (21).

HRMS: for C₁₀H₇NS: Calculated 173.0299, observed 173.0295.

Synthesis of 3-Benzothiophene acetic acid (**99**)

A mixture of 3-cyanomethyl benzothiophene (**98**) (5.04 g, 29.1 mmol) in 5 ml of 20% sodium hydroxide solution was stirred overnight at room temperature. The reaction mixture was then diluted to 25 ml with water and extracted with 2 x 10 ml portions of ether. The aqueous solution was then acidified with 12N hydrochloric acid (congo red) and extracted with 3 x 50 ml portions of ethyl acetate. The ethyl acetate extracts were then combined, dried with magnesium sulfate and treated with activated charcoal. The solvent was then removed under a reduced pressure to obtain a white crystalline product. The yield was 51% (2.86 g, 14.9 mmol). The product showed:



^1H NMR: (CDCl_3 , 300 MHz); δ 3.89 (2H, s, CH_2), 7.33-7.42 (3H, m, 3ArH), 7.75 (1H, dd, $J=6.8$, 1.9 Hz, ArH), 7.86 (1H, dd, $J=6.8$, 2.1 Hz, ArH), ~11 (1H, broad, COOH).

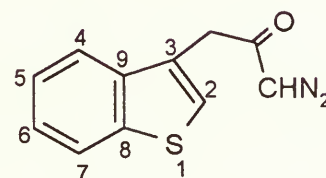
^{13}C NMR: (CDCl_3 , 75 MHz); δ 34.11 (CH_2), 121.63, 122.86, 124.25, 124.47, 125.04, 127.31, 128.33, 140.12 (Ar), 177.15 (COOH).

MS[EI $^+$]: m/z (RI%); 173 [M] $^+$ (100), 147 [$\text{M}-\text{COOH}$] $^+$ (21).

HRMS: for $\text{C}_{10}\text{H}_7\text{NS}$: Calculated 173.0299, observed 173.0295.

Synthesis of 1-Diazo-3-(3-Benzothieryl)-2-Propanone (**100**)

The diazoketone (**100**) was prepared following the procedure employed for the synthesis of 1-diazo-3-(3-



benzofuran)-2-propanone (**84**). The reaction mixture was purified by column

chromatography using silica gel and 33% hexanes in dichloromethane as the eluent. TLC of the product (**100**) with 50% ethyl acetate in hexanes gave an $R_f = 0.61$. The yield was 77%.

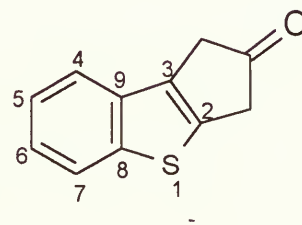
^1H NMR: (CDCl_3 , 300 MHz); δ 3.82 (s, 2H, CH_2), 5.11 (s, 1H, CHN_2), 7.27 (s, 1H, Ar-H), 7.33-7.39 (m, 2H, Ar-H), 7.72 (dd, 1H, $J=6.7, 2.2$ Hz, Ar-H), 7.85 (dd, 1H, $J=6.7, 2.2$ Hz, Ar-H).

^{13}C NMR: (CDCl_3 , 75 MHz); δ 40.93 (CH_2), 54.59 (CHN_2), 121.68, 122.82, 124.33, 124.56, 124.90, 128.96, 138.28, 140.21 (C_{Ar}), 191.78(CO).

MS[EI $^+$]: m/z (RI%); 216 [M] $^+$ (13), 187 [$\text{M}-\text{N}_2-\text{H}$] $^+$ (28), 160 [$\text{M}-\text{CO}-\text{N}_2$] $^+$ (40), 147 [$\text{M}-\text{COCHN}_2$] $^+$ (100), 115 (52).

HRMS: for $\text{C}_{11}\text{H}_8\text{N}_2\text{OS}$: calculated 216.0357, observed 216.0364.

Rhodium(II) Acetate Catalyzed Decomposition of 1-Diazo-3-(3-Benzothieryl)-2-Propanone (**100**)



To a stirred solution of rhodium acetate (~1 mg) in dichloromethane (100 ml) under argon atmosphere, was added a solution of the diazoketone (**100**) (100 mg, 0.5 mmol) in dichloromethane (1 ml) over 10 hours using a syringe pump. The reaction mixture was stirred for an additional five hours after the addition is complete. The solvent was evaporated under a reduced pressure and the residue purified by column chromatography using silica gel and 67% dichloromethane in hexanes as eluent, yielding 2,3-dihydro-1*H*-benzo[*b*]cyclopenta[*d*] thiophen-2-one (**102**) as

the only isolable product in 73%. The compound shows identical spectroscopic properties (MS and NMR) as the minor product isolated in the previous system.

X-RAY CRYSTALLOGRAPHY

All crystallographic determinations were made by Dr. Christopher S. Frampton (Roche Products Ltd., 40 Broadwater Road, Welwyn Garden City, Herts., AL7 3AY, U.K.)

Crystal data for (3): C_7H_6OS , $M = 138.18$, monoclinic, space group $P2_1/c$, $a = 6.414(2)$, $b = 13.309(2)$, $c = 7.542(1)$ Å, $\beta = 106.90(2)^\circ$, $V = 616.0(2)$ Å³, $Z = 4$, $D_c = 1.490$ g cm⁻³, $F(000) = 288$, $\mu(\text{Mo-K}\alpha) = 0.421$ mm⁻¹, $T = 123$ K. Intensities ($h k \pm l$) of a colourless prism (dimensions 0.10 x 0.20 x 0.25 mm) were collected by the ω -2 θ scan method to $2\theta_{\text{max}} = 54^\circ$. A total of 1463 reflections were collected of which 1348 were unique ($R_{\text{int}} = 0.0176$). Data collected for Lorentz polarization and decay (0.64%) but not for absorption. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms located by difference synthesis were included in the model but not refined. Full-matrix least-squares refinement of 82 parameters gave $R1 = 0.0349$ and $wR2 = 0.1030$ for $I \geq 2\sigma(I)$ and $R1 = 0.0433$, $wR2 = 0.1099$, $S = 1.055$ for all data. The largest difference peak and hole = 0.455 and -0.434 eÅ⁻³ respectively.

Crystal data for (20): $C_{14}H_{12}O_2S_2$, $M = 276.36$, monoclinic, space group $P2_1/n$, $a = 9.837(2)$, $b = 5.890(2)$, $c = 21.6728(14)$ Å, $\beta = 94.219(9)^\circ$, $V = 1252.4(4)$ Å³, $Z = 4$, $D_c = 1.466$ g cm⁻³, $F(000) = 576$, $\mu(\text{Mo-K}\alpha) = 0.414$ mm⁻¹, $T = 123$ K. Intensities ($h k \pm l$) of a cream coloured prism (dimensions 0.10 x 0.22 x 0.45 mm) were collected by the ω -2 θ

scan method to $2\theta_{\max} = 54^\circ$. A total of 2905 reflections were collected of which 2746 were unique ($R_{\text{int}} = 0.0386$). Data collected for Lorentz polarization and decay (0.71%) but not for absorption. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms located by difference synthesis were included in the model but not refined. Full-matrix least-squares refinement of 163 parameters gave $R1 = 0.0356$ and $wR2 = 0.0899$ for $I \geq 2\sigma(I)$ and $R1 = 0.0569$, $wR2 = 0.0980$, $S = 1.036$ for all data. The largest difference peak and hole = 0.364 and -0.299 e \AA^{-3} respectively.

Tables of crystallographic information for **3** and **20** appear in Appendices I and II, respectively.

Appendix I

Table 1. Crystal data and structure refinement for rwx0226.

| | |
|-----------------------------------|--|
| Identification code | rwx0226 |
| Empirical formula | C(7) H(6) O S |
| Formula weight | 138.18 |
| Temperature | 123(1) K |
| Wavelength | 0.71069 Å |
| Crystal system | Monoclinic |
| Space group | P 2 ₁ /c |
| Unit cell dimensions | a = 6.414(2) Å alpha = 90 deg. b = 13.309(2) Å beta = 106.90(2) deg. c = 7.5423(12) Å gamma = 90 deg. |
| Volume | 616.0(2) Å ³ |
| Z | 4 |
| Density (calculated) | 1.490 Mg/m ³ |
| Absorption coefficient | 0.421 mm ⁻¹ |
| F(000) | 288 |
| Crystal size | 0.25 x 0.20 x 0.10 mm |
| Theta range for data collection | 3.06 to 27.00 deg. |
| Index ranges | 0 ≤ h ≤ 8, 0 ≤ k ≤ 16, -9 ≤ l ≤ 9 |
| Reflections collected | 1463 |
| Independent reflections | 1348 [R(int) = 0.0176] |
| Absorption correction | None |
| Refinement method | Full-matrix least-squares on F ² |
| Data / restraints / parameters | 1348 / 0 / 82 |
| Goodness-of-fit on F ² | 1.055 |
| Final R indices [I > 2sigma(I)] | R1 = 0.0349, wR2 = 0.1030 |
| R indices (all data) | R1 = 0.0433, wR2 = 0.1099 |
| Largest diff. peak and hole | 0.455 and -0.434 e.Å ⁻³ |

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for rwx0226. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

| | x | y | z | $U(\text{eq})$ |
|------|----------|---------|----------|----------------|
| S(1) | 4594(1) | 3799(1) | 1278(1) | 18(1) |
| O(1) | -1903(2) | 3766(1) | -4785(2) | 26(1) |
| C(1) | 3150(3) | 3723(1) | 2874(2) | 18(1) |
| C(2) | 929(3) | 3685(1) | 2080(2) | 14(1) |
| C(3) | 431(3) | 3718(1) | 88(2) | 14(1) |
| C(4) | -1623(3) | 3686(1) | -1493(2) | 16(1) |
| C(5) | -770(3) | 3772(1) | -3188(2) | 17(1) |
| C(6) | 1730(3) | 3865(1) | -2584(2) | 16(1) |
| C(7) | 2237(3) | 3791(1) | -519(2) | 15(1) |

Table 3. Selected bond lengths [\AA] and angles [deg] for rwx0226.

| | |
|----------------|------------|
| S(1)-C(7) | 1.712(2) |
| S(1)-C(1) | 1.722(2) |
| O(1)-C(5) | 1.213(2) |
| C(1)-C(2) | 1.376(3) |
| C(2)-C(3) | 1.443(2) |
| C(3)-C(7) | 1.367(2) |
| C(3)-C(4) | 1.498(2) |
| C(4)-C(5) | 1.534(2) |
| C(5)-C(6) | 1.539(3) |
| C(6)-C(7) | 1.499(2) |
| C(7)-S(1)-C(1) | 91.27(9) |
| C(2)-C(1)-S(1) | 113.42(13) |
| C(1)-C(2)-C(3) | 109.8(2) |
| C(7)-C(3)-C(2) | 113.5(2) |
| C(7)-C(3)-C(4) | 111.7(2) |
| C(2)-C(3)-C(4) | 134.8(2) |
| C(3)-C(4)-C(5) | 102.53(14) |
| O(1)-C(5)-C(4) | 124.9(2) |
| O(1)-C(5)-C(6) | 124.5(2) |
| C(4)-C(5)-C(6) | 110.64(14) |
| C(7)-C(6)-C(5) | 101.23(14) |
| C(3)-C(7)-C(6) | 113.8(2) |
| C(3)-C(7)-S(1) | 112.02(14) |
| C(6)-C(7)-S(1) | 134.17(13) |

Symmetry transformations used to generate equivalent atoms:

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for rwx0226. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

| | x | y | z | U(eq) |
|------|----------|---------|----------|-------|
| S(1) | 4594(1) | 3799(1) | 1278(1) | 18(1) |
| O(1) | -1903(2) | 3766(1) | -4785(2) | 26(1) |
| C(1) | 3150(3) | 3723(1) | 2874(2) | 18(1) |
| C(2) | 929(3) | 3685(1) | 2080(2) | 14(1) |
| C(3) | 431(3) | 3718(1) | 88(2) | 14(1) |
| C(4) | -1623(3) | 3686(1) | -1493(2) | 16(1) |
| C(5) | -770(3) | 3772(1) | -3188(2) | 17(1) |
| C(6) | 1730(3) | 3865(1) | -2584(2) | 16(1) |
| C(7) | 2237(3) | 3791(1) | -519(2) | 15(1) |

Table 3. Selected bond lengths [\AA] and angles [deg] for rwx0226.

| | |
|----------------|------------|
| S(1)-C(7) | 1.712(2) |
| S(1)-C(1) | 1.722(2) |
| O(1)-C(5) | 1.213(2) |
| C(1)-C(2) | 1.376(3) |
| C(2)-C(3) | 1.443(2) |
| C(3)-C(7) | 1.367(2) |
| C(3)-C(4) | 1.498(2) |
| C(4)-C(5) | 1.534(2) |
| C(5)-C(6) | 1.539(3) |
| C(6)-C(7) | 1.499(2) |
| C(7)-S(1)-C(1) | 91.27(9) |
| C(2)-C(1)-S(1) | 113.42(13) |
| C(1)-C(2)-C(3) | 109.8(2) |
| C(7)-C(3)-C(2) | 113.5(2) |
| C(7)-C(3)-C(4) | 111.7(2) |
| C(2)-C(3)-C(4) | 134.8(2) |
| C(3)-C(4)-C(5) | 102.53(14) |
| O(1)-C(5)-C(4) | 124.9(2) |
| O(1)-C(5)-C(6) | 124.5(2) |
| C(4)-C(5)-C(6) | 110.64(14) |
| C(7)-C(6)-C(5) | 101.23(14) |
| C(3)-C(7)-C(6) | 113.8(2) |
| C(3)-C(7)-S(1) | 112.02(14) |
| C(6)-C(7)-S(1) | 134.17(13) |

Symmetry transformations used to generate equivalent atoms:

Table 4. Bond lengths [Å] and angles [deg] for rwx0226.

| | |
|----------------|------------|
| S(1)-C(7) | 1.712(2) |
| S(1)-C(1) | 1.722(2) |
| O(1)-C(5) | 1.213(2) |
| C(1)-C(2) | 1.376(3) |
| C(2)-C(3) | 1.443(2) |
| C(3)-C(7) | 1.367(2) |
| C(3)-C(4) | 1.498(2) |
| C(4)-C(5) | 1.534(2) |
| C(5)-C(6) | 1.539(3) |
| C(6)-C(7) | 1.499(2) |
| C(1)-H(1) | 0.919(2) |
| C(2)-H(2) | 0.897(2) |
| C(4)-H(3) | 0.971(2) |
| C(4)-H(4) | 0.994(2) |
| C(6)-H(5) | 0.979(2) |
| C(6)-H(6) | 1.021(2) |
| | |
| C(7)-S(1)-C(1) | 91.27(9) |
| C(2)-C(1)-S(1) | 113.42(13) |
| C(1)-C(2)-C(3) | 109.8(2) |
| C(7)-C(3)-C(2) | 113.5(2) |
| C(7)-C(3)-C(4) | 111.7(2) |
| C(2)-C(3)-C(4) | 134.8(2) |
| C(3)-C(4)-C(5) | 102.53(14) |
| O(1)-C(5)-C(4) | 124.9(2) |
| O(1)-C(5)-C(6) | 124.5(2) |
| C(4)-C(5)-C(6) | 110.64(14) |
| C(7)-C(6)-C(5) | 101.23(14) |
| C(3)-C(7)-C(6) | 113.8(2) |
| C(3)-C(7)-S(1) | 112.02(14) |
| C(6)-C(7)-S(1) | 134.17(13) |
| C(2)-C(1)-H(1) | 130.5(2) |
| S(1)-C(1)-H(1) | 116.1(2) |
| C(1)-C(2)-H(2) | 121.8(2) |
| C(3)-C(2)-H(2) | 128.3(2) |
| C(3)-C(4)-H(3) | 116.7(2) |
| C(5)-C(4)-H(3) | 107.1(2) |
| C(3)-C(4)-H(4) | 116.1(2) |
| C(5)-C(4)-H(4) | 107.1(2) |
| H(3)-C(4)-H(4) | 106.5(2) |
| C(7)-C(6)-H(5) | 111.6(2) |
| C(5)-C(6)-H(5) | 110.5(2) |
| C(7)-C(6)-H(6) | 109.3(2) |
| C(5)-C(6)-H(6) | 112.8(2) |
| H(5)-C(6)-H(6) | 111.1(2) |

Symmetry transformations used to generate equivalent atoms:

Table 5. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for rwx0226. The anisotropic displacement factor exponent takes the form:
 $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

| | U11 | U22 | U33 | U23 | U13 | U12 |
|------|-------|-------|-------|-------|-------|-------|
| S(1) | 16(1) | 22(1) | 15(1) | 1(1) | 2(1) | 0(1) |
| O(1) | 24(1) | 37(1) | 13(1) | -2(1) | -1(1) | 1(1) |
| C(1) | 21(1) | 20(1) | 10(1) | 1(1) | 1(1) | 0(1) |
| C(2) | 18(1) | 12(1) | 11(1) | 1(1) | 2(1) | 0(1) |
| C(3) | 17(1) | 13(1) | 12(1) | 0(1) | 3(1) | 0(1) |
| C(4) | 15(1) | 17(1) | 15(1) | 1(1) | 2(1) | -1(1) |
| C(5) | 20(1) | 15(1) | 14(1) | -1(1) | 2(1) | 0(1) |
| C(6) | 18(1) | 19(1) | 11(1) | 0(1) | 4(1) | -1(1) |
| C(7) | 16(1) | 15(1) | 12(1) | 0(1) | 2(1) | -1(1) |

Table 6. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for rwx0226.

| | x | y | z | U(eq) |
|------|-------|------|-------|-------|
| H(1) | 3962 | 3708 | 4097 | 27 |
| H(2) | 0 | 3670 | 2768 | 27 |
| H(3) | -2647 | 4233 | -1568 | 27 |
| H(4) | -2481 | 3054 | -1634 | 27 |
| H(5) | 2173 | 4515 | -2962 | 27 |
| H(6) | 2471 | 3287 | -3055 | 27 |

| h | k | l | 10Fo | 10Fc | 10s | h | k | l | 10Fo | 10Fc | 10s | h | k | l | 10Fo | 10Fc | 10s | h | k | l | 10Fo | 10Fc | 10s |
|---|----|---|------|------|-----|----|----|---|------|------|-----|----|----|---|------|------|-----|----|----|---|------|------|-----|
| 1 | 0 | 0 | 296 | 284 | 1 | 5 | 13 | 0 | 113 | 113 | 2 | -1 | 6 | 1 | 731 | 699 | 5 | 3 | 13 | 1 | 191 | 191 | 3 |
| 2 | 0 | 0 | 27 | 42 | 1 | 0 | 14 | 0 | 66 | 64 | 1 | 0 | 6 | 1 | 185 | 193 | 4 | 4 | 13 | 1 | 81 | 83 | 1 |
| 3 | 0 | 0 | 517 | 517 | 1 | 1 | 14 | 0 | 86 | 83 | 1 | 1 | 6 | 1 | 61 | 72 | 1 | -4 | 14 | 1 | 108 | 103 | 2 |
| 4 | 0 | 0 | 113 | 140 | 1 | 2 | 14 | 0 | 22 | 20 | 3 | 2 | 6 | 1 | 332 | 326 | 2 | -3 | 14 | 1 | 67 | 66 | 1 |
| 5 | 0 | 0 | 8 | 12 | 8 | 3 | 14 | 0 | 77 | 80 | 1 | 3 | 6 | 1 | 183 | 175 | 1 | -2 | 14 | 1 | 89 | 84 | 1 |
| 6 | 0 | 0 | 52 | 52 | 1 | 4 | 14 | 0 | 50 | 48 | 1 | 4 | 6 | 1 | 45 | 42 | 1 | -1 | 14 | 1 | 258 | 252 | 3 |
| 7 | 0 | 0 | 57 | 46 | 1 | 1 | 15 | 0 | 93 | 91 | 1 | 5 | 6 | 1 | 97 | 100 | 1 | 0 | 14 | 1 | 81 | 81 | 2 |
| 1 | 1 | 0 | 240 | 244 | 1 | 2 | 15 | 0 | 74 | 73 | 1 | 6 | 6 | 1 | 32 | 36 | 2 | 1 | 14 | 1 | 56 | 53 | 1 |
| 2 | 1 | 0 | 255 | 272 | 1 | 3 | 15 | 0 | 49 | 45 | 1 | 7 | 6 | 1 | 143 | 138 | 2 | 2 | 14 | 1 | 122 | 126 | 2 |
| 3 | 1 | 0 | 193 | 197 | 1 | 0 | 16 | 0 | 372 | 379 | 3 | -7 | 7 | 1 | 80 | 78 | 1 | 3 | 14 | 1 | 87 | 87 | 1 |
| 4 | 1 | 0 | 35 | 38 | 1 | 1 | 16 | 0 | 11 | 11 | 10 | -6 | 7 | 1 | 117 | 115 | 2 | 4 | 14 | 1 | 13 | 11 | 12 |
| 5 | 1 | 0 | 228 | 232 | 2 | 2 | 16 | 0 | 75 | 71 | 1 | -5 | 7 | 1 | 39 | 39 | 1 | -3 | 15 | 1 | 54 | 53 | 1 |
| 6 | 1 | 0 | 129 | 139 | 2 | -8 | 1 | 1 | 109 | 102 | 2 | -4 | 7 | 1 | 86 | 82 | 1 | -2 | 15 | 1 | 100 | 107 | 1 |
| 7 | 1 | 0 | 125 | 115 | 2 | -7 | 1 | 1 | 100 | 100 | 1 | -3 | 7 | 1 | 149 | 137 | 2 | -1 | 15 | 1 | 123 | 130 | 2 |
| 0 | 2 | 0 | 41 | 37 | 1 | -6 | 1 | 1 | 185 | 184 | 2 | -2 | 7 | 1 | 221 | 212 | 2 | 0 | 15 | 1 | 89 | 90 | 1 |
| 1 | 2 | 0 | 38 | 36 | 1 | -5 | 1 | 1 | 97 | 98 | 1 | -1 | 7 | 1 | 175 | 155 | 2 | 1 | 15 | 1 | 89 | 90 | 1 |
| 2 | 2 | 0 | 0 | 0 | 1 | -4 | 1 | 1 | 170 | 169 | 2 | 0 | 7 | 1 | 188 | 175 | 2 | 2 | 15 | 1 | 10 | 4 | 10 |
| 3 | 2 | 0 | 35 | 39 | 1 | -3 | 1 | 1 | 229 | 227 | 1 | 1 | 7 | 1 | 217 | 220 | 2 | 3 | 15 | 1 | 89 | 92 | 1 |
| 4 | 2 | 0 | 11 | 12 | 10 | -2 | 1 | 1 | 221 | 230 | 1 | 2 | 7 | 1 | 118 | 120 | 2 | -2 | 16 | 1 | 59 | 59 | 2 |
| 5 | 2 | 0 | 0 | 0 | 9 | -1 | 1 | 1 | 122 | 115 | 1 | 3 | 7 | 1 | 229 | 229 | 2 | -1 | 16 | 1 | 109 | 113 | 2 |
| 6 | 2 | 0 | 17 | 5 | 3 | 0 | 1 | 1 | 387 | 385 | 1 | 4 | 7 | 1 | 49 | 56 | 1 | 0 | 16 | 1 | 10 | 18 | 10 |
| 7 | 2 | 0 | 0 | 0 | 0 | 1 | 1 | 1 | 401 | 402 | 1 | 5 | 7 | 1 | 69 | 69 | 1 | 1 | 16 | 1 | 39 | 41 | 2 |
| 1 | 3 | 0 | 256 | 251 | 1 | 2 | 1 | 1 | 305 | 314 | 1 | 6 | 7 | 1 | 88 | 89 | 1 | 2 | 16 | 1 | 32 | 30 | 2 |
| 2 | 3 | 0 | 230 | 238 | 2 | 3 | 1 | 1 | 336 | 338 | 2 | -7 | 8 | 1 | 17 | 8 | 4 | -8 | 0 | 2 | 37 | 41 | 2 |
| 3 | 3 | 0 | 167 | 176 | 2 | 4 | 1 | 1 | 95 | 101 | 1 | -6 | 8 | 1 | 31 | 29 | 2 | -7 | 0 | 2 | 146 | 138 | 2 |
| 4 | 3 | 0 | 100 | 102 | 1 | 5 | 1 | 1 | 164 | 169 | 2 | -5 | 8 | 1 | 4 | 21 | 3 | -6 | 0 | 2 | 262 | 277 | 2 |
| 5 | 3 | 0 | 231 | 229 | 2 | 6 | 1 | 1 | 123 | 124 | 2 | -4 | 8 | 1 | 95 | 98 | 1 | -5 | 0 | 2 | 381 | 387 | 2 |
| 6 | 3 | 0 | 135 | 147 | 2 | 7 | 1 | 1 | 69 | 65 | 1 | -3 | 8 | 1 | 30 | 32 | 1 | -4 | 0 | 2 | 132 | 149 | 2 |
| 7 | 3 | 0 | 140 | 135 | 2 | -7 | 2 | 1 | 113 | 110 | 1 | -2 | 8 | 1 | 60 | 62 | 1 | -3 | 0 | 2 | 250 | 233 | 1 |
| 0 | 4 | 0 | 1946 | 1947 | 4 | -6 | 2 | 1 | 35 | 38 | 2 | -1 | 8 | 1 | 142 | 135 | 2 | -2 | 0 | 2 | 113 | 126 | 1 |
| 1 | 4 | 0 | 204 | 167 | 1 | -5 | 2 | 1 | 486 | 503 | 2 | 0 | 8 | 1 | 30 | 25 | 1 | -1 | 0 | 2 | 101 | 91 | 1 |
| 2 | 4 | 0 | 120 | 128 | 1 | -4 | 2 | 1 | 303 | 317 | 2 | 1 | 8 | 1 | 44 | 45 | 1 | 0 | 0 | 2 | 186 | 189 | 1 |
| 3 | 4 | 0 | 420 | 430 | 2 | -3 | 2 | 1 | 29 | 43 | 1 | 2 | 8 | 1 | 35 | 35 | 1 | 1 | 0 | 2 | 113 | 97 | 1 |
| 4 | 4 | 0 | 83 | 103 | 1 | -2 | 2 | 1 | 268 | 300 | 1 | 3 | 8 | 1 | 0 | 12 | 1 | 2 | 0 | 2 | 45 | 57 | 1 |
| 5 | 4 | 0 | 22 | 22 | 2 | -1 | 2 | 1 | 1001 | 1049 | 3 | 4 | 8 | 1 | 30 | 25 | 2 | 3 | 0 | 2 | 301 | 297 | 2 |
| 6 | 4 | 0 | 50 | 51 | 1 | 0 | 2 | 1 | 132 | 124 | 1 | 5 | 8 | 1 | 10 | 19 | 9 | 4 | 0 | 2 | 416 | 431 | 2 |
| 7 | 4 | 0 | 49 | 44 | 2 | 1 | 2 | 1 | 141 | 159 | 1 | 6 | 8 | 1 | 26 | 23 | 2 | 5 | 0 | 2 | 7 | 24 | 7 |
| 1 | 5 | 0 | 135 | 129 | 1 | 2 | 2 | 1 | 568 | 560 | 1 | -6 | 9 | 1 | 148 | 146 | 1 | 6 | 0 | 2 | 226 | 221 | 3 |
| 2 | 5 | 0 | 211 | 214 | 1 | 3 | 2 | 1 | 292 | 266 | 2 | -5 | 9 | 1 | 125 | 123 | 2 | 7 | 0 | 2 | 207 | 209 | 3 |
| 3 | 5 | 0 | 147 | 154 | 2 | 4 | 2 | 1 | 80 | 82 | 1 | -4 | 9 | 1 | 110 | 111 | 2 | -8 | 1 | 2 | 78 | 70 | 1 |
| 4 | 5 | 0 | 21 | 22 | 2 | 5 | 2 | 1 | 91 | 99 | 1 | -3 | 9 | 1 | 101 | 99 | 1 | -7 | 1 | 2 | 21 | 22 | 3 |
| 5 | 5 | 0 | 204 | 208 | 2 | 6 | 2 | 1 | 42 | 40 | 1 | -2 | 9 | 1 | 81 | 81 | 1 | -6 | 1 | 2 | 114 | 117 | 2 |
| 6 | 5 | 0 | 102 | 112 | 1 | 7 | 2 | 1 | 171 | 161 | 3 | -1 | 9 | 1 | 51 | 56 | 1 | -5 | 1 | 2 | 217 | 224 | 2 |
| 7 | 5 | 0 | 86 | 81 | 1 | -7 | 3 | 1 | 92 | 94 | 1 | 0 | 9 | 1 | 193 | 184 | 1 | -4 | 1 | 2 | 19 | 13 | 2 |
| 0 | 6 | 0 | 62 | 63 | 1 | -6 | 3 | 1 | 156 | 156 | 2 | 1 | 9 | 1 | 221 | 218 | 2 | -3 | 1 | 2 | 218 | 229 | 1 |
| 1 | 6 | 0 | 84 | 79 | 1 | -5 | 3 | 1 | 70 | 71 | 1 | 2 | 9 | 1 | 220 | 223 | 2 | -2 | 1 | 2 | 484 | 479 | 1 |
| 2 | 6 | 0 | 6 | 13 | 6 | -4 | 3 | 1 | 126 | 129 | 2 | 3 | 9 | 1 | 252 | 246 | 2 | -1 | 1 | 2 | 39 | 27 | 1 |
| 3 | 6 | 0 | 73 | 76 | 1 | -3 | 3 | 1 | 194 | 191 | 1 | 4 | 9 | 1 | 107 | 109 | 2 | 0 | 1 | 2 | 297 | 285 | 1 |
| 4 | 6 | 0 | 32 | 34 | 1 | -2 | 3 | 1 | 267 | 266 | 1 | 5 | 9 | 1 | 147 | 149 | 2 | 1 | 1 | 2 | 406 | 395 | 1 |
| 5 | 6 | 0 | 19 | 18 | 3 | -1 | 3 | 1 | 238 | 220 | 1 | 6 | 9 | 1 | 104 | 99 | 2 | 2 | 1 | 2 | 335 | 328 | 1 |
| 6 | 6 | 0 | 14 | 11 | 5 | 0 | 3 | 1 | 325 | 316 | 1 | -6 | 10 | 1 | 16 | 25 | 16 | 3 | 1 | 2 | 80 | 85 | 1 |
| 7 | 6 | 0 | 11 | 1 | 10 | 1 | 3 | 1 | 365 | 369 | 1 | -5 | 10 | 1 | 328 | 337 | 3 | 4 | 1 | 2 | 156 | 152 | 2 |
| 1 | 7 | 0 | 156 | 143 | 2 | 2 | 3 | 1 | 207 | 214 | 1 | -4 | 10 | 1 | 187 | 185 | 2 | 5 | 1 | 2 | 0 | 16 | 1 |
| 2 | 7 | 0 | 180 | 174 | 2 | 3 | 3 | 1 | 299 | 299 | 2 | -3 | 10 | 1 | 71 | 74 | 1 | 6 | 1 | 2 | 0 | 2 | 1 |
| 3 | 7 | 0 | 130 | 140 | 2 | 4 | 3 | 1 | 81 | 89 | 1 | -2 | 10 | 1 | 121 | 125 | 1 | 7 | 1 | 2 | 45 | 47 | 2 |
| 4 | 7 | 0 | 124 | 129 | 1 | 5 | 3 | 1 | 120 | 127 | 2 | -1 | 10 | 1 | 437 | 416 | 2 | -8 | 2 | 2 | 0 | 3 | 1 |
| 5 | 7 | 0 | 190 | 193 | 2 | 6 | 3 | 1 | 111 | 110 | 1 | 0 | 10 | 1 | 124 | 130 | 1 | -7 | 2 | 2 | 13 | 10 | 6 |
| 6 | 7 | 0 | 129 | 137 | 2 | 7 | 3 | 1 | 65 | 62 | 1 | 1 | 10 | 1 | 67 | 68 | 1 | -6 | 2 | 2 | 19 | 21 | 3 |
| 7 | 7 | 0 | 142 | 135 | 2 | -7 | 4 | 1 | 0 | 4 | 1 | 2 | 10 | 1 | 199 | 199 | 2 | -5 | 2 | 2 | 5 | 5 | 5 |
| 0 | 8 | 0 | 1058 | 1011 | 2 | -6 | 4 | 1 | 0 | 15 | 1 | 3 | 10 | 1 | 129 | 125 | 2 | -4 | 2 | 2 | 16 | 13 | 2 |
| 1 | 8 | 0 | 70 | 41 | 1 | -5 | 4 | 1 | 11 | 18 | 11 | 4 | 10 | 1 | 23 | 23 | 3 | -3 | 2 | 2 | 25 | 25 | 1 |
| 2 | 8 | 0 | 148 | 147 | 2 | -4 | 4 | 1 | 60 | 65 | 1 | 5 | 10 | 1 | 84 | 81 | 1 | -2 | 2 | 2 | 35 | 34 | 1 |
| 3 | 8 | 0 | 288 | 294 | 2 | -3 | 4 | 1 | 16 | 12 | 2 | 6 | 10 | 1 | 12 | 19 | 11 | -1 | 2 | 2 | 17 | 16 | 1 |
| 4 | 8 | 0 | 63 | 73 | 1 | -2 | 4 | 1 | 43 | 45 | 1 | -6 | 11 | 1 | 76 | 77 | 1 | 0 | 2 | 2 | 0 | 4 | 1 |
| 5 | 8 | 0 | 34 | 32 | 2 | -1 | 4 | 1 | 128 | 120 | 1 | -5 | 11 | 1 | 24 | 17 | 3 | 1 | 2 | 2 | 7 | 4 | 6 |
| 6 | 8 | 0 | 35 | 36 | 2 | 0 | 4 | 1 | 44 | 38 | 1 | -4 | 11 | 1 | 59 | 59 | 1 | 2 | 2 | 2 | 25 | 24 | 1 |
| 1 | 9 | 0 | 80 | 73 | 1 | 1 | 4 | 1 | 35 | 36 | 1 | -3 | 11 | 1 | 93 | 86 | 1 | 3 | 2 | 2 | 14 | 2 | 2 |
| 2 | 9 | 0 | 129 | 126 | 2 | 2 | 4 | 1 | 26 | 26 | 1 | -2 | 11 | 1 | 149 | 145 | 2 | 4 | 2 | 2 | 13 | 14 | 4 |
| 3 | 9 | 0 | 97 | 101 | 1 | 3 | 4 | 1 | 17 | 5 | 2 | -1 | 11 | 1 | 142 | 134 | 2 | 5 | 2 | 2 | 23 | 20 | 2 |
| 4 | 9 | 0 | 48 | 48 | 1 | 4 | 4 | 1 | 16 | 15 | 3 | 0 | 11 | 1 | 128 | 124 | 1 | 6 | 2 | 2 | 0 | 6 | 1 |
| 5 | 9 | 0 | 170 | 163 | 3 | 5 | 4 | 1 | 0 | 10 | 1 | 1 | 11 | 1 | 139 | 139 | 2 | 7 | 2 | 2 | 11 | 12 | 10 |
| 6 | 9 | 0 | 68 | 70 | 1 | 6 | 4 | 1 | 11 | 16 | 11 | 2 | 11 | 1 | 47 | 45 | 1 | -8 | 3 | 2 | 67 | 64 | 2 |
| 0 | 10 | 0 | 69 | 72 | 1 | 7 | 4 | 1 | 13 | 23 | 13 | -5 | 11 | 1 | 156 | 152 | 2 | -7 | 3 | 2 | 49 | 44 | 1 |
| 1 | 10 | 0 | 91 | 88 | 1 | -7 | 5 | 1 | 94 | 92 | 1 | 4 | 11 | 1 | 28 | 27 | 2 | -6 | 3 | 2 | 95 | 100 | 1 |
| 2 | 10 | 0 | 14 | 20 | 14 | -6 | 5 | 1 | 179 | 175 | 3 | 5 | 11 | 1 | 25 | 24 | 3 | -5 | 3 | 2 | 221 | 227 | 2 |

| h | k | l | 10Fo | 10Fc | 10s | h | k | l | 10Fo | 10Fc | 10s | h | k | l | 10Fo | 10Fc | 10s | h | k | l | 10Fo | 10Fc | 10s |
|----|---|---|------|------|-----|----|----|---|------|------|-----|----|----|---|------|------|-----|----|----|---|------|------|-----|
| 0 | 4 | 2 | 81 | 77 | 1 | 1 | 11 | 2 | 208 | 206 | 2 | -1 | 4 | 3 | 15 | 11 | 2 | 2 | 11 | 3 | 18 | 22 | 4 |
| 1 | 4 | 2 | 27 | 20 | 1 | 2 | 11 | 2 | 211 | 210 | 2 | 0 | 4 | 3 | 77 | 74 | 1 | 1 | 11 | 3 | 127 | 130 | 2 |
| 2 | 4 | 2 | 26 | 31 | 1 | 3 | 11 | 2 | 88 | 91 | 1 | 1 | 4 | 3 | 8 | 11 | 7 | 4 | 11 | 3 | 118 | 126 | 2 |
| 3 | 4 | 2 | 297 | 292 | 2 | 4 | 11 | 2 | 117 | 116 | 1 | 2 | 4 | 3 | 34 | 32 | 1 | -5 | 12 | 3 | 12 | 14 | 11 |
| 4 | 4 | 2 | 388 | 406 | 3 | 5 | 11 | 2 | 0 | 17 | 1 | 3 | 4 | 3 | 50 | 54 | 1 | -4 | 12 | 3 | 47 | 43 | 1 |
| 5 | 4 | 2 | 22 | 32 | 3 | -5 | 12 | 2 | 194 | 193 | 3 | 4 | 4 | 3 | 12 | 7 | 12 | -3 | 12 | 3 | 9 | 15 | 8 |
| 6 | 4 | 2 | 210 | 205 | 3 | -4 | 12 | 2 | 70 | 70 | 1 | 5 | 4 | 3 | 21 | 22 | 2 | -2 | 12 | 3 | 4 | 5 | 4 |
| 7 | 4 | 2 | 0 | 7 | 1 | -3 | 12 | 2 | 141 | 136 | 2 | 6 | 4 | 3 | 29 | 28 | 2 | -1 | 12 | 3 | 0 | 2 | 2 |
| 8 | 4 | 2 | 129 | 130 | 2 | -2 | 12 | 2 | 76 | 73 | 1 | -7 | 5 | 3 | 88 | 87 | 1 | 0 | 12 | 3 | 99 | 100 | 1 |
| 9 | 4 | 2 | 180 | 188 | 2 | -1 | 12 | 2 | 27 | 26 | 2 | -6 | 5 | 3 | 141 | 145 | 2 | 1 | 12 | 3 | 28 | 27 | 2 |
| 10 | 4 | 2 | 21 | 28 | 2 | 0 | 12 | 2 | 32 | 28 | 9 | -5 | 5 | 3 | 33 | 34 | 1 | 2 | 12 | 3 | 52 | 52 | 1 |
| 11 | 4 | 2 | 137 | 147 | 1 | 1 | 12 | 2 | 0 | 9 | 1 | -4 | 5 | 3 | 248 | 268 | 2 | 3 | 12 | 3 | 89 | 93 | 1 |
| 12 | 4 | 2 | 301 | 296 | 2 | 2 | 12 | 2 | 38 | 37 | 2 | -3 | 5 | 3 | 398 | 404 | 1 | 4 | 12 | 3 | 24 | 12 | 2 |
| 13 | 4 | 2 | 8 | 2 | 8 | 3 | 12 | 2 | 148 | 147 | 2 | -2 | 5 | 3 | 83 | 87 | 1 | -5 | 13 | 3 | 37 | 30 | 2 |
| 14 | 4 | 2 | 199 | 196 | 1 | 4 | 12 | 2 | 246 | 244 | 3 | -1 | 5 | 3 | 266 | 272 | 2 | -4 | 13 | 3 | 164 | 162 | 2 |
| 15 | 4 | 2 | 258 | 259 | 1 | -5 | 13 | 2 | 86 | 92 | 1 | 0 | 5 | 3 | 169 | 166 | 1 | -3 | 13 | 3 | 215 | 208 | 3 |
| 16 | 4 | 2 | 263 | 262 | 2 | -4 | 13 | 2 | 36 | 34 | 2 | 1 | 5 | 3 | 169 | 167 | 2 | -2 | 13 | 3 | 95 | 93 | 1 |
| 17 | 4 | 2 | 49 | 53 | 2 | -3 | 13 | 2 | 32 | 34 | 2 | 2 | 5 | 3 | 54 | 56 | 1 | -1 | 13 | 3 | 175 | 172 | 3 |
| 18 | 4 | 2 | 103 | 105 | 2 | -2 | 13 | 2 | 90 | 91 | 1 | 3 | 5 | 3 | 146 | 143 | 1 | 0 | 13 | 3 | 66 | 62 | 1 |
| 19 | 4 | 2 | 0 | 4 | 1 | -1 | 13 | 2 | 16 | 13 | 4 | 4 | 5 | 3 | 170 | 174 | 2 | 1 | 13 | 3 | 126 | 125 | 2 |
| 20 | 4 | 2 | 0 | 5 | 1 | 0 | 13 | 2 | 51 | 50 | 1 | 5 | 5 | 3 | 51 | 48 | 1 | 2 | 13 | 3 | 54 | 52 | 1 |
| 21 | 4 | 2 | 26 | 22 | 1 | 1 | 13 | 2 | 65 | 59 | 1 | 6 | 5 | 3 | 30 | 25 | 1 | 3 | 13 | 3 | 52 | 48 | 2 |
| 22 | 4 | 2 | 55 | 56 | 2 | 2 | 13 | 2 | 141 | 142 | 2 | -7 | 6 | 3 | 29 | 27 | 3 | -4 | 14 | 3 | 25 | 17 | 2 |
| 23 | 4 | 2 | 27 | 24 | 2 | 3 | 13 | 2 | 0 | 5 | 1 | -6 | 6 | 3 | 182 | 183 | 2 | -3 | 14 | 3 | 69 | 75 | 1 |
| 24 | 4 | 2 | 27 | 30 | 2 | 4 | 13 | 2 | 16 | 15 | 15 | -6 | 6 | 3 | 192 | 193 | 2 | -2 | 14 | 3 | 74 | 79 | 1 |
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| h | k | l | 10Fo | 10Fc | 10s | h | k | l | 10Fo | 10Fc | 10s | h | k | l | 10Fo | 10Fc | 10s | h | k | l | 10Fo | 10Fc | 10s |
|----|---|---|------|------|-----|------|----|---|------|------|-----|----|----|----|------|------|-----|----|---|---|------|------|-----|
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| 0 | 4 | 4 | 23 | 5 | 1 | -2 | 12 | 4 | 223 | 219 | 3 | -1 | 6 | 6 | 170 | 173 | 2 | -2 | 1 | 6 | 0 | 9 | 1 |
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| -1 | 9 | 4 | 89 | 85 | 1 | -6 | 4 | 5 | 28 | 29 | 2 | -1 | 12 | 12 | 36 | 35 | 2 | 2 | 6 | 6 | 14 | 8 | 13 |
| 0 | 9 | 4 | 23 | 26 | 4 | -5 | 4 | 5 | 0 | 6 | 1 | 0 | 12 | 12 | 117 | 119 | 1 | -6 | 7 | 6 | 52 | 49 | 3 |
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| h | k | l | 10Fo | 10Fc | 10s | h | k | l | 10Fo | 10Fc | 10s | h | k | l | 10Fo | 10Fc | 10s | h | k | l | 10Fo | 10Fc | 10s | |
|----|----|---|------|------|-----|----|---|---|------|------|-----|----|----|---|------|------|-----|----|----|---|------|------|-----|---|
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| -3 | 11 | 6 | 37 | 36 | 2 | -6 | 5 | 7 | 152 | 152 | 2 | -4 | 0 | 8 | 125 | 128 | 2 | -4 | 7 | 8 | 93 | 95 | 1 | |
| -2 | 11 | 6 | 0 | 3 | 1 | -5 | 5 | 7 | 151 | 149 | 2 | -3 | 0 | 8 | 172 | 168 | 3 | -3 | 7 | 8 | 117 | 115 | 2 | |
| -1 | 11 | 6 | 279 | 285 | 3 | -4 | 5 | 7 | 121 | 116 | 2 | -2 | 0 | 8 | 55 | 54 | 1 | -2 | 7 | 8 | 46 | 48 | 2 | |
| 0 | 11 | 6 | 118 | 117 | 1 | -3 | 5 | 7 | 50 | 49 | 1 | -1 | 0 | 8 | 194 | 192 | 3 | -1 | 7 | 8 | 57 | 57 | 1 | |
| 1 | 11 | 6 | 100 | 103 | 1 | -2 | 5 | 7 | 276 | 284 | 2 | 0 | 0 | 8 | 189 | 189 | 2 | 0 | 7 | 8 | 23 | 28 | 2 | |
| -4 | 12 | 6 | 131 | 132 | 2 | -1 | 5 | 7 | 73 | 72 | 1 | 1 | 0 | 8 | 123 | 125 | 2 | -4 | 8 | 8 | 93 | 98 | 1 | |
| -3 | 12 | 6 | 21 | 15 | 3 | 0 | 5 | 7 | 157 | 156 | 2 | 2 | 0 | 8 | 240 | 242 | 3 | -3 | 8 | 8 | 118 | 123 | 2 | |
| -2 | 12 | 6 | 135 | 143 | 2 | 1 | 5 | 7 | 160 | 164 | 2 | -6 | 1 | 8 | 95 | 95 | 1 | -2 | 8 | 8 | 48 | 47 | 1 | |
| -1 | 12 | 6 | 60 | 57 | 1 | 2 | 5 | 7 | 12 | 14 | 11 | -5 | 1 | 8 | 131 | 130 | 2 | -1 | 8 | 8 | 139 | 145 | 2 | |
| 0 | 12 | 6 | 85 | 90 | 1 | -3 | 5 | 7 | 26 | 23 | 3 | -4 | 1 | 8 | 93 | 93 | 1 | 0 | 8 | 8 | 137 | 138 | 4 | |
| 1 | 12 | 6 | 180 | 182 | 3 | -6 | 6 | 7 | 128 | 120 | 2 | -3 | 1 | 8 | 95 | 97 | 1 | -3 | 9 | 8 | 34 | 32 | 3 | |
| -2 | 13 | 6 | 19 | 27 | 18 | -5 | 6 | 7 | 120 | 111 | 2 | -2 | 1 | 8 | 53 | 54 | 1 | -2 | 9 | 8 | 27 | 27 | 3 | |
| -1 | 13 | 6 | 157 | 167 | 2 | -4 | 6 | 7 | 9 | 13 | 9 | -1 | 1 | 8 | 49 | 49 | 1 | -1 | 9 | 8 | 19 | 21 | 4 | |
| -7 | 1 | 7 | 63 | 58 | 1 | -3 | 6 | 7 | 37 | 38 | 2 | 0 | 0 | 1 | 8 | 17 | 23 | 4 | -4 | 1 | 9 | 105 | 107 | 1 |
| -6 | 1 | 7 | 164 | 162 | 2 | -2 | 6 | 7 | 80 | 84 | 1 | -3 | 1 | 8 | 45 | 41 | 1 | -3 | 1 | 9 | 33 | 32 | 2 | |
| -5 | 1 | 7 | 144 | 140 | 2 | -1 | 6 | 7 | 40 | 44 | 1 | -2 | 1 | 8 | 24 | 26 | 3 | -2 | 1 | 9 | 128 | 125 | 2 | |
| -4 | 1 | 7 | 132 | 126 | 2 | 0 | 6 | 7 | 189 | 183 | 7 | -6 | 2 | 8 | 14 | 0 | 14 | -1 | 1 | 9 | 0 | 11 | 1 | |
| -3 | 1 | 7 | 43 | 39 | 1 | 1 | 6 | 7 | 123 | 126 | 2 | -5 | 2 | 8 | 17 | 4 | 4 | 0 | 1 | 9 | 31 | 31 | 1 | |
| -2 | 1 | 7 | 274 | 281 | 2 | 2 | 6 | 7 | 179 | 184 | 3 | -4 | 2 | 8 | 6 | 6 | 5 | -4 | 2 | 9 | 177 | 171 | 3 | |
| -1 | 1 | 7 | 68 | 64 | 1 | -6 | 7 | 7 | 134 | 135 | 2 | -3 | 2 | 8 | 8 | 8 | 1 | -3 | 2 | 9 | 110 | 114 | 2 | |
| 0 | 1 | 7 | 169 | 169 | 2 | -5 | 7 | 7 | 73 | 69 | 1 | -2 | 2 | 8 | 0 | 1 | 1 | -2 | 2 | 9 | 221 | 220 | 3 | |
| 1 | 1 | 7 | 170 | 170 | 3 | -4 | 7 | 7 | 99 | 99 | 1 | -1 | 2 | 8 | 17 | 18 | 4 | -1 | 2 | 9 | 126 | 128 | 2 | |
| 2 | 1 | 7 | 29 | 27 | 2 | -3 | 7 | 7 | 16 | 9 | 3 | 0 | 0 | 8 | 12 | 15 | 12 | 0 | 2 | 9 | 4 | 4 | 4 | |
| 3 | 1 | 7 | 24 | 20 | 3 | -2 | 7 | 7 | 176 | 180 | 3 | 1 | 2 | 8 | 0 | 2 | 1 | -4 | 3 | 9 | 106 | 105 | 2 | |
| -7 | 2 | 7 | 162 | 159 | 2 | -1 | 7 | 7 | 38 | 39 | 1 | 2 | 2 | 8 | 14 | 9 | 14 | -3 | 3 | 9 | 25 | 21 | 3 | |
| -6 | 2 | 7 | 139 | 137 | 2 | 0 | 7 | 7 | 116 | 116 | 1 | -6 | 3 | 8 | 102 | 104 | 1 | -2 | 3 | 9 | 125 | 126 | 2 | |
| -5 | 2 | 7 | 132 | 128 | 2 | 1 | 7 | 7 | 100 | 104 | 1 | -5 | 3 | 8 | 142 | 136 | 2 | -1 | 3 | 9 | 11 | 6 | 10 | |
| -4 | 2 | 7 | 18 | 13 | 4 | 2 | 7 | 7 | 26 | 30 | 3 | -4 | 3 | 8 | 105 | 102 | 2 | 0 | 3 | 9 | 34 | 33 | 2 | |
| -3 | 2 | 7 | 44 | 45 | 1 | -5 | 8 | 7 | 6 | 16 | 6 | -3 | 3 | 8 | 120 | 116 | 2 | -4 | 4 | 9 | 17 | 6 | 4 | |
| -2 | 2 | 7 | 94 | 101 | 1 | -4 | 8 | 7 | 10 | 22 | 10 | -2 | 3 | 8 | 55 | 55 | 1 | -3 | 4 | 9 | 11 | 7 | 10 | |
| -1 | 2 | 7 | 38 | 45 | 1 | -3 | 8 | 7 | 45 | 47 | 1 | -1 | 3 | 8 | 57 | 57 | 1 | -2 | 4 | 9 | 45 | 43 | 2 | |
| 0 | 2 | 7 | 230 | 219 | 2 | -2 | 8 | 7 | 52 | 51 | 1 | 0 | 3 | 8 | 23 | 28 | 6 | -1 | 4 | 9 | 12 | 5 | 11 | |
| 1 | 2 | 7 | 144 | 150 | 2 | -1 | 8 | 7 | 0 | 1 | 1 | 1 | 3 | 8 | 28 | 28 | 2 | -3 | 5 | 9 | 46 | 40 | 2 | |
| 2 | 2 | 7 | 203 | 201 | 3 | 0 | 8 | 7 | 16 | 17 | 15 | 2 | 3 | 8 | 18 | 18 | 4 | -2 | 5 | 9 | 107 | 107 | 2 | |
| 3 | 2 | 7 | 182 | 176 | 3 | 1 | 8 | 7 | 40 | 44 | 2 | -5 | 4 | 8 | 25 | 24 | 3 | -1 | 5 | 9 | 24 | 27 | 3 | |
| -6 | 3 | 7 | 161 | 157 | 2 | 2 | 8 | 7 | 16 | 16 | 6 | -4 | 4 | 8 | 117 | 120 | 2 | -2 | 6 | 9 | 189 | 191 | 3 | |

Appendix II

Table 1. Crystal data and structure refinement for csf43.

| | |
|-----------------------------------|--|
| Identification code | csf43 |
| Empirical formula | C14 H12 O2 S2 |
| Formula weight | 276.36 |
| Temperature | 123(1) K |
| Wavelength | 0.71069 Å |
| Crystal system | Monoclinic |
| Space group | P 21/n |
| Unit cell dimensions | a = 9.837(2) Å alpha = 90 deg. b = 5.890(2) Å beta = 94.219(9) deg. c = 21.6728(14) Å gamma = 90 deg. |
| Volume | 1252.4(4) Å ³ |
| Z | 4 |
| Density (calculated) | 1.466 Mg/m ³ |
| Absorption coefficient | 0.414 mm ⁻¹ |
| F(000) | 576 |
| Crystal size | 0.450 x 0.220 x 0.100 mm |
| Theta range for data collection | 3.38 to 26.99 deg. |
| Index ranges | 0 ≤ h ≤ 12, 0 ≤ k ≤ 7, -27 ≤ l ≤ 27 |
| Reflections collected | 2905 |
| Independent reflections | 2746 [R(int) = 0.0386] |
| Absorption correction | None |
| Refinement method | Full-matrix least-squares on F ² |
| Data / restraints / parameters | 2746 / 0 / 163 |
| Goodness-of-fit on F ² | 1.036 |
| Final R indices [I > 2sigma(I)] | R1 = 0.0356, wR2 = 0.0899 |
| R indices (all data) | R1 = 0.0569, wR2 = 0.0980 |
| Largest diff. peak and hole | 0.364 and -0.299 e.Å ⁻³ |

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for csf43. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

| | x | y | z | U(eq) |
|-------|----------|----------|----------|-------|
| S(1) | 1814(1) | 1678(1) | 9617(1) | 23(1) |
| S(2) | 2489(1) | -518(1) | 10310(1) | 26(1) |
| O(1) | -3760(2) | -5083(3) | 8486(1) | 35(1) |
| O(2) | 4267(2) | -2236(3) | 7284(1) | 30(1) |
| C(1) | -2676(2) | -4099(4) | 8472(1) | 24(1) |
| C(2) | -2355(2) | -2207(4) | 8063(1) | 24(1) |
| C(3) | -1104(2) | -1390(3) | 8230(1) | 21(1) |
| C(4) | -448(2) | -2655(3) | 8749(1) | 19(1) |
| C(5) | -1392(2) | -4576(4) | 8885(1) | 24(1) |
| C(6) | 739(2) | -2215(3) | 9069(1) | 21(1) |
| C(7) | 1671(2) | -280(3) | 8956(1) | 18(1) |
| C(8) | 3117(2) | -1070(3) | 8806(1) | 17(1) |
| C(9) | 3978(2) | 911(3) | 8616(1) | 19(1) |
| C(10) | 4472(2) | 658(3) | 8064(1) | 21(1) |
| C(11) | 3983(2) | -1473(4) | 7783(1) | 21(1) |
| C(12) | 3031(2) | -2571(3) | 8214(1) | 24(1) |
| C(13) | 3884(2) | -2267(3) | 9345(1) | 20(1) |
| C(14) | 3703(2) | -2099(3) | 9945(1) | 23(1) |

Table 3. Selected bond lengths [Å] and angles [deg] for csf43.

| | |
|-------------------|------------|
| S(1)-C(7) | 1.836(2) |
| S(1)-S(2) | 2.0549(8) |
| S(2)-C(14) | 1.749(2) |
| O(1)-C(1) | 1.216(2) |
| O(2)-C(11) | 1.222(2) |
| C(1)-C(2) | 1.472(3) |
| C(1)-C(5) | 1.519(3) |
| C(2)-C(3) | 1.346(3) |
| C(3)-C(4) | 1.459(3) |
| C(4)-C(6) | 1.339(3) |
| C(4)-C(5) | 1.507(3) |
| C(6)-C(7) | 1.494(3) |
| C(7)-C(8) | 1.553(3) |
| C(8)-C(13) | 1.517(2) |
| C(8)-C(9) | 1.516(3) |
| C(8)-C(12) | 1.555(3) |
| C(9)-C(10) | 1.333(3) |
| C(10)-C(11) | 1.461(3) |
| C(11)-C(12) | 1.516(3) |
| C(13)-C(14) | 1.329(3) |
| | |
| C(7)-S(1)-S(2) | 100.16(7) |
| C(14)-S(2)-S(1) | 101.51(7) |
| O(1)-C(1)-C(2) | 127.1(2) |
| O(1)-C(1)-C(5) | 126.1(2) |
| C(2)-C(1)-C(5) | 106.8(2) |
| C(3)-C(2)-C(1) | 109.9(2) |
| C(2)-C(3)-C(4) | 111.6(2) |
| C(6)-C(4)-C(3) | 128.3(2) |
| C(6)-C(4)-C(5) | 124.8(2) |
| C(3)-C(4)-C(5) | 106.9(2) |
| C(4)-C(5)-C(1) | 104.1(2) |
| C(4)-C(6)-C(7) | 125.9(2) |
| C(6)-C(7)-C(8) | 112.9(2) |
| C(6)-C(7)-S(1) | 111.38(13) |
| C(8)-C(7)-S(1) | 109.43(12) |
| C(13)-C(8)-C(9) | 108.08(14) |
| C(13)-C(8)-C(7) | 112.93(14) |
| C(9)-C(8)-C(7) | 111.4(2) |
| C(13)-C(8)-C(12) | 111.3(2) |
| C(9)-C(8)-C(12) | 102.2(2) |
| C(7)-C(8)-C(12) | 110.3(2) |
| C(10)-C(9)-C(8) | 113.9(2) |
| C(9)-C(10)-C(11) | 109.8(2) |
| O(2)-C(11)-C(10) | 126.5(2) |
| O(2)-C(11)-C(12) | 125.5(2) |
| C(10)-C(11)-C(12) | 108.0(2) |
| C(11)-C(12)-C(8) | 105.5(2) |
| C(14)-C(13)-C(8) | 128.5(2) |
| C(13)-C(14)-S(2) | 128.9(2) |

Symmetry transformations used to generate equivalent atoms:

Table 4. Bond lengths [Å] and angles [deg] for csf43.

| | |
|-------------------|------------|
| S(1)-C(7) | 1.836(2) |
| S(1)-S(2) | 2.0549(8) |
| S(2)-C(14) | 1.749(2) |
| O(1)-C(1) | 1.216(2) |
| O(2)-C(11) | 1.222(2) |
| C(1)-C(2) | 1.472(3) |
| C(1)-C(5) | 1.519(3) |
| C(2)-C(3) | 1.346(3) |
| C(3)-C(4) | 1.459(3) |
| C(4)-C(6) | 1.339(3) |
| C(4)-C(5) | 1.507(3) |
| C(6)-C(7) | 1.494(3) |
| C(7)-C(8) | 1.553(3) |
| C(8)-C(13) | 1.517(2) |
| C(8)-C(9) | 1.516(3) |
| C(8)-C(12) | 1.555(3) |
| C(9)-C(10) | 1.333(3) |
| C(10)-C(11) | 1.461(3) |
| C(11)-C(12) | 1.516(3) |
| C(13)-C(14) | 1.329(3) |
| C(2)-H(1) | 0.997(2) |
| C(3)-H(2) | 0.901(2) |
| C(5)-H(3) | 0.968(2) |
| C(5)-H(4) | 1.000(2) |
| C(6)-H(5) | 1.007(2) |
| C(7)-H(6) | 0.953(2) |
| C(9)-H(7) | 0.994(2) |
| C(10)-H(8) | 0.995(2) |
| C(12)-H(9) | 0.934(2) |
| C(12)-H(10) | 1.019(2) |
| C(13)-H(11) | 0.948(2) |
| C(14)-H(12) | 1.012(2) |
| | |
| C(7)-S(1)-S(2) | 100.16(7) |
| C(14)-S(2)-S(1) | 101.51(7) |
| O(1)-C(1)-C(2) | 127.1(2) |
| O(1)-C(1)-C(5) | 126.1(2) |
| C(2)-C(1)-C(5) | 106.8(2) |
| C(3)-C(2)-C(1) | 109.9(2) |
| C(2)-C(3)-C(4) | 111.6(2) |
| C(6)-C(4)-C(3) | 128.3(2) |
| C(6)-C(4)-C(5) | 124.8(2) |
| C(3)-C(4)-C(5) | 106.9(2) |
| C(4)-C(5)-C(1) | 104.1(2) |
| C(4)-C(5)-C(6) | 125.9(2) |
| C(6)-C(5)-C(4) | 112.9(2) |
| C(6)-C(7)-S(1) | 111.33(13) |
| C(8)-C(7)-S(1) | 109.43(12) |
| C(13)-C(8)-C(7) | 103.03(14) |
| C(13)-C(8)-C(9) | 112.93(14) |
| C(9)-C(8)-C(7) | 111.4(2) |
| C(13)-C(8)-C(12) | 111.3(2) |
| C(9)-C(8)-C(12) | 102.2(2) |
| C(7)-C(8)-C(12) | 110.3(2) |
| C(10)-C(9)-C(8) | 113.9(2) |
| C(9)-C(10)-C(11) | 109.8(2) |
| O(2)-C(11)-C(10) | 126.5(2) |
| O(2)-C(11)-C(12) | 125.5(2) |
| C(10)-C(11)-C(12) | 103.0(2) |
| C(11)-C(12)-C(8) | 105.5(2) |
| C(14)-C(13)-C(8) | 123.6(2) |
| C(13)-C(14)-S(2) | 123.9(2) |

| | |
|-------------------|------------|
| C(3)-C(2)-H(1) | 126.7(2) |
| C(1)-C(2)-H(1) | 123.1(2) |
| C(2)-C(3)-H(2) | 125.6(2) |
| C(4)-C(3)-H(2) | 122.7(2) |
| C(4)-C(5)-H(3) | 111.6(2) |
| C(1)-C(5)-H(3) | 106.8(2) |
| C(4)-C(5)-H(4) | 111.9(2) |
| C(1)-C(5)-H(4) | 112.0(2) |
| H(3)-C(5)-H(4) | 110.2(2) |
| C(4)-C(6)-H(5) | 117.0(2) |
| C(7)-C(6)-H(5) | 117.1(2) |
| C(6)-C(7)-H(6) | 110.6(2) |
| C(8)-C(7)-H(6) | 107.2(2) |
| S(1)-C(7)-H(6) | 104.94(14) |
| C(10)-C(9)-H(7) | 122.4(2) |
| C(8)-C(9)-H(7) | 123.5(2) |
| C(9)-C(10)-H(8) | 130.5(2) |
| C(11)-C(10)-H(8) | 119.6(2) |
| C(11)-C(12)-H(9) | 110.1(2) |
| C(8)-C(12)-H(9) | 111.8(2) |
| C(11)-C(12)-H(10) | 109.0(2) |
| C(8)-C(12)-H(10) | 111.2(2) |
| H(9)-C(12)-H(10) | 109.2(2) |
| C(14)-C(13)-H(11) | 119.9(2) |
| C(8)-C(13)-H(11) | 111.6(2) |
| C(13)-C(14)-H(12) | 121.5(2) |
| S(2)-C(14)-H(12) | 109.1(2) |

Symmetry transformations used to generate equivalent atoms:

Table 5. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for csf43. The anisotropic displacement factor exponent takes the form:
 $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

| | U11 | U22 | U33 | U23 | U13 | U12 |
|-------|-------|-------|-------|-------|-------|--------|
| S(1) | 26(1) | 20(1) | 23(1) | -1(1) | 4(1) | 0(1) |
| S(2) | 30(1) | 31(1) | 18(1) | 2(1) | 2(1) | -4(1) |
| O(1) | 21(1) | 41(1) | 43(1) | -6(1) | 4(1) | -12(1) |
| O(2) | 31(1) | 39(1) | 21(1) | -8(1) | 0(1) | 7(1) |
| C(1) | 18(1) | 28(1) | 25(1) | -9(1) | 4(1) | -4(1) |
| C(2) | 19(1) | 32(1) | 22(1) | -3(1) | 0(1) | 0(1) |
| C(3) | 19(1) | 26(1) | 19(1) | 0(1) | 3(1) | -2(1) |
| C(4) | 17(1) | 20(1) | 21(1) | 0(1) | 4(1) | -2(1) |
| C(5) | 21(1) | 23(1) | 27(1) | -1(1) | 2(1) | -6(1) |
| C(6) | 18(1) | 21(1) | 23(1) | 5(1) | -1(1) | -2(1) |
| C(7) | 16(1) | 20(1) | 17(1) | 1(1) | -2(1) | -1(1) |
| C(8) | 18(1) | 18(1) | 16(1) | -1(1) | -1(1) | -3(1) |
| C(9) | 16(1) | 20(1) | 19(1) | 1(1) | -2(1) | -4(1) |
| C(10) | 18(1) | 26(1) | 20(1) | 1(1) | 0(1) | -1(1) |
| C(11) | 17(1) | 27(1) | 19(1) | -2(1) | -5(1) | 6(1) |
| C(12) | 24(1) | 24(1) | 22(1) | -6(1) | -2(1) | -4(1) |
| C(13) | 15(1) | 19(1) | 25(1) | 0(1) | -2(1) | -1(1) |
| C(14) | 23(1) | 23(1) | 22(1) | 4(1) | -6(1) | -2(1) |

Table 6. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for csf43.

| | x | y | z | U(eq) |
|-------|-------|-------|-------|-------|
| H(1) | -3029 | -1558 | 7745 | 37 |
| H(2) | -682 | -263 | 8033 | 37 |
| H(3) | -1043 | -6023 | 8755 | 37 |
| H(4) | -1577 | -4632 | 9332 | 37 |
| H(5) | 1038 | -3303 | 9410 | 37 |
| H(6) | 1313 | 616 | 8616 | 37 |
| H(7) | 4207 | 2240 | 8887 | 37 |
| H(8) | 5038 | 1698 | 7827 | 37 |
| H(9) | 2146 | -2625 | 8026 | 37 |
| H(10) | 3357 | -4182 | 8312 | 37 |
| H(11) | 4584 | -3213 | 9210 | 37 |
| H(12) | 4207 | -3118 | 10260 | 37 |

| h k l 10Fo 10Fc 10s | | | | | | h k l 10Fo 10Fc 10s | | | | | | h k l 10Fo 10Fc 10s | | | | | |
|---------------------|---|---|------|------|----|---------------------|---|---|-----|------|----|---------------------|---|---|------|------|----|
| 2 | 0 | 0 | 891 | 904 | 4 | -2 | 1 | 1 | 135 | 150 | 2 | 1 | 5 | 1 | 281 | 286 | 4 |
| 4 | 0 | 0 | 463 | 433 | 5 | -1 | 1 | 1 | 15 | 14 | 14 | 2 | 5 | 1 | 18 | 26 | 18 |
| 6 | 0 | 0 | 423 | 418 | 6 | 0 | 1 | 1 | 928 | 967 | 26 | 3 | 5 | 1 | 180 | 182 | 4 |
| 8 | 0 | 0 | 56 | 54 | 5 | 1 | 1 | 1 | 52 | 47 | 2 | 4 | 5 | 1 | 71 | 77 | 5 |
| 10 | 0 | 0 | 61 | 55 | 6 | 2 | 1 | 1 | 995 | 1018 | 4 | 5 | 5 | 1 | 21 | 18 | 21 |
| 12 | 0 | 0 | 89 | 75 | 6 | 3 | 1 | 1 | 163 | 155 | 3 | 6 | 5 | 1 | 140 | 133 | 4 |
| 1 | 1 | 0 | 113 | 121 | 2 | 4 | 1 | 1 | 17 | 9 | 17 | 7 | 5 | 1 | 13 | 43 | 13 |
| 2 | 1 | 0 | 1160 | 1186 | 5 | 5 | 1 | 1 | 130 | 143 | 3 | 8 | 5 | 1 | 41 | 24 | 40 |
| 3 | 1 | 0 | 359 | 363 | 4 | 6 | 1 | 1 | 75 | 79 | 4 | 9 | 5 | 1 | 63 | 61 | 6 |
| 4 | 1 | 0 | 319 | 317 | 5 | 7 | 1 | 1 | 382 | 399 | 7 | -7 | 6 | 1 | 0 | 67 | 1 |
| 5 | 1 | 0 | 212 | 208 | 3 | 8 | 1 | 1 | 154 | 153 | 3 | -6 | 6 | 1 | 57 | 56 | 8 |
| 6 | 1 | 0 | 84 | 83 | 3 | 9 | 1 | 1 | 100 | 95 | 4 | -5 | 6 | 1 | 137 | 125 | 4 |
| 7 | 1 | 0 | 48 | 48 | 6 | 10 | 1 | 1 | 143 | 148 | 5 | -4 | 6 | 1 | 17 | 0 | 17 |
| 8 | 1 | 0 | 20 | 2 | 20 | 11 | 1 | 1 | 137 | 139 | 5 | -3 | 6 | 1 | 117 | 121 | 5 |
| 9 | 1 | 0 | 0 | 5 | 1 | 12 | 1 | 1 | 127 | 128 | 5 | -2 | 6 | 1 | 68 | 65 | 6 |
| 10 | 1 | 0 | 0 | 22 | 1 | -12 | 2 | 1 | 119 | 114 | 5 | -1 | 6 | 1 | 104 | 108 | 5 |
| 11 | 1 | 0 | 0 | 22 | 1 | -11 | 2 | 1 | 0 | 21 | 1 | 0 | 6 | 1 | 41 | 39 | 7 |
| 12 | 1 | 0 | 164 | 166 | 5 | -10 | 2 | 1 | 175 | 166 | 4 | 1 | 6 | 1 | 90 | 87 | 5 |
| 0 | 0 | 0 | 310 | 294 | 4 | -9 | 2 | 1 | 24 | 38 | 24 | 2 | 6 | 1 | 60 | 69 | 7 |
| 1 | 1 | 2 | 128 | 127 | 2 | -8 | 2 | 1 | 0 | 23 | 1 | 3 | 6 | 1 | 350 | 361 | 7 |
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| 4 | 6 | 0 | 168 | 157 | 4 | -7 | 4 | 1 | 106 | 106 | 5 | 9 | 1 | 2 | 168 | 173 | 4 |
| 5 | 6 | 0 | 42 | 39 | 9 | -6 | 4 | 1 | 191 | 200 | 4 | 10 | 1 | 2 | 23 | 14 | 23 |
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| 11 | 0 | 1 | 119 | 115 | 4 | 10 | 4 | 1 | 35 | 74 | 34 | 1 | 2 | 2 | 40 | 47 | 4 |
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| h | k | l | 10Fo | 10Fc | 10s | h | k | l | 10Fo | 10Fc | 10s | h | k | l | 10Fo | 10Fc | 10s | h | k | l | 10Fo | 10Fc | 10s |
|-----|---|---|------|------|-----|-----|---|---|------|------|-----|-----|---|---|------|------|-----|-----|---|---|------|------|-----|
| 3 | 0 | 0 | 553 | 522 | 4 | 7 | 4 | 3 | 59 | 54 | 5 | -3 | 2 | 4 | 556 | 548 | 5 | -3 | 7 | 4 | 62 | 54 | 8 |
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| 7 | 0 | 0 | 145 | 150 | 3 | 9 | 4 | 3 | 81 | 78 | 5 | -1 | 2 | 4 | 454 | 460 | 5 | -1 | 7 | 4 | 58 | 52 | 9 |
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| 10 | 1 | 1 | 248 | 251 | 4 | -3 | 6 | 6 | 27 | 12 | 26 | 1 | 3 | 4 | 533 | 530 | 6 | -5 | 1 | 5 | 45 | 35 | 5 |
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| 0 | 2 | 2 | 521 | 536 | 17 | 0 | 7 | 7 | 65 | 63 | 10 | -6 | 4 | 4 | 308 | 292 | 5 | 10 | 1 | 5 | 112 | 111 | 5 |
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| 2 | 2 | 2 | 463 | 471 | 5 | 2 | 7 | 7 | 78 | 73 | 6 | -4 | 4 | 4 | 151 | 164 | 3 | 12 | 1 | 5 | 44 | 45 | 44 |
| 3 | 2 | 2 | 277 | 268 | 4 | 3 | 7 | 7 | 44 | 47 | 13 | -3 | 4 | 4 | 394 | 425 | 7 | -12 | 2 | 5 | 112 | 109 | 5 |
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| 7 | 2 | 2 | 165 | 160 | 3 | -8 | 0 | 4 | 0 | 16 | 1 | 1 | 4 | 4 | 90 | 102 | 4 | -8 | 2 | 5 | 157 | 142 | 4 |
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| 0 | 3 | 3 | 80 | 78 | 2 | -7 | 1 | 4 | 360 | 353 | 5 | -3 | 5 | 4 | 69 | 77 | 5 | 8 | 2 | 5 | 0 | 54 | 1 |
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| 5 | 3 | 3 | 268 | 271 | 5 | -2 | 1 | 4 | 353 | 341 | 3 | 2 | 5 | 4 | 87 | 83 | 4 | -10 | 3 | 5 | 222 | 223 | 5 |
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| 7 | 3 | 3 | 352 | 360 | 6 | 0 | 1 | 4 | 515 | 521 | 3 | 4 | 5 | 4 | 230 | 234 | 4 | -8 | 3 | 5 | 72 | 74 | 6 |
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| h k l 10Fo 10Fc 10s | | | | | | h k l 10Fo 10Fc 10s | | | | | | h k l 10Fo 10Fc 10s | | | | | |
|---------------------|---|---|-----|-----|----|---------------------|---|---|-----|-----|----|---------------------|---|---|-----|-----|----|
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| h | k | l | 10Fo | 10Fc | 10s | h | k | l | 10Fo | 10Fc | 10s | h | k | l | 10Fo | 10Fc | 10s | h | k | l | 10Fo | 10Fc | 10s |
|-----|---|---|------|------|-----|-----|---|---|------|------|-----|-----|---|----|------|------|-----|-----|---|----|------|------|-----|
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|-----|---|----|------|------|-----|-----|---|----|------|------|-----|-----|---|----|------|------|-----|-----|---|----|------|------|-----|
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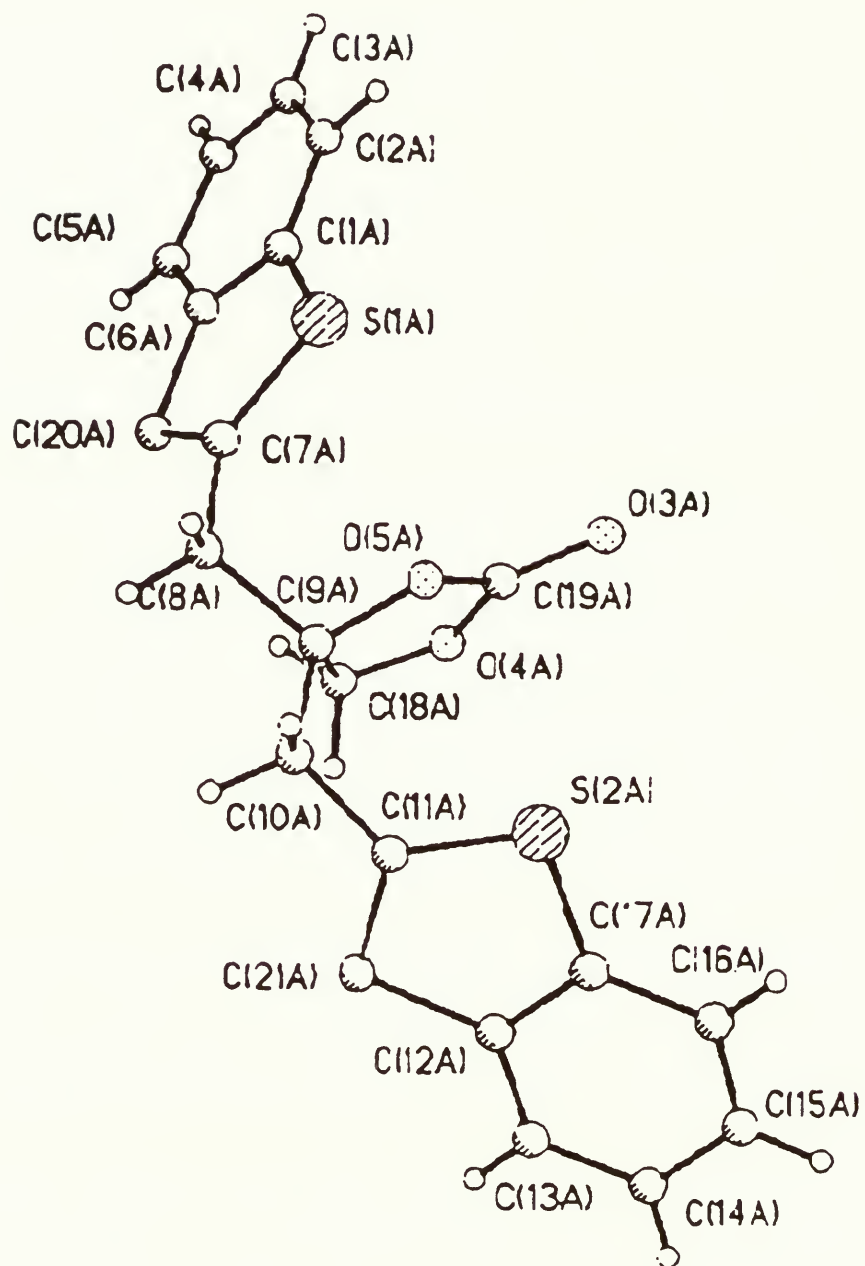
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| -2 | 1 | 18 | 340 | 355 | 5 | 7 | 1 | 19 | 14 | 86 | 14 | 7 | 2 | 20 | 0 | 1 | 1 | -6 | 0 | 22 | 0 | 50 | 1 |
| -1 | 1 | 18 | 81 | 94 | 5 | 8 | 1 | 19 | 127 | 142 | 6 | -7 | 3 | 20 | 0 | 11 | 1 | -4 | 0 | 22 | 250 | 249 | 5 |
| 0 | 1 | 18 | 330 | 329 | 8 | -9 | 2 | 19 | 63 | 71 | 8 | -6 | 3 | 20 | 124 | 120 | 5 | -2 | 0 | 22 | 123 | 123 | 4 |
| 1 | 1 | 18 | 123 | 119 | 3 | -8 | 2 | 19 | 48 | 32 | 7 | -5 | 3 | 20 | 38 | 22 | 38 | 0 | 0 | 22 | 112 | 119 | 3 |
| 2 | 1 | 18 | 26 | 13 | 25 | -7 | 2 | 19 | 0 | 46 | 1 | -4 | 3 | 20 | 24 | 24 | 24 | 2 | 0 | 22 | 135 | 135 | 4 |
| 3 | 1 | 18 | 26 | 12 | 26 | -6 | 2 | 19 | 37 | 24 | 9 | -3 | 3 | 20 | 12 | 49 | 11 | 4 | 0 | 22 | 84 | 87 | 6 |
| 4 | 1 | 18 | 110 | 108 | 4 | -5 | 2 | 19 | 79 | 85 | 5 | -2 | 3 | 20 | 129 | 134 | 5 | 6 | 0 | 22 | 0 | 31 | 1 |
| 5 | 1 | 18 | 99 | 93 | 5 | -4 | 2 | 19 | 120 | 120 | 4 | -1 | 3 | 20 | 224 | 223 | 4 | -8 | 1 | 22 | 45 | 36 | 8 |
| 6 | 1 | 18 | 68 | 64 | 6 | -3 | 2 | 19 | 133 | 130 | 4 | 0 | 3 | 20 | 240 | 240 | 3 | -7 | 1 | 22 | 212 | 214 | 5 |
| 7 | 1 | 18 | 62 | 66 | 6 | -2 | 2 | 19 | 155 | 154 | 4 | 1 | 3 | 20 | 180 | 182 | 4 | -6 | 1 | 22 | 51 | 26 | 5 |
| 8 | 1 | 18 | 100 | 103 | 6 | -1 | 2 | 19 | 0 | 42 | 1 | 2 | 3 | 20 | 140 | 145 | 5 | -5 | 1 | 22 | 99 | 98 | 5 |
| -9 | 2 | 18 | 162 | 157 | 5 | 0 | 2 | 19 | 429 | 431 | 5 | 3 | 3 | 20 | 158 | 155 | 4 | -4 | 1 | 22 | 140 | 139 | 4 |
| -8 | 2 | 18 | 107 | 113 | 6 | 1 | 2 | 19 | 197 | 192 | 4 | 4 | 3 | 20 | 188 | 185 | 4 | -3 | 1 | 22 | 47 | 23 | 5 |
| -7 | 2 | 18 | 123 | 134 | 5 | 2 | 2 | 19 | 137 | 141 | 4 | 5 | 3 | 20 | 67 | 62 | 7 | -2 | 1 | 22 | 330 | 329 | 6 |
| -6 | 2 | 18 | 121 | 128 | 4 | 3 | 2 | 19 | 172 | 172 | 4 | 6 | 3 | 20 | 44 | 49 | 43 | -1 | 1 | 22 | 186 | 189 | 4 |
| -5 | 2 | 18 | 102 | 104 | 4 | 4 | 2 | 19 | 0 | 11 | 1 | -6 | 4 | 20 | 83 | 79 | 7 | 0 | 1 | 22 | 139 | 140 | 3 |
| -4 | 2 | 18 | 43 | 45 | 7 | 5 | 2 | 19 | 22 | 8 | 21 | -5 | 4 | 20 | 171 | 166 | 4 | 1 | 1 | 22 | 187 | 189 | 4 |
| -3 | 2 | 18 | 88 | 101 | 5 | 6 | 2 | 19 | 29 | 1 | 28 | -4 | 4 | 20 | 0 | 35 | 1 | 2 | 1 | 22 | 112 | 113 | 4 |
| -2 | 2 | 18 | 82 | 90 | 5 | 7 | 2 | 19 | 103 | 100 | 6 | -3 | 4 | 20 | 166 | 169 | 5 | 3 | 1 | 22 | 114 | 120 | 5 |
| -1 | 2 | 18 | 142 | 152 | 4 | -8 | 3 | 19 | 96 | 87 | 6 | -2 | 4 | 20 | 0 | 5 | 1 | 4 | 1 | 22 | 0 | 25 | 1 |
| 0 | 2 | 18 | 184 | 182 | 2 | -7 | 3 | 19 | 104 | 108 | 5 | -1 | 4 | 20 | 126 | 123 | 5 | 5 | 1 | 22 | 200 | 202 | 4 |
| 1 | 2 | 18 | 32 | 37 | 32 | -6 | 3 | 19 | 94 | 94 | 5 | 0 | 4 | 20 | 33 | 41 | 33 | 6 | 1 | 22 | 69 | 60 | 6 |
| 2 | 2 | 18 | 114 | 114 | 4 | -5 | 3 | 19 | 224 | 232 | 4 | 1 | 4 | 20 | 0 | 14 | 1 | -7 | 2 | 22 | 73 | 77 | 7 |
| 3 | 2 | 18 | 320 | 309 | 6 | -4 | 3 | 19 | 32 | 51 | 32 | -6 | 2 | 20 | 29 | 12 | 28 | -6 | 2 | 22 | 60 | 60 | 7 |
| 4 | 2 | 18 | 101 | 101 | 5 | -3 | 3 | 19 | 81 | 77 | 5 | 3 | 4 | 20 | 0 | 40 | 1 | -5 | 2 | 22 | 177 | 174 | 4 |
| 5 | 2 | 18 | 152 | 150 | 4 | -2 | 3 | 19 | 294 | 299 | 5 | 4 | 4 | 20 | 279 | 277 | 5 | -4 | 2 | 22 | 188 | 191 | 4 |
| 6 | 2 | 18 | 281 | 278 | 5 | -1 | 3 | 19 | 125 | 131 | 4 | -3 | 5 | 20 | 57 | 52 | 8 | -3 | 2 | 22 | 0 | 33 | 1 |
| 7 | 2 | 18 | 52 | 59 | 8 | 0 | 3 | 19 | 89 | 86 | 3 | -2 | 5 | 20 | 52 | 58 | 10 | -2 | 2 | 22 | 12 | 18 | 11 |
| 8 | 2 | 18 | 111 | 112 | 6 | 1 | 3 | 19 | 169 | 170 | 4 | -1 | 5 | 20 | 97 | 87 | 6 | -1 | 2 | 22 | 102 | 102 | 5 |
| -8 | 3 | 18 | 0 | 12 | 1 | 2 | 3 | 19 | 312 | 326 | 5 | 0 | 5 | 20 | 47 | 37 | 8 | 0 | 2 | 22 | 274 | 280 | 3 |
| -7 | 3 | 18 | 134 | 120 | 4 | 3 | 3 | 19 | 176 | 179 | 4 | 1 | 5 | 20 | 29 | 43 | 28 | 1 | 2 | 22 | 284 | 285 | 5 |
| -6 | 3 | 18 | 69 | 73 | 7 | 4 | 3 | 19 | 113 | 112 | 5 | -7 | 0 | 21 | 93 | 100 | 5 | 2 | 2 | 22 | 169 | 162 | 4 |
| -5 | 3 | 18 | 0 | 12 | 1 | 5 | 3 | 19 | 98 | 104 | 5 | -5 | 0 | 21 | 79 | 77 | 5 | 3 | 3 | 22 | 196 | 191 | 4 |
| -4 | 3 | 18 | 32 | 10 | 32 | 6 | 3 | 19 | 70 | 73 | 6 | -3 | 0 | 21 | 27 | 24 | 27 | 4 | 4 | 22 | 181 | 176 | 5 |
| -3 | 3 | 18 | 26 | 7 | 25 | -6 | 4 | 19 | 239 | 239 | 5 | -1 | 0 | 21 | 97 | 96 | 5 | 5 | 5 | 22 | 72 | 78 | 6 |
| -2 | 3 | 18 | 49 | 35 | 6 | -5 | 4 | 19 | 91 | 97 | 6 | 1 | 0 | 21 | 92 | 87 | 5 | 6 | 2 | 22 | 36 | 33 | 36 |
| -1 | 3 | 18 | 8 | 41 | 8 | -4 | 4 | 19 | 173 | 186 | 5 | 3 | 0 | 21 | 188 | 182 | 4 | -6 | 3 | 22 | 0 | 41 | 1 |
| 0 | 3 | 18 | 35 | 27 | 8 | -3 | 4 | 19 | 48 | 54 | 48 | -5 | 0 | 21 | 224 | 220 | 4 | -5 | 3 | 22 | 89 | 80 | 6 |
| 1 | 3 | 18 | 281 | 272 | 5 | -2 | 4 | 19 | 29 | 32 | 28 | 7 | 0 | 21 | 208 | 205 | 5 | -4 | 3 | 22 | 113 | 110 | 5 |
| 2 | 3 | 18 | 28 | 47 | 28 | -1 | 4 | 19 | 141 | 154 | 5 | -8 | 1 | 21 | 77 | 90 | 7 | -3 | 3 | 22 | 193 | 197 | 4 |
| 3 | 3 | 18 | 169 | 158 | 4 | 0 | 4 | 19 | 12 | 26 | 11 | -7 | 1 | 21 | 30 | 29 | 29 | -2 | 3 | 22 | 69 | 62 | 6 |
| 4 | 3 | 18 | 0 | 8 | 1 | 1 | 4 | 19 | 108 | 105 | 5 | -6 | 1 | 21 | 207 | 187 | 4 | -1 | 3 | 22 | 284 | 290 | 5 |
| 5 | 3 | 18 | 43 | 42 | 9 | 2 | 4 | 19 | 50 | 48 | 7 | -5 | 1 | 21 | 152 | 150 | 5 | 0 | 3 | 22 | 52 | 58 | 6 |
| 6 | 3 | 18 | 26 | 25 | 25 | 3 | 4 | 19 | 81 | 86 | 6 | -4 | 1 | 21 | 189 | 194 | 4 | 1 | 3 | 22 | 235 | 229 | 4 |
| 7 | 3 | 18 | 0 | 16 | 1 | 4 | 4 | 19 | 214 | 215 | 4 | -3 | 1 | 21 | 66 | 60 | 5 | 2 | 3 | 22 | 171 | 169 | 5 |
| -7 | 4 | 18 | 168 | 159 | 5 | 5 | 4 | 19 | 18 | 22 | 17 | -2 | 1 | 21 | 141 | 138 | 4 | 3 | 3 | 22 | 0 | 23 | 1 |
| -6 | 4 | 18 | 0 | 46 | 1 | -4 | 5 | 19 | 25 | 25 | 24 | -1 | 1 | 21 | 97 | 102 | 5 | 4 | 3 | 22 | 199 | 194 | 5 |
| -5 | 4 | 18 | 277 | 280 | 5 | -3 | 5 | 19 | 259 | 252 | 5 | 0 | 1 | 21 | 9 | 31 | 9 | 5 | 3 | 22 | 45 | 59 | 12 |
| -4 | 4 | 18 | 29 | 14 | 29 | -2 | 5 | 19 | 87 | 86 | 5 | 1 | 1 | 21 | 213 | 209 | 4 | -4 | 4 | 22 | 121 | 116 | 5 |
| -3 | 4 | 18 | 376 | 370 | 6 | -1 | 5 | 19 | 228 | 219 | 4 | 2 | 1 | 21 | 161 | 160 | 4 | -3 | 4 | 22 | 0 | 36 | 1 |
| -2 | 4 | 18 | 71 | 70 | 6 | 0 | 5 | 19 | 108 | 110 | 4 | 3 | 1 | 21 | 232 | 234 | 4 | -2 | 4 | 22 | 57 | 56 | 7 |
| -1 | 4 | 18 | 197 | 203 | 4 | 1 | 5 | 19 | 0 | 16 | 1 | 4 | 1 | 21 | 75 | 67 | 6 | -1 | 4 | 22 | 84 | 79 | 6 |
| 0 | 4 | 18 | 30 | 3 | 17 | 2 | 5 | 19 | 96 | 99 | 6 | 5 | 1 | 21 | 184 | 179 | 4 | 0 | 4 | 22 | 43 | 37 | 13 |
| 1 | 4 | 18 | 143 | 136 | 4 | 3 | 5 | 19 | 36 | 22 | 11 | 1 | 2 | 21 | 0 | 12 | 1 | 1 | 4 | 22 | 89 | 92 | 7 |
| 2 | 4 | 18 | 20 | 28 | 19 | -8 | 0 | 20 | 35 | 44 | 34 | 7 | 1 | 21 | 112 | 117 | 5 | 2 | 4 | 22 | 31 | 24 | 30 |
| 3 | 4 | 18 | 27 | 40 | 27 | -6 | 0 | 20 | 167 | 161 | 4 | -8 | 2 | 21 | 102 | 105 | 6 | -7 | 0 | 23 | 161 | 165 | 5 |
| 4 | 4 | 18 | 177 | 172 | 4 | -4 | 0 | 20 | | | | | | | | | | | | | | | |

Table 7. Observed and calculated structure factors for csf43

| h | k | l | 10Fo | 10Fc | 10s | h | k | l | 10Fo | 10Fc | 10s | h | k | l | 10Fo | 10Fc | 10s | h | k | l | 10Fo | 10Fc | 10s |
|----|---|----|------|------|-----|----|---|----|------|------|-----|----|---|----|------|------|-----|----|---|----|------|------|-----|
| -5 | 2 | 23 | 28 | 25 | 28 | 2 | 0 | 24 | 164 | 167 | 5 | 0 | 3 | 24 | 12 | 24 | 11 | 0 | 3 | 25 | 98 | 93 | 6 |
| -4 | 2 | 23 | 118 | 117 | 5 | 4 | 0 | 24 | 116 | 115 | 6 | 1 | 3 | 24 | 17 | 23 | 16 | 1 | 3 | 25 | 182 | 174 | 5 |
| -3 | 2 | 23 | 259 | 259 | 5 | -6 | 1 | 24 | 93 | 100 | 6 | 2 | 3 | 24 | 0 | 10 | 1 | -4 | 0 | 26 | 47 | 53 | 9 |
| -2 | 2 | 23 | 274 | 271 | 5 | -5 | 1 | 24 | 176 | 183 | 4 | -5 | 0 | 25 | 26 | 44 | 26 | -2 | 0 | 26 | 208 | 210 | 4 |
| -1 | 2 | 23 | 187 | 194 | 4 | -4 | 1 | 24 | 105 | 99 | 5 | -3 | 0 | 25 | 147 | 155 | 5 | 0 | 0 | 26 | 286 | 293 | 3 |
| 0 | 2 | 23 | 203 | 209 | 3 | -3 | 1 | 24 | 147 | 149 | 4 | -1 | 0 | 25 | 131 | 128 | 4 | 2 | 0 | 26 | 137 | 147 | 5 |
| 1 | 2 | 23 | 79 | 78 | 7 | -2 | 1 | 24 | 110 | 101 | 5 | 1 | 0 | 25 | 218 | 226 | 5 | -4 | 1 | 26 | 165 | 159 | 5 |
| 2 | 2 | 23 | 16 | 19 | 15 | -1 | 1 | 24 | 0 | 19 | 1 | 3 | 0 | 25 | 318 | 312 | 6 | -3 | 1 | 26 | 94 | 101 | 6 |
| 3 | 2 | 23 | 154 | 154 | 5 | 0 | 1 | 24 | 167 | 173 | 3 | -5 | 1 | 25 | 26 | 52 | 26 | -2 | 1 | 26 | 160 | 153 | 5 |
| 4 | 2 | 23 | 25 | 4 | 24 | 1 | 1 | 24 | 97 | 92 | 5 | -4 | 1 | 25 | 0 | 26 | 1 | -1 | 1 | 26 | 114 | 108 | 6 |
| 5 | 2 | 23 | 29 | 31 | 28 | 2 | 1 | 24 | 35 | 36 | 12 | -3 | 1 | 25 | 45 | 45 | 8 | 0 | 1 | 26 | 54 | 59 | 6 |
| -5 | 3 | 23 | 36 | 29 | 13 | 3 | 1 | 24 | 107 | 111 | 5 | -2 | 1 | 25 | 26 | 62 | 25 | 1 | 1 | 26 | 64 | 63 | 7 |
| -4 | 3 | 23 | 100 | 102 | 6 | 4 | 1 | 24 | 158 | 157 | 5 | -1 | 1 | 25 | 30 | 41 | 30 | 2 | 1 | 26 | 124 | 129 | 6 |
| -3 | 3 | 23 | 0 | 14 | 1 | 5 | 1 | 24 | 123 | 117 | 5 | 0 | 1 | 25 | 0 | 22 | 1 | 3 | 1 | 26 | 175 | 179 | 5 |
| -2 | 3 | 23 | 75 | 70 | 5 | -6 | 2 | 24 | 144 | 138 | 5 | 1 | 1 | 25 | 233 | 234 | 5 | -3 | 2 | 26 | 41 | 40 | 40 |
| -1 | 3 | 23 | 17 | 55 | 17 | -5 | 2 | 24 | 69 | 67 | 7 | 2 | 1 | 25 | 92 | 81 | 6 | -2 | 2 | 26 | 0 | 43 | 1 |
| 0 | 3 | 23 | 155 | 153 | 3 | -4 | 2 | 24 | 106 | 113 | 6 | 3 | 1 | 25 | 25 | 20 | 25 | -1 | 2 | 26 | 0 | 2 | 1 |
| 1 | 3 | 23 | 148 | 150 | 5 | -3 | 2 | 24 | 41 | 65 | 41 | 4 | 1 | 25 | 147 | 150 | 5 | 0 | 2 | 26 | 0 | 14 | 1 |
| 2 | 3 | 23 | 174 | 170 | 4 | -2 | 2 | 24 | 28 | 16 | 28 | -5 | 2 | 25 | 224 | 205 | 5 | 1 | 2 | 26 | 0 | 29 | 1 |
| 3 | 3 | 23 | 115 | 124 | 6 | -1 | 2 | 24 | 0 | 38 | 1 | -4 | 2 | 25 | 266 | 258 | 4 | -3 | 0 | 27 | 47 | 57 | 8 |
| 4 | 3 | 23 | 0 | 10 | 1 | 0 | 2 | 24 | 106 | 112 | 4 | -3 | 2 | 25 | 150 | 149 | 5 | -1 | 0 | 27 | 108 | 105 | 5 |
| -2 | 4 | 23 | 85 | 90 | 6 | 1 | 2 | 24 | 156 | 153 | 4 | -2 | 2 | 25 | 211 | 202 | 4 | 1 | 0 | 27 | 66 | 65 | 6 |
| -1 | 4 | 23 | 144 | 137 | 5 | 2 | 2 | 24 | 70 | 76 | 7 | -1 | 2 | 25 | 203 | 204 | 4 | -3 | 1 | 27 | 66 | 68 | 7 |
| 0 | 4 | 23 | 61 | 55 | 5 | 3 | 2 | 24 | 133 | 132 | 5 | 0 | 2 | 25 | 149 | 147 | 3 | -2 | 1 | 27 | 80 | 72 | 7 |
| 1 | 4 | 23 | 158 | 147 | 4 | 4 | 2 | 24 | 57 | 56 | 9 | 1 | 2 | 25 | 74 | 71 | 7 | -1 | 1 | 27 | 96 | 99 | 6 |
| -6 | 0 | 24 | 118 | 109 | 5 | -4 | 3 | 24 | 142 | 146 | 5 | 2 | 2 | 25 | 42 | 13 | 41 | 0 | 1 | 27 | 110 | 112 | 3 |
| -4 | 0 | 24 | 0 | 42 | 1 | -3 | 3 | 24 | 257 | 268 | 5 | 3 | 2 | 25 | 8 | 49 | 8 | 1 | 1 | 27 | 12 | 16 | 11 |
| -2 | 0 | 24 | 42 | 51 | 7 | -2 | 3 | 24 | 134 | 129 | 5 | -2 | 3 | 25 | 115 | 114 | 6 | | | | | | |
| 0 | 0 | 24 | 22 | 44 | 21 | -1 | 3 | 24 | 180 | 186 | 5 | -1 | 3 | 25 | 17 | 4 | 16 | | | | | | |

Appendix III



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