THE PREPARATION AND REACTIONS OF SOME
1,2-DIPOLAR SPECIES

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ABSTRACT

This research was directed mainly towards the investigation of the reactions of allylic amineimides. The work can be divided into two main sections.

Section 1 of the thesis deals mainly with thermolysis studies of amineimides. Sections 1a and 1b represent a comprehensive survey of amineimide literature up to 1971.

N-ALLYL-N,N-DIMETHYLAMINE-BENZIMIDE was prepared and rearranged at 140° to 1-allyl-1-benzoyl-2,2-dimethylhydrazine. A tentative mechanism involving an initial migration to the carbonyl oxygen was disproved by incorporating the amineimide system into a five-membered ring.

N,N-DIMETHYL-N-PROPARGYLAMINE-BENZIMIDE did not rearrange on heating; but the hydrobromide, on heating, disproportionated to give 1-benzoyl-2,2,2-trimethylhydrazinium bromide and 1-benzoyl-2,2-dimethylhydrazine. 1-ALLYL-1,1-DIMETHYL-2-BENZOYLHYDRAZINUM BROMIDE and 1-benzoyl-2,2,2-trimethylhydrazinium iodide both disproportionated to give 1-benzoyl-2,2-dimethylhydrazine.

Section 1 concludes with a discussion of the mechanisms of allylic migrations in amineimides proposed by J. E. Baldwin.

Section 2 deals with the formation of five-membered heterocyclic compounds from amineimides by bromination. 1,1-DIMETHYL-2-BENZOYL-4-BROMOPYRAZOLIDINIUM BROMIDE was formed from N-ALLYL-N,N-DIMETHYLAMINE-BENZIMIDE, 1,1-DIMETHYL-2-BENZOYL-4-BROMOPYRAZOL-3-ENIUM BROMIDE from N,N-DIMETHYL-N-PROPARGYLAMINE-BENZIMIDE via the
unusual acetylenic "bromonium" ion. Hydrogenolysis of both heterocyclic compounds gave the same product. The preparation was extended by forming 2,2-dimethyl-4-bromoisoaxazolinium bromide from N-allyl-N,N-dimethylamine-N-oxide.

Sections 3 and 4 cover a number of unsuccessful attempts to synthesise other amineimides and 1,2-dipolar species.
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INTRODUCTION
In the last 50 years, a multitude of 1,2-dipolar species have been prepared and their reactions investigated. This discussion will be limited to 1,2-dipolar compounds formed from elements in the first main row of the periodic table, where reactions are not complicated by \( p_\pi-d_\pi \) overlap.

1) **THE MEISENHEIMER REARRANGEMENT**

The Meisenheimer rearrangement is the thermal isomerisation of a tertiary amine oxide to a substituted hydroxylamine.* The reaction is typified by the transformations (1) \( \rightarrow \) (2) and (3) \( \rightarrow \) (4).

\[
R_1R_2N-\text{O} \quad \rightarrow \quad R_1R_2N-\text{O} \quad CH_2\text{Ar}
\]

\[
| \quad \text{CH}_2\text{Ar}
\]

(1) \hspace{2cm} (2)

Pinner\(^{(2)}\) described the first rearrangement of an amine oxide, nicotine-1'-oxide (5) but incorrectly ascribed the structure of the rearranged product to the tetrahydrofuran derivative (6). This was later \(^{(3)}\) shown to be 2-methyl-6-3'-pyridyltetrahydro-1,2-oxazine (7).

* The literature up to 1967 is reviewed by Johnstone\(^{(1)}\).
Meisenheimer et al\textsuperscript{(4,5)} investigated the rearrangement of a variety of allylic amine oxides in strongly basic solution and found that the O-allylhydroxylamines were formed in good yield except in the case of the N,N-dialkyl-N-allylamine-N-oxide; subsequently it was found that these will rearrange under anhydrous conditions\textsuperscript{(6)}. Hydration of the oxygen, causing a reduction in the effective charge, was suggested as the reason for the lack of success in aqueous solutions.

Kleinschmidt and Cope\textsuperscript{(7)} studied the rearrangement of N-crotyl-N-methylaniline-N-oxide (8) and found that the product was O-2-but-3-enyl-N-methyl-N-phenylhydroxylamine (9) and not O-crotyl-N-methyl-N-phenylhydroxylamine (10).
The reaction was postulated to proceed via a five-membered transition state (11) by analogy with the Claisen rearrangement of O-allylphenols.

If a group has hydrogens β to the quaternary nitrogen a β elimination occurs, giving an olefin. This reaction limits the scope of the Meisenheimer rearrangement. Thus when N,N-dimethyl-N-α-phenethylamine-N-oxide (12) was heated, the only products were styrene and N,N-dimethylhydroxylamine (8).
2) THE WITTIG REARRANGEMENT

The Wittig\(^{(9)}\) rearrangement involves the migration of a group from oxygen to carbon. A typical example reported by Wittig and Löhmann\(^{(10)}\) involves treatment of dibenzyl ether (13) with phenyllithium to give 1,2-diphenylethan-1-ol. The reaction is viewed as proceeding via the carbanion (14), the driving force being the formation of the alkoxide ion (15). Similarly\(^{(11)}\) allyl-9-fluorenyl ether (17) gave the corresponding tertiary alcohol (18) on treatment with phenyllithium in ether at room temperature. The benzyl-methyl and -ethyl ethers
rearranged at 100° but the 9-fluorenyl-phenyl ether could not be induced to rearrange. A phenyl migration was accomplished when benzhydryl phenyl ether was treated with potassium piperidide or potassium amide in liquid ammonia, or with phenyl or butyllithium in tetrahydrofuran (12).
3) THE STEVENS REARRANGEMENT

The Stevens rearrangement has many structural similarities to the Wittig rearrangement, the major difference being that the driving force for reaction in this case is the complete neutralisation of charge instead of the establishment of a more stable charged species. Typically, N-benzyl-N,N-dimethyl-N-phenacylammonium bromide rearranges in aqueous alkali to give α-dimethylamino-β-phenylpropiophenone (20) and N-allyl-N,N-dimethyl-N-phenacylammonium bromide (21) gives 1-benzoyl-1-(N,N-dimethylamino)-but-3-ene (22).

At lower temperatures, the Stevens rearrangement of benzyl substituted ammonium compounds can be superseded by a Sommelet rearrangement, in which the negatively charged carbon atom attacks the benzylic phenyl ring. Thus treatment of N,N-dibenzyl-N,N-dimethyl-
ammonium bromide (23) with phenyllithium in ether at room temperature gives a mixture of \( \text{N,N-dimethyl-N-(1,2-diphenylethyl)amine} \) (24) and \( \text{(o-methylbenzhydryl)dimethylamine} \) (25)\(^{(14)} \). When the reaction was performed in liquid ammonia with potassium amide\(^{(15)} \), (25) was the only product formed, with no evidence of formation of (24).
4) **MECHANISMS IN 1,2-DIPOLAR REARRANGEMENTS**

(i) Benzylic and Alkyl Rearrangements

Many mechanisms have been postulated for rearrangements in 1,2-dipolar systems. Hauser and Kantor\(^{(16)}\) initially suggested that benzylic migration is effected by "an intramolecular nucleophilic displacement" at the same side at which the migrating group is attached \((26)\). This view is supported by the observation\(^{(17)}\) that rearrangement of \(N,N\)-dimethyl-\(N\)-\(\alpha\)-phenethyl-\(N\)-phenacylammonium bromide (27) occurs with retention of configuration of the \(\alpha\)-phenethyl group. However this interpretation in general terms does not readily explain the observation\(^{(18)}\) that 1-norbornyl and 1-apocamphyl benzyl ethers do not undergo the Wittig rearrangement.

In 1959, Stevens\(^{(19)}\) suggested that the 1,2-rearrangement of \(N\)-benzyl-\(N\),\(N\)-dimethyl-\(N\)-phenacylammonium bromide (19) proceeded
by a heterolytic mechanism via the intermediate (28).

This heterolytic, dissociation - recombination reaction was used by Schollkopf and Fabian (20) to explain the Wittig rearrangement. However this process seems a little suspicious. Hauser and Kantor (16) showed that, in the Wittig rearrangement of dibenzylether (13) in liquid ammonia with potassium amide, the products of the reaction include benzaldehyde and toluene. They also showed that benzaldehyde
in toluene in the presence of potassium amide does not react to give (15), the normal product of a Wittig rearrangement; also it is noted that benzyl potassium is more likely to react with ammonia to give toluene, than with benzaldehyde to give (15).

Support for a cleavage – recombination pathway came from the observation of a "trapped" intermediate, 1-phenylethanol, in the Wittig rearrangement of dibenzyl ether in the presence of methyllithium(21); again, it is pointed out(18) that this ionic mechanism will not explain the failure of 1-norbornyl and 1-apocamphyl benzyl ethers to undergo the Wittig rearrangement, since it has been shown(22) that the 1-norbornyl carbanion is quite stable.

Lansbury et al(18) suggested that the Wittig rearrangement proceeds via a homolytic, dissociation – recombination reaction. The absence of rearrangement by 1-norbornyl and 1-apocamphyl benzyl ethers is rationalised by the observation that the 1-norbornyl radical is very strained by comparison with acyclic t-alkyl radicals. Thus the mechanism, in general terms, would proceed via formation of a radical anion and an alkyl radical; subsequent electron shift and recoupling to give the product (Scheme 1).

\[
\begin{align*}
\text{R} - \cdot X & \longrightarrow \text{R} - \cdot X - Y + \cdot \text{CH}_2 - \text{R} \\
\text{Y} - \text{CH}_2 - \text{R} & \\
\text{R} - \cdot X - Y - \text{or ..} & \leftarrow \text{R} - \cdot X - Y - \text{or ..} + \cdot \text{CH}_2 - \text{R} \\
& \text{CH}_2 \text{R}
\end{align*}
\]

Scheme 1
Several recent publications indicate that this mechanism is a general one. Thus Castagnoli et al\(^{(23)}\) found that heating a mixture of (29a) and (29b) gave rise to a mixture of products including considerable amounts of crossover products (30c) and (30d).

(a) \(n = 3, R = H\)
(b) \(n = 2, R = \text{CH}_3\)
(c) \(n = 3, R = \text{CH}_3\)
(d) \(n = 2, R = H\)

Similarly, when (29c) and (29d) were heated, (30a) and (30b) were found in substantial yield.

When the Meisenheimer rearrangement of N-benzyl-N,N-dimethyl-amine-N-oxide (31) was carried out under oxygen at high pressure, the rearranged product (32) was obtained in 30% yield\(^{(24)}\). The rate constant for reaction was the same as for the Meisenheimer rearrangement and indicates that the transition state is the same for both reactions. Lorand\(^{(24)}\) suggested that the rearrangement takes place in a solvent cage.

A convincing demonstration of the radical nature of the Meisenheimer rearrangement was the observation\(^{(25)}\) of the Chemically Induced Dynamic Nuclear Polarisation (CIDNP) effect\(^{(26)}\) in the
isomerisation of (31); the effect was observed in both the benzylic methylene and the methyl groups in (32).

Recently, the isolation of some benzylic, carbonyl stabilized intermediates (33) in the Stevens rearrangement has been reported and the CIDNP effect associated with (34) has been observed in the isomerisation. This supports the view that the radical, dissociation - recombination process is general in the thermal reorganisation of benzylic and, most likely, alkyl 1,2-dipolar species.
(ii) **Allylic Rearrangements**

The rearrangement of allyl groups in 1,2-dipolar systems seems to be dependent upon the conditions under which the rearrangement takes place. Thus Stevens *et al* (28) report that both crottyl-(35) and 1'-methallyl(36)-9-fluorenyl ethers rearrange in the presence of sodium t-butoxide at 100° to give 9-crotyl-9-fluorenol (37) and suggest that the reaction (35) → (37) occurs by an internal nucleophilic displacement (see (26)) and the reaction (36) → (37) occurs by an internal $S_{N}^{2'}$ reaction. The internal nucleophilic reaction seems unlikely in view of our previous discussion and would seem more likely to proceed via a radical, dissociation - recombination mechanism. When the reaction was repeated at lower temperatures (29,30) with sodium amide in liquid ammonia, (35) rearranged to give 9-(α-methallyl)-9-fluorenol (38).
In a study of the Stevens rearrangement of allylic ammonium salts, Millard and Stevens\(^{(31)}\) showed that a variety of ammonium salts with variously substituted allyl groups undergo rearrangement with inversion of the allyl group. Although two exceptions, N-cinnamyl\(^{(39b)}\) and 3-(o-tolyl)-allyl\(^{(39c)}\)-N,N-dimethyl-N-phenacylamine-N-oxide, are quoted, later workers\(^{(32)}\) showed that these too rearrange with inversion.

\[
\begin{array}{c}
\text{Ph} \quad \text{O} \\
\text{N}(\text{CH}_{3})_2 \\
R^2 \\
R^1 \\
\hline
(a) \text{CH}_3 & \text{H} \\
(b) \text{Ph} & \text{H} \\
(c) \text{o-} \text{H}_3 \text{C}_6 \text{H}_4 & \text{H} \\
(d) \text{p-} \text{H}_3 \text{COC}_6 \text{H}_4 & \text{H} \\
(e) \text{o-} \text{O}_2 \text{NC}_6 \text{H}_4 & \text{H} \\
(f) \text{CH}_3 & \text{CH}_3
\end{array}
\]

In a study of the Wittig rearrangement of allyl ethers, Rantensrauch\(^{(33)}\) illustrated the temperature and steric effects on the mechanism of the allylic rearrangement. Thus when (40) was formed at \(-80^\circ\), the rearranged mixture gave (45) and (46) in the ratio 8:1, at \(-25^\circ\) the ratio was 7.5:1 and at \(23^\circ\), fell to 6:1.
(41) Gave, at $-25^\circ$, a mixture of (45) and (46) in the ratio 1:1.4.
It is interesting to note that, though the gem-dimethylallyl compounds rearrange to some extent via a cleavage-recombination pathway, the methallyl compounds rearrange in a concerted fashion with no evidence of cleavage.

Baldwin and Patrick\(^{(34)}\) studied the Wittig rearrangement using the optically active 1,3-dimethylallyl benzyl ether (47). Isomerisation of (47b) at $0^\circ$ gave a product which contained 14% deuterium on the double bond, indicating that 28% of the reaction proceeded via the radical, dissociation - recombination process and 72% via the concerted process. This is also borne out by the
observation that the ketone (48) formed from the alcohol had 72% optical purity.

The Meisenheimer rearrangement in allylic systems was studied by Kleinschmidt and Cope\(^7\), as previously noted. Although they were able to isolate the 1-methallyl hydroxylamine (9) from the pyrolysis of (8), pyrolysis of the cinnamyl compound (49) gave a product which could not be separated.
In view of the temperature at which the reaction takes place, it may be possible that the product is a mixture of (50) and (51) and as Johnstone\(^{(1)}\) notes, the reaction should be investigated.

The stereospecific nature of the concerted process in allyl rearrangements has recently been used to transfer chirality from an optically active nitrogen to a carbon atom\(^{(35)}\). Thus when (+)-N-trans-2-butenyl-N-ethyl-p-toluidine-N-oxide (52) is warmed in alkali, the product is (+)-O-1-methallyl-N-ethyl-N-p-tolylhydroxylamine (53).

![Chemical structures](image)

Hydrogenolysis of (+)-(53) gave (+)-2-butanol. The optical purity of the (+)-2-butanol was 7.7% but since the optical purity of (52) was not known, the degree of selectivity could not be determined.

Another 1,2-dipolar species, amineimides, has been known since 1959. A detailed review of the reactions and isomerisation of amineimides comprises the main body of this work.
la) NOMENCLATURE

Three types of nomenclature are currently in use in amine-imide chemistry. The Chemical Society presently favours the term amido-ammonium compounds, or ammonio-amidates; the American Chemical Society favours the term amine-imides. Where the $-N-N-$ system is incorporated in a ring, these are referred to as the "-inium hydroxide-inner salt".\(^{(48)}\)

In this work the term "amine-imide" will be used since this indicates the structural similarities to amine oxides. For cyclic amine-imides, the term "-inium hydroxide-inner salt" will be used.

lb) REACTIONS OF AMINEIMIDES

In 1954, Wawzonek and Meyer\(^{(36)}\) reported the synthesis of the first amineimide, trimethylamine-$p$-toluenesulphonimide (54).

![Chemical structure of (54)](image)

$\text{SO}_2 - N \rightarrow N(CH_3)_3^+$

(54)

Reaction of (54) with benzyl chloride produced 1-benzyl-1-$p$-toluenesulphonyl-2,2,2-trimethylhydrazinium chloride, but reaction with methyl iodide in ethanol gave 1,1,1-trimethyl-2-$p$-toluenesulphonyl-hydrazinium iodide. Wawzonek rationalised the reaction to proceed
via the ethyl alcohohate (55), although this was not isolated. The same result could accrue by an initial alkylation, followed by a nucleophilic displacement involving water or alcohol.

\[
\begin{array}{c}
\text{(55a)} \\
\text{(55b)}
\end{array}
\]

Pyrolysis of (54) gave an intractable gum and small amounts of trimethylamine, ammonia, formaldehyde and p-toluenesulphonamide.

Trimethylamine-benzimide (56) was synthesised by Hinman and Flores (37); the structure was proved by hydrogenolysis to trimethylamine and benzamide, but no investigations of its reactions were carried out.

\[
\begin{array}{c}
\text{(56)}
\end{array}
\]
Structural similarities between amineimides and sulphilimines\(^{(38)}\) prompted an investigation into the rearrangement of benzyl amineimides\(^{(39)}\). Thus when \(N,N\)-dimethyl-\(N\)-\(p\)-nitrobenzylamine-acetimide (57) was pyrolysed at 180-185\(^\circ\), the main product was 1-acetyl-2,2-dimethyl-1-\(p\)-nitrobenzyl-hydrazine (58).

\[
\begin{align*}
\text{(57)} & \quad \text{(a) } X = \text{H} \\
\text{(58)} & \quad \text{(b) } X = \text{NO}_2
\end{align*}
\]

The isomerisation (57) \(\rightarrow\) (58) was originally conceived to proceed via a three membered transition state involving a concerted nucleophilic displacement of the benzyl group by the negatively charged nitrogen. However, in a later paper\(^{(40)}\), Jemison and Morris observed the chemically induced dynamic nuclear polarisation (CIDNP) effect\(^{(26)}\) in the pyrolysis of (57b) which suggested that the reaction proceeds via a homolytic cleavage-recombination pathway (Scheme 2).
Alkylation of (57b) with methyl iodide gave 1,1-dimethyl-1-
p-nitrobenzyl-2-α-methoxyethylidenehydrazonium iodide (59) indicating
that the resonance form (60) contributes significantly to the structure of the amineimide (39).

In a series of experiments (41) conducted prior to the work by Jemison and Morris, the benzyl group was incorporated in a heterocyclic ring (61). By analogy with previous results, the product of thermolysis was expected to be 1-methyl-2-acetyl-3-phenylhexahydropyridazine (62). Also, it had been previously found (42) that pyrolysis of 1-methyl-2-phenylpyrroline-N-oxide (63) produced 2-methyl-6-phenyltetrahydro-1,2-oxazine (64) (c.f. Pinner (2)). Electronic simi-
larities suggested a similar reaction course. In fact, pyrolysis of (61) gave (62) in only 17% yield, the major portion (40%) being converted into methyl isocyanate (65) and 1-methyl-2-phenylpyrrolidine (66).

\[
\text{CH}_3\text{N}==\text{C}==\text{O} + \quad \text{CH}_{3}\text{N}==\text{C}==\text{N}\text{CH}_3
\]

(65) (66)

(61)

Wawzonek and Gueldner\(^{(41)}\) surmise that the transformation \((61) \rightarrow (62)\) is inhibited because delocalisation of the negative charge decreases the nucleophilicity of the imide nitrogen. On the other hand the charge is localised on the oxygen in the amine-oxide (63). The competing reaction which gives (65) and (66) was considered analogous to the Curtius, Schmidt, Hofmann and Lössen rearrangements which proceed via a similar transition state (67)\(^{(43)}\).

\[
\begin{align*}
R & \quad \begin{array}{c}
\text{N} - \text{X} \\
\text{C} \\
\text{O}
\end{array} \\
\end{align*} \quad \begin{array}{c}
\text{O}==\text{C}==\text{N} - \text{R} + \text{X}
\end{array}
\]

\((X = \text{N}_2, \text{Cl}, \text{Br, OCOR})\)

(67)
In a series of papers\(^{(44-47)}\), the Curtius-type reaction was investigated in the pyrolysis of trimethylamine-benzimide (56). The major products of the reaction are trimethylamine and phenyl isocyanate which, under the basic conditions of the reaction, trimerises to triphenylisocyanurate (68). Photolysis of (56) gave 22% benzamide\(^{(45)}\).

Small amounts of benzanilide (69), \(N,N'\)-diphenyl urea (70) and 2-phenylbenzimidazole (71) were also formed. Diphenyl urea could be produced by hydration of phenyl isocyanate, but all three by-products could be derived from a common precursor (72), produced by the reaction of phenyl isocyanate with trimethylamine-benzimide (Scheme 3).

The involvement of phenyl isocyanate and hence (72) in the formation of (69) and (71) was convincingly demonstrated by heating trimethylamine-benzimide in the presence of \(\alpha\)-napthyl isocyanate.
(Scheme 3)
This thermolysis resulted in the formation of 2-phenyl-1H-naph[1,2-d]imidazole (73) in 5-10% yield.

Smith and Briggs\(^\text{(45)}\) postulated that an acyl nitrene may be involved in the formation of phenyl isocyanate and not a concerted rearrangement. Later work\(^\text{(47)}\) suggests that the process is concerted. Thus when trimethylamine-dodecanimide (74) was thermolysed in dimethyl sulphoxide, the only observed product was di-n-undecyl urea. If a nitrene were produced, it would either form an adduct with dimethyl sulphoxide or would abstract hydrogen from the solvent to give dodecanamide.

\[
\begin{align*}
\text{C}_{11}\text{H}_{23} & - \text{N} - \text{N(CH}_3\text{)}_3 \\
& \quad \text{(74)}
\end{align*}
\]
Wadsworth\(^{(48)}\) investigated the possibility of involvement of an acyl nitrene intermediate in the thermolysis of amineimides. By incorporating an amineimide system in a ring (75), the possibility of a concerted reaction is diminished since this would involve a bicyclic intermediate. In fact, when 1,1,4-trimethyl-3-oxopyrazolidinium inner salt (75) was pyrolysed at 245\(^\circ\), the product was (77) in almost quantitative yield with no evidence of (76), the expected product via a nitrene intermediate. However, the transformation (75) \(\rightarrow\) (77) could be enhanced via an intermediate (78), formed by a prototropic shift.
Thermolysis of 1-benzyl-1,4-dimethyl-3-oxopyrazolidinium inner salt (79) gave the normal product from a Wawzonek rearrangement (80) at 190°C, with no evidence of cleavage of the N-N bond.

\[
\text{CH}_3-\text{N}^+\text{N}^{-}\text{CH}_2-\text{N}^+\text{N}^{-}\text{CH}_3
\]

\(\text{190°C}\)

\[
\text{CH}_3\text{N}^+\text{N}^{-}\text{CH}_2\text{N}^+\text{N}^{-}\text{CH}_3
\]

In subsequent work, Wadsworth and Emmons\(^{49}\) prepared an interesting dimer of \(N\),\(N\)-dimethylamino isocyanate (81). The triazole (81)

\[
\text{(CH}_3\text{)}^2\text{N}^+\text{N}^{-}\text{N}^+\text{N}^{-}\text{N}^+\text{N}^{-}\text{N}^+\text{N}^{-}\text{N}(\text{CH}_3\text{)}^2
\]

\(\text{200°C}\)

\[
\text{CH}_3\text{N}^+\text{N}^{-}\text{N}^{-}\text{CH}_3
\]

\[
\text{N}(\text{CH}_3\text{)}^2
\]

was rapidly transformed to (82) at 200°C in excellent yield. This
methyl migration is surprising since no methyl migration is observed in trimethylamine-benzimide or the cyclic \((75)\). Presumably the adjacent, electron withdrawing carbonyl group may serve to labilise the methyl group. Also, this may be an intermolecular reaction.

A more striking illustration of an alkyl migration was obtained by the pyrolysis of the spiro analogues \((29\text{a and b)}^{(50)}\). On heating \((83\text{a})\) at \(200^\circ\), only the starting material was recovered and no trace of \((84\text{a})\). On the other hand, \((83\text{b})\) was converted to \((84\text{b})\) in quantitative yield. The dependence of the reaction on ring size led Wadsworth to suggest that the migrating carbon atom is attached to the negative nitrogen on the same side from which it leaves. However, no details of the structure of \((84\text{b})\) are presented in the communication and no subsequent paper has yet appeared.
A methyl migration in an acyclic system has recently been reported\(^{(51)}\). Thus when trimethylamine-carboethoxyimide (85) is heated at \(175^\circ\), the product is (86).

\[
\begin{align*}
\text{C}_2\text{H}_5\text{O} & - \text{C} - \overset{\delta^-}{\text{N}} - \overset{\delta^+}{\text{N(CH}_3)_3} \rightarrow \text{C}_2\text{H}_5\text{O} - \text{C} - \overset{\delta^-}{\text{N}} - \overset{\delta^+}{\text{N(CH}_3)_2} \\
\text{(85)} & \quad \text{(86)}
\end{align*}
\]

This seems to be an unusual case since there is no activation for the migration, but if the transition state for isocyanate formation (87) is considered, it can be seen that this involves a nucleophilic attack at a partially negative nitrogen. This would raise the energy of the transition state for the Curtius-type reaction and allow competition from the reaction (85) \(\rightarrow\) (86). In this context it is interesting to note that thermolysis of ethoxycarbonyl azide (88) yields the acyl nitrene\(^{(52)}\), which can be trapped by olefins to give aziridines (89), one of the few reactions which seem to proceed via an acyl nitrene.

\[
\begin{align*}
\text{C}_2\text{H}_5\text{O} & - \overset{\delta^-}{\text{C}} = \overset{\delta^+}{\text{O}} \rightarrow \text{C}_2\text{H}_5\text{O} - \overset{\delta^-}{\text{C}} = \overset{\delta^+}{\text{N}} - \overset{\delta^-}{\text{N}} = \overset{\delta^+}{\text{N}}(\text{CH}_3)_3 \\
\text{(88)} & \quad \text{(89)}
\end{align*}
\]
Morris et al (53) pyrolysed amineimides containing β hydrogens in an alkyl group on the quaternised nitrogen and found that a facile cis-elimination takes place. Thus when N,N-dimethyl-2-phenylpropylamine-acetimide (90) and N,N-dimethylcyclooctylamine-acetimide (91) were heated at 125° in vacuo, 2-phenylpropene and cyclooctene were obtained in good yield; the cyclooctene was almost completely in the cis form. As the authors point out, this fills a gap in the series of isoelectronic, dipolar species (92), (93) and (94) which can take part in a thermal cis elimination, the stereospecificity of the elimination varies, in accordance with the expected nucleophilicity of the negatively charged atom. Thus (92) give 100% cis-cyclooctene (54), (93) 96.5% cis : 3.5% trans and (94) 85% cis : 15% trans (55). The elimination seems most likely to proceed via a five membered transition state (95).
It has recently been shown\(^{(56)}\) that the dimer of diethylamino isocyanate (96) and related compounds undergo a thermal cis-elimination to give the urazole (97) and ethylene.

In studies of elimination reactions, Wawzonek and Paschke\(^{(57)}\) observed that thermolysis of \(N,N\)-dihexylmethylamine-benzimide (98)
leads to a mixture of N-hexyl-N-methylbenzamide, 1-hexene, 2-phenylbenzimidazole (71), N,N-dihexylmethyamine, N,N'-diphenylurea and 1-phenyl-3-methylurazole (99). The formation of the urazole (99) is rationalised in a reaction of 1-benzoyl-2-hexyl-2-methylhydrazine with phenyl isocyanate (Scheme 4). This was verified by heating 1-benzoyl-2-hexyl-2-methylhydrazine with phenyl isocyanate and observing that (99) is formed. It is interesting to note that no urazole

\[
\begin{align*}
\text{Ph} & \quad \text{C} \quad \text{NH} \quad \text{N} \quad \text{CH}_3 \quad \text{PhNCO} \\
& \quad \text{O} \quad \text{C}_6\text{H}_{13} \\
\rightarrow & \quad \text{Ph} \quad \text{NH} \quad \text{C} \quad \text{O} \\
& \quad \text{O} \quad \text{C}_6\text{H}_{13} \\
\text{Ph} & \quad \text{C} \quad \text{NHPh} \\
& \quad \text{O} \\
+ & \\
\text{CH}_3 \quad \text{N} \quad \text{N} \quad \text{C} \quad \text{O} \\
& \quad \text{O} \quad \text{C}_6\text{H}_{13} \\
\downarrow & \\
\text{Ph} \quad \text{N} \quad \text{C} \quad \text{O} \\
\text{CH}_3 & \\
\text{C}_6\text{H}_{13} \\
\Delta & \\
\text{Me} \quad \text{N} \quad \text{N} \quad \text{H} \\
& \quad \text{O} \quad \text{Ph} \\
& \quad \text{O} \quad \text{Ph} \\
& \quad \text{O} \quad \text{Ph} \\
\text{(Scheme 4)}
\end{align*}
\]
### Table I

**Methods of Preparation of Amineimides**

<table>
<thead>
<tr>
<th>Method of Preparation</th>
<th>References</th>
</tr>
</thead>
</table>
| 1. \[
\begin{align*}
R^1\text{CONHR}^2\text{R}^3 & \xrightarrow{\text{R}^4\text{X}} R^1\text{CONHR}^2\text{R}^3 & \xrightarrow{\text{base}} R^1\text{CONHR}^2\text{R}^3 & \xrightarrow{X^-} \\
\end{align*}
\]
\(R^1 = \text{Aryl or alkyl; } R^2, R^3, R^4 = \text{alkyl, allyl, benzyl}\)           | 37, 39, 41, 44, 47, 48, 57-59, 61, 62a, 64, 65. |
| 2. \[
\begin{align*}
R^1\text{R}^2\text{R}^3\text{NNH}_2 & \xrightarrow{\text{base}} R^1\text{R}^2\text{R}^3\text{NNH} & \xrightarrow{\text{R}^4\text{COR}^5} R^1\text{R}^2\text{R}^3\text{NNCOR}^4 \\
\end{align*}
\(R^1, R^2, R^3 = \text{alkyl, or } R^1\text{R}^2\text{R}^3\text{N} = \text{pyridyl, } R^4 = \text{alkyl, aryl or carboalkoxy, } R^5 = 0\text{Alkyl or Cl.}\) | 60, 62b, 63, 67, 68 |
| 3. \[
\begin{align*}
[R^1\text{R}^2\text{NNCO}] & \xrightarrow{R^3\text{NCO}} R^1\text{R}^2\text{N} & \xrightarrow{X^-} \\
\end{align*}
\(R^1, R^2 = \text{alkyl, } R^3 = \text{alkyl or } NR^1R^2\)                              | 49, 50, 57. |
is produced in the thermolysis of N,N-dihexylmethylamine-acetimide; this is ascribed to the reduced basicity of the nitrogen in the benzimide compared with that of the acetimide, indicated by the difference in the carbonyl stretching frequencies (acetimide 1580 cm\(^{-1}\), benzimide 1560 cm\(^{-1}\)).

A number of papers have appeared in which a large variety of amineimides are reported\(^{58-65}\). These were synthesised for possible detergent properties, as precursors to isocyanates and as insecticides\(^{63}\).

The use of pyridinium imides in the preparation of pyrazolo-[1,5-a]pyridine derivatives has recently been reported\(^{66}\). Thus when (100) was refluxed in toluene, (101) was obtained in good yield.

A photochemical rearrangement of an amineimide has recently been reported\(^{67,68}\) which involves the formation of diazapines (103) from pyridinium-carboethoxyimides (102)\(^{67}\) and related compounds\(^{68}\). The reaction is considered to proceed via the bicyclic intermediate (104).
1c) ISOMERISATION OF ALLYLIC AMINEIMIDES

In previously published work, no investigation of allylic rearrangements of amineimides* was carried out. N-Allyl-N,N-dimethylamine-benzimide (105) is a stable, hygroscopic crystalline solid, the infra-red spectrum shows absorption at 1600 cm\(^{-1}\) (c.f. 1600 cm\(^{-1}\) for trimethylamine-benzimide) ascribed\(^{(39)}\) to the C=N stretching mode.

\[
\begin{align*}
R &= \text{OC}_2\text{H}_5, \text{SO}_2\text{C}_7\text{H}_7, \text{Ph} \\
(102) &\quad \rightarrow \quad (104) &\quad \rightarrow \quad (103)
\end{align*}
\]

\* Wadsworth\(^{(48)}\) claims that this was investigated by Wawzonek and Yeakey\(^{(39)}\), but this seems to be a mistake.
Thermolysis of (105) at 140° gave an essentially quantitative yield of 1-allyl-1-benzoyl-2,2-dimethylhydrazine (106).

The reaction was originally thought to proceed via a five membered transition state, similar to the elimination reaction (95) and similar to allylic migrations in the base catalysed rearrangements of allylic amine oxides (7) and allylic phenacyl ammonium salts (31)*. Another possibility (69) was that the allyl group could be transposed first to the oxygen via a five membered transition state and then to nitrogen via a six membered transition state (Scheme 5).

(Scheme 5)

To test this mechanism, the imide system was incorporated in a heterocyclic ring (107), in this way the oxygen is constrained to lie away from the migrating allyl group. Although (107) was

* The mechanism of rearrangements of allylic amineimides is discussed more fully in section 1d.
not isolated, its existence was inferred when treatment of the hydrobromide with triethylamine caused the NMR methyl absorption to shift upfield by 0.5 ppm. (c.f. 0.7 ppm. for the hydrobromide of (105)). On heating (107) to 150°, the allyl group migrated to give (108) in 74% yield indicating that the carbonyl oxygen is not directly involved in the isomerisation. Although an unsatisfactory analysis for (108) was obtained, the NMR spectrum indicated that this was the correct structure.

Before the mechanism of this reaction could be investigated further, Baldwin et al.(70) and Morris(71) published communications which established the mechanism of the allylic rearrangements, these results are discussed in section 1c.

1-Benzoyl-2,2-diallylhydrazine (109) was prepared with a view to preparing N,N-diallyl-N-methylamine-benzimide. (109) Could not be methylated however, which is in agreement with the findings of
Hinman and Flores (37) who could not methylate 1-benzoyl-2,2-di-n-propylhydrazine.

An attempt to isomerise N,N-dimethyl-N-propargylamine-benzimide (110) resulted in the formation of a tar. During the course of preparing (110), it was observed that the hydrobromide (111) evolved a gas above its melting point. The gas was identi-
fied as acetylenic and the other products from the reaction were 1-benzoyl-2,2-dimethylhydrazine (112) and 1,1,1-trimethyl-2-benzoylhydrazinium bromide (113). The reaction to produce (113) can be viewed as proceeding via homolysis of the C-C bond in the propargyl group, which is known to be relatively weak (72). Subsequent hydrogen abstraction from the starting material resulting in the formation of (113) (Scheme 6). (112) Could be derived via an $S_N^2$ reaction with bromide ion as the nucleophile; in this context, both 1-allyl-1,1-dimethyl-2-benzoylhydrazinium bromide and 1-benzoyl-2,2,2-trimethylhydrazinium iodide give (112) as the sole product of thermolysis.

The formation of (113) could also arise from (112) by a nucleophilic attack of the tertiary nitrogen on a quarternary methyl group in (111) leaving 1-benzoyl-2-methyl-2-propargyl hydrazine, though the last of these was not identified.
<table>
<thead>
<tr>
<th>Parent Compound</th>
<th>PhCONHN(CH$_3$)$_3$</th>
<th>PhCONHN(CH$_3$)$_2$</th>
<th>PhCONHN(CH$_3$)$_2$</th>
<th>PhCONHN(CH$_3$)$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salt</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I.R. C=O stretch (cm$^{-1}$)</td>
<td>1650</td>
<td>1680</td>
<td>1680</td>
<td>1725</td>
</tr>
<tr>
<td>N.M.R. CH$_3$ signal (δ)</td>
<td>3.85</td>
<td>3.80</td>
<td>3.85</td>
<td>3.82, 3.85</td>
</tr>
<tr>
<td>Amineimide</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I.R. (C=N) stretch (cm$^{-1}$)</td>
<td>1600</td>
<td>1600</td>
<td>1600</td>
<td>---</td>
</tr>
<tr>
<td>N.M.R. CH$_3$ signal (δ)</td>
<td>3.40</td>
<td>3.23</td>
<td>3.48</td>
<td>3.32, 3.35</td>
</tr>
<tr>
<td>Rearranged Product</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I.R. C=O stretch (cm$^{-1}$)</td>
<td>---</td>
<td>1640</td>
<td>---</td>
<td>1700</td>
</tr>
<tr>
<td>N.M.R. CH$_3$ signal (δ)</td>
<td>---</td>
<td>2.50</td>
<td>---</td>
<td>2.51</td>
</tr>
</tbody>
</table>
1d) **REARRANGEMENT MECHANISMS FOR ALLYLIC AMINEIMIDES**

Shortly after the publication of the initial results (69), communications by Baldwin et al (70) and Morris (71) were published in which a variety of allylic amineimides were studied.

Baldwin showed that when the negatively charged nitrogen is not part of a delocalised system, the isomerism is concerted (path A). When the compounds (114a-c) were prepared, they spontaneously isomerised (115a-c) at 35°C.

\[
\begin{align*}
\text{(a)} & \quad \text{H} \quad \text{H} \quad \text{H} \\
\text{(b)} & \quad \text{H} \quad \text{CH}_3 \quad \text{CH}_3 \\
\text{(c)} & \quad \text{H} \quad \text{H} \quad \text{Ph} \\
\text{(d)} & \quad \text{Ac} \quad \text{H} \quad \text{CH}_3 \\
\text{(e)} & \quad \text{Ac} \quad \text{CH}_3 \quad \text{CH}_3 \\
\text{(f)} & \quad \text{Ac} \quad \text{H} \quad \text{Ph}
\end{align*}
\]

The compounds (114d-f) are stable at room temperature, but at elevated temperature the isomerisation proceeds via a homolytic, dissociation – recombination reaction (path B) to give (116d-f) in similar fashion to the Wawzonek rearrangement (40) (Scheme 7). In the absence of any constraints, such as solvent cage effects, the product will be the most thermodynamically stable.
Although the same result could obtain by reaction [A] followed by reaction [C], as suggested by Morris (71), this was eliminated by preparing (115f) and showing that isomerisation to (116f) occurs at only one tenth of the rate of (114f) under the same conditions. Also the observation of the CIDNP (26) emission of the methylene protons in (116f) during the isomerisation reaction lends support for path [B].

Baldwin argues that the delocalisation of the negative charge in the amidate, decreases the nucleophilicity of the negative nitrogen, thus raising the activation energy for reaction [A] and allowing competition from reaction [B]. It is also noted that the initial geometry of the product corresponds to the conformer of maximum energy in the rotation of amides and hence would destabilise the transition state for reaction [A].
2) PREPARATION OF FIVE-MEMBERED HETEROCYCLES FROM AMINEIMIDES AND AMINE OXIDES

Although N-allyl-N,N-dimethylamine-benzimide (105) does not appear to isomerise via a five-membered transition state, it seemed quite probable that the presence of a good leaving group on the terminal carbon atom could lead to closure to form a five-membered ring. Such an example (73) is the amide assisted formation of the bromohydrin (118) of 3-benzamido cyclohexene (117).

\[
\begin{align*}
\text{Bromination of (105) at room temperature resulted in the formation of 1,1-dimethyl-2-benzoyl-4-bromopyrazolidinium bromide (119).}
\end{align*}
\]
In a similar fashion, the propargyl amineimide (110) gave 1,1-dimethyl-2-benzoyl-4-bromopyrazol-3-enium bromide (120).

\[
\begin{align*}
\text{(120)}
\end{align*}
\]

It could be argued that the oxygen end of the ambident amido group could intercept the bromonium ion to give rise to (121) and (122).

\[
\begin{align*}
\text{(121)} \\
\text{(122)}
\end{align*}
\]

However, it has been shown\(^{(74,75)}\) that whenever an amidate ion participates in a reaction to form five-membered rings, the more nucleophilic nitrogen reacts and there is no evidence of oxygen participation. Thus (123) in the presence of ethoxide ion is transformed exclusively to (124).
Since the bromination of allyl amineimides was successful, it seemed reasonable to apply the same reaction to an allylic amine oxide. Thus bromination of N-allyl-N,N-dimethylamine-N-oxide (125) produced 2,2-dimethyl-4-bromoisoxazolinium bromide (126). The yield of (126) was low (3%), but since the reaction was performed only once, the loss could have resulted from an improper workup procedure, also hydration of the amine oxide could reduce the nucleophilicity of the oxygen, resulting in a lower yield of (126).

An attempt was made to displace the bromine in the pyrazolidinium salt by thiocyanate but without success. Hydrolysis of
(120) with hydrochloric acid gave benzoic acid and 1,1-dimethylhydrazine hydrochloride. A possible mechanism for the reaction is outlined below (Scheme 8).

Hydrogenolysis of (119) and (120) gave (127), identified as the picrate. The displacement of the bromide in both cases could be explained by an assisted displacement (S_N) of bromide by nitrogen and subsequent hydrolysis by water in the ethanol to give (127).

The parent peak for (127) appeared at m/e 205 corresponding to (127) minus H_2O in the mass spectrum of the picrate.
3) **ATTEMPTED PREPARATION OF SOME AMINEIMIDES**

The preparation of the thiobenzoyl analogue of (105) was attempted, but the product of the reaction was 1,1-dimethyl-2-thiobenzoylhydrazinium bromide (128). The reaction possibly proceeds by an initial allylation on the nucleophilic sulphur, followed by an $S_N2'$ reaction by traces of water to give (128) although no evidence of the fate of the allyl moiety was obtained.

An attempt was made to prepare trimethylamine-thiobenzimide by a variation of the method of McKillip and Slagel\(^{(62b)}\), but without success.

1,1-Dimethyl-2-(2,4-dinitrophenyl)hydrazine (129) was prepared in an attempt to prepare the amineimine (130). Unfortunately, no alkylated product was obtained. Presumably the electron withdrawing power of the two nitro groups considerably decreases the nucleophilicity of the terminal nitrogen (131).
In an attempt to prepare the amineimide (132) by a one step reaction (Scheme 9), a product was produced in small yield, which smelled like pyridine but could not be isolated.

(Scheme 9)
4) **FURTHER 1,2-DIPOLAR SPECIES**

When S-benzamido-S,S-dimethylsulphonium bromide (133) was treated with sodium hydroxide gave benzamide in almost quantitative yield. In this context it is interesting to note that in a recent publication, Oae et al\(^{(76)}\) have shown that treatment of (134) with cyanide ion gives the urea (135) and the sulphide.

![Chemical Structure](image)

\((133)\)

Dimethyl sulphonium acetimide (136) was prepared and thermolysed\(^{(74)}\) after the inception of this work. The products of thermolysis are unusual and are postulated to arise via an initial prototropic shift to give a Stevens-type intermediate (Scheme 10).
An attempt was made to isolate the ylide (137) by treating \( N-p \)-bromophenacyl-\( N,N,N \)-triethylammonium bromide (138) with sodium hydroxide at room temperature. The product turned out to be \( p \)-bromophenacyl alcohol (139).
Carbonyl-stabilised ylides of the type (140) have since been reported\(^{(27)}\) and are discussed more fully in the introduction.

\[
\begin{align*}
\text{O} & \quad \text{CH}_2 \quad \text{Ar}'' \\
\| & \quad \| \\
\text{Ar}' & \quad \text{C} \quad \text{CH} \quad +\text{N(CH}_3\text{)}_2
\end{align*}
\]

(140)
EXPERIMENTAL
**Spectroscopic Data**

Mass spectra were obtained on an AEI MS-30 mass spectrometer. The $^1$H n.m.r. spectra were recorded at room temperature on a Varian A-60 spectrometer operating at 60 MHz/sec.

All infra-red spectra were recorded on a Perkin Elmer 237-B double beam spectrometer. Solids were measured as KBr discs, liquids as thin films between KBr plates. Spectra were calibrated using a polystyrene film. Abbreviations used in quoting infra-red data are: br = broad, s = sharp, sh = shoulder.

**Thin Layer Chromatography**

This was carried out on microscope slides coated with silica gel Gf-254 (Merck). The slides were visualised by exposure to ultraviolet light.

**Other Physical Data**

Melting point determinations were carried out on an Electro-thermal melting point apparatus and all values quoted are uncorrected. Micro analyses were carried out by Dr. F. Pascher, Bonn, West Germany.
**1-BENZOYL-2,2-DIMETHYLHYDRAZINE**

This was prepared by a modification of the method used by Meyer and Cummings (78). A solution of benzoyl chloride (70 g., 0.5 mole) in dry ether (100 ml.) was added dropwise over 1 hour to 1,1-dimethylhydrazine (66 g., 1.1 mole) dissolved in dry ether (500 ml.). A white crystalline solid was formed which was filtered off. The solid was dissolved in water and treated with saturated sodium carbonate solution until the evolution of carbon dioxide subsided. The solution was extracted with chloroform (3 x 100 ml.). After drying with anhydrous sodium carbonate the solvent was removed in vacuo to leave a yellow oil, which, on triturating with a small amount of ether yielded 1-benzoyl-2,2-dimethylhydrazine (65 g., 80%) as a white microcrystalline solid. A sample crystallised from benzene-pentane as white needles, m.p. 106.5 - 107.5° (lit., (78) m.p. 105-106°) (Found: C, 65.99; H, 7.26%. Calc. for C₉H₁₂N₂O: C, 65.85; H, 7.32%); ν<sub>max</sub> 3250br (N-H), 1640 (C=O), 1540, 1480, 1295, 1305, 1165, 1020, 915, 720, 690 cm<sup>-1</sup>. This was also synthesised by the method of Smith et al (79) from dimethylhydrazine and benzoic acid in the presence of dicyclohexylcarbodiimide, the infra-red spectra and melting points of the products from both reactions were identical.

**1-ALLYL-1,1-DIMETHYL-2-BENZOYLHYDRAZINIUM BROMIDE**

A solution of 1-benzoyl-2,2-dimethylhydrazine (20 g., 0.12 mole) and allyl bromide (23 g., 0.2 mole) in absolute ethanol
(300 ml.) was stirred at room temperature for 24 hours when
1-allyl-1,1-dimethyl-2-benzoylhydrazinium bromide (30 g., 86%)
separated as a white microcrystalline solid. An analytical
sample crystallised from ethanol as colourless prisms, m.p. 149-
151° (Found: Br, 28.07%. \( \text{C}_{12}\text{H}_{17}\text{BrN}_2\text{O} \) requires Br, 28.07%);
\( \nu \)\_max. 2970, 1680 (C=O), 1580, 1460, 1445, 1435, 1280, 1225, 900,
720 cm\(^{-1}\). \( ^1\text{H} \) n.m.r. (\( \text{D}_2\text{O} \)); 3.80 \( \delta \) singlet (6 protons).

**1-ALLYL-1,1-DIMETHYL-2-BENZOYLHYDRAZINIUM p-TOLUENESULPHONATE**

Allyl \( p \)-toluenesulphonate (11.0 g., 0.05 mole) and 1-
benzoyl-2,2-dimethylhydrazine (8.2 g., 0.05 mole) were stirred
in chloroform (100 ml.) for two days at room temperature, when
ether was added to precipitate 1-allyl-1,1-dimethyl-2-benzoyl-
hydrazinium \( p \)-toluenesulphonate (14.0 g., 73%) as an off-white
solid. An analytical sample crystallised from 2-propanol as white
needles, m.p. 152-155° (Found: C, 60.60; H, 6.41%. \( \text{C}_{19}\text{H}_{24}\text{N}_2\text{O}_4\text{S} \)
requires C, 60.64; H, 6.38%); \( \nu \)\_max. 3020, 1685 (C=O), 1460, 1305,
1290, 1230, 1185, 1175, 1125, 1040, 825, 685, 680.

**N-ALLYL-N,N-DIMETHYLAMINE-BENZIMIDE**

1-Allyl-1,1-dimethyl-2-benzoylhydrazinium bromide (2.3 g.,
0.08 mole) was triturated with sodium hydroxide (e.g. in 5 ml. water)
to give a colourless oil. This was extracted with chloroform (4 \times
10 ml.). The chloroform solution was dried with anhydrous sodium
carbonate and the solvent removed in vacuo to leave a colourless oil, which on triturating with a little ether gave N-allyl-N,N-dimethylamine-benzimide (1.48 g., 75%) as white granular crystals. Crystallisation from 1-bromopropane produced white, hygroscopic, granular crystals, m.p. 86-88° (Found: C, 70.57; H, 7.80; N, 13.68%. C_{12}H_{16}N_{2}O requires C, 70.58; H, 7.84; N, 13.72%); \nu_{\text{max}} 1600 (C=N), 1555, 1480, 1455, 1440, 1340, 1310, 1300, 940, 750 cm\(^{-1}\).

\(^1\)H n.m.r. (CDCl\(_3\)), 3.32 \delta singlet (6 protons).

**THERMOLYSIS OF N-ALLYL-N,N-DIMETHYLAMINE-BENZIMIDE**

N-Allyl-N,N-dimethylamine-benzimide (5.0 g., 0.024 mole) was placed in a sealed tube, in vacuo, and heated at 140° for 18 hours, when 1-allyl-1-benzoyl-2,2-dimethylhydrazine (5.0 g., 100%) was formed as a brown oil. The oil was distilled under reduced pressure to give a water-white oil, (3.8 g., 76%) b.p. 158/7 m.m., n\(_D^{25}\) 1.5329. The infra-red spectra of the crude and distilled product were identical (Found: C, 70.70; H, 7.98; N, 13.91%. C\(_{12}\)H\(_{16}\)N\(_2\)O requires C, 70.58; H, 7.84; N, 13.72%); \nu_{\text{max}} 2980, 2950, 1640 (C=O), 1460, 1445, 1430, 1390, 1290, 690 cm\(^{-1}\). \(^1\)H n.m.r. (CDCl\(_3\)); 2.50 \delta singlet (6 protons).

**1-BENZOYL-2,2-DIALYLHYDRAZINE**

**Method 1**

Sodium (4.6 g., 0.2 g. atom) was dissolved in absolute ethanol (75 ml.); benzhydrazide\(^{37}\) (13.6 g., 0.1 mole) was dissolved in the solution and allyl bromide (48 g., 0.4 mole) was added dropwise
over half an hour. The mixture was refluxed for 2 hours, after which time the solvent was removed, in vacuo. To the remaining solid was added 2-butanone (25 ml.) and the mixture was refluxed for 10 minutes and then the solution was filtered. On standing the filtrate deposited 1-benzoyl-2,2-diallylhydrazine (7.5 g., 35%) as a brown microcrystalline solid. Recrystallisation from 2-butanone gave buff plates, m.p. 115-116° (Found: C, 72.07; H, 7.57; N, 12.83%. C₁₃H₁₆N₂O requires C, 72.22; H, 7.41; N, 12.96%); \( v_{\text{max.}} \) 3245 (N-H), 1640 (C=O), 1570, 1540, 1435, 1305, 930 sh, 920, 690 cm\(^{-1}\).

Method 2

To a mixture of benzhydrazide (13.6 g., 0.1 mole) and triethylamine (20.2 g., 0.2 mole) in absolute ethanol (75 ml.) was added allyl bromide (36.3 g., 0.3 mole) dropwise over 1 hour. The mixture was refluxed for 2.5 hours and allowed to stand overnight when needles of triethylamine hydrobromide were deposited. The solid was filtered off and the filtrate treated with 2 M sodium carbonate to decompose any hydrobromide in solution. The solvent was removed, in vacuo, and the remaining solid was treated as in method 1 to give 1-benzoyl-2,2-diallylhydrazine (5.0 g., 23%), m.p. 115-116°. The infra-red spectra of both products were identical.

1-ALLYL-1,4-DIMETHYL-3-OXOPYRAZOLIDINIUM p-TOLUENESULPHONATE

Allyl p-toluenesulphonate (4.2 g., 0.02 mole) and 1,4-dimethyl-3-pyrazolidinone \(^{(48)}\) (2.3 g., 0.02 mole) were dissolved in ether (50 ml.). After standing for a week at room temperature, a gummy, semicrystalline
solid separated out which was crystallised from 2-propanol to give colourless needles of 1-allyl-1,4-dimethyl-3-oxopyrazolidinium p-toluenesulphonate monohydrate (1.3 g., 20%), m.p. 82-84° (Found: C, 52.34; H, 7.09; S, 9.04%. C₁₅H₂₃N₂O₅S requires C, 52.32; H, 6.98; S, 9.30%); ν\text{max.} \text{cm}^{-1} 1725 (C=O), 1205 sh, 1185, 1120, 1030, 1010, 810, 675. \text{H n.m.r.} D₂O: 1.56, 1.66 δ doublet (3 protons); 2.66 δ singlet (3 protons); 3.82, 3.85 δ doublet (3 protons).

2-ALLYL-1,4-DIMETHYL-3-PYRAZOLIDINONE

A mixture of 1,4-dimethyl-3-pyrazolidinone (48) (4.6 g., 0.04 mole) and allyl bromide (4.8 g., 0.04 mole) in ether (50 ml.) was stirred overnight at room temperature. The ether and any excess allyl bromide were removed, in vacuo, leaving a yellow glass which was taken into water and extracted with chloroform (3 x 20 ml.). The water was removed, in vacuo, to yield a colourless glass of 1-allyl-1,4-dimethyl-3-oxopyrazolidinium bromide. The N.M.R. spectrum in deuterium oxide indicated that the pyrazolidinium moiety was identical with that of the p-toluenesulphonate prepared above. Basifying the solution in the N.M.R. tube caused the methyl doublet (3.82, 3.85 δ) to move upfield (3.32, 3.35 δ); in contrast, the absorption of the methyl group attached to carbon moved upfield by only 0.05 p.p.m. The bromide was treated with excess triethylamine and the resulting mixture heated to 150°, on an oil bath, for 30 minutes, when the mixture was taken into water (50 ml.) and extracted with chloroform (3 x 20 ml.). The extract was dried with anhydrous sodium carbonate and the chloroform removed in vacuo. The
residue was distilled under reduced pressure to give 2-allyl-1,4-
dimethyl-3-pyrazolidinone as a colourless oil (3.4 g., 74%, based
on 1,4-dimethyl-3-pyrazolidinone), b.p. 110-115° (30 m.m.). (Found:
C, 59.12; H, 8.91; N, 18.18%. C8H14N2O requires C, 62.29; H, 9.09;
N, 18.19%); \( \nu \) \(_{\text{max.}} \) 2975, 2945, 1700 br. C=O, 1650 sh, 1450, 1400 br.,
1260, 1200, 935 cm\(^{-1}\). \(^1\)H n.m.r. (CDCl\(_3\)) 1.1, 1.2 \( \delta \) doublet (3 protons),
2.51 \( \delta \) singlet (3 protons).

1-BENZOYL-2,2-DIMETHYL-2-PROPARGYLHYDRAZINIUM BROMIDE

A solution of 1-benzoyl-2,2-dimethylhydrazine (16.4 g., 0.1 mole)
and propargyl bromide (11.5 g., 0.1 mole) in ethanol (50 ml.) was
stirred overnight. On adding ether and scratching, 1-benzoyl-2,2-
dimethyl-2-propargylhydrazinium bromide (25.6 g., 91%), was deposited
as white microcrystals. An analytical sample crystallised from 2-
propanol as white microcrystals, m.p. 142.5-144° (with gas evolution)
(Found: C, 50.83; H, 5.26; Br, 28.35%. C\(_{12}\)H\(_{15}\)BrN\(_2\)O requires: C,
50.88; H, 5.30; Br, 28.27%); \( \nu \) \(_{\text{max.}} \) 3280 (\( \equiv \)C-H), 3075 (N-H), 2900-2700 br,
2120 s (C=C), 1680 (C=O), 1540, 1450, 1430 s, 1410 s, 1320, 1280, 740,
700 cm\(^{-1}\). \(^1\)H n.m.r. (D\(_2\)O); 3.85 \( \delta \) singlet (6 protons).

N,N-DIMETHYL-N-PROPARGYLAMINE-BENZIMIDE

A solution of 1-benzoyl-2,2-dimethyl-2-propargylhydrazinium
bromide (10 g., 0.035 mole) in water (25 ml.) was treated with excess
2 M sodium carbonate solution. The solution was extracted with chloro-
form (3 x 20 ml.). After drying with anhydrous sodium carbonate, the
solvent was removed, in vacuo, to leave N,N-dimethyl-N-propargylamine-
benzimide (7.2 g., 100%) as white, granular crystals. An analytical sample crystallised from 1-bromopropane as white needles, m.p. 100-102°C (Found: C, 71.22; H, 6.79; N, 14.02%. C₁₂H₁₄N₂O requires: C, 71.29; H, 6.93; N, 13.86%); ν max. 3200 (≡C-H), 2125 (C≡C), 1600 (C=N), 1555, 1460, 1340, 1290, 715, 690 cm⁻¹. ¹H n.m.r. (CDCl₃); 3.48 δ singlet (6 protons).

THERMOLYSIS OF N,N-DIMETHYL-N-PROPARGYLAMINE-BENZIMIDE

N,N-Dimethyl-N-propargylamine-benzimide was heated on an oil bath at 140°C under a stream of dry nitrogen to yield an intractable, black tar which could not be separated or identified.

THERMOLYSIS OF 1-BENZOYL-2,2-DIMETHYL-2-PROPARGYLHYDRAZINIUM BROMIDE

1-Benzoyl-2,2-dimethyl-2-propargylhydrazinium bromide (10 g., 0.035 mole) was heated on an oil bath at 145°C under a stream of dry nitrogen for two hours. During the course of the reaction, a gas was evolved which was passed through a condenser and a cold trap, immersed in melting carbon tetrachloride (-23°C) and into a solution of ammoniacal cupric sulphate; the formation of a brown precipitate indicated the evolution of a terminal acetylenic compound. At the end of the reaction a black oil remained, which was dissolved in boiling 2-propanol (50 ml.). Addition of a small amount of ether to the solution precipitated a buff solid which was identified (see below) as 1-benzoyl-2,2,2-trimethylhydrazinium bromide (2.5 g., 30%). An analytical sample crystallised from 2-propanol as off-white micro-crystals, m.p. 184-186°C decomp. (inserted at 170°C); (Found: C, 45.71; H, 5.89; Br, 30.87%. C₁₀H₁₅BrN₂O requires: C, 46.33;
H, 5.79; Br, 30.89%); \nu_{\text{max.}} \text{ 3315 br(N-H), 1650 (C=O), 1540, 1400, 1260, 1240, 1230 sh, 1200 cm}^{-1}. \text{ The structure was proved by treating the salt with a 10\% solution of sodium hydroxide; subsequent extraction with chloroform, drying with sodium carbonate and removal of the solvent, in vacuo, gave trimethylamine-benzimide. Crystallisation from 1-bromopropane gave white, granular crystals, m.p. 169-170° (lit. (44), 169-170°), not depressed by mixing with an authentic sample prepared by the method of Gibson and Murray (44). The infra-red spectra of both samples were also identical; \nu_{\text{max.}} \text{ 1600 (C=N), 1565, 1480, 1335, 1070 s, 900 s, 815 s, 730 cm}^{-1}.

Thin-layer chromatography (2-propanol) of the mother liquor from the thermolysis showed four spots corresponding to starting material (R_f, 0.54; standard R_f 0.54), 1-benzoyl-2,2,2-trimethylhydrazinium bromide (R_f, 0.17; standard R_f 0.17), 1-benzoyl-2,2-dimethylhydrazine (R_f, 0.70; standard R_f 0.70) and an unknown compound (R_f, 0.84). The solvent was removed from the mother liquor and water (25 ml.) was added. This solution was then extracted with chloroform (3 x 10 ml.). The extract was dried with anhydrous sodium sulphate and the solvent removed, in vacuo, leaving a small amount of oil which was tritiated with a small amount of ether to give 1-benzoyl-2,2-dimethylhydrazine (1.8 g., 30\%) m.p. 105-106°, mixed m.p. 106-107°. Thin layer chromatography (2-propanol) of the ether washings showed a single spot (R_f, 0.84) corresponding to the unknown compound. Evaporation of the ether gave a smear of an oil, insufficient for an infra-red spectrum. The infra-red spectrum of the liquid in the cold trap was identical with that of propargyl bromide.
THERMOLYSIS OF 1-BENZOYL-2,2,2-TRIMETHYLHYDRAZINIUM IODIDE

1-Benzyol-2,2,2-trimethylhydrazinium iodide (37) (3.5 g., 0.008 mole) was heated on an oil bath at 190-200° under a stream of dry nitrogen for 15 minutes. The resulting tar was taken into water (25 ml.) and extracted with chloroform (3 x 10 ml.). The solution was dried with anhydrous sodium carbonate and the solvent removed, in vacuo, leaving an oil which, on triturating with a little ether, gave 1-benzyol-2,2-dimethylhydrazine (0.8 g., 60%) m.p. and mixed m.p. 105-106°. Thin-layer chromatography (2-propanol) of the mother liquor and the ether washings indicated that this was the only product of thermolysis.

THERMOLYSIS OF 1-ALLYL-1,1-DIMETHYL-2-BENZOYLHYDRAZINIUM BROMIDE

This reaction was carried out in similar fashion to the previous one. Again 1-benzyol-2,2-dimethylhydrazine was the only solid product of thermolysis in 64% yield.
SECTION 2

1,1-DIMETHYL-2-BENZOYL-4-BROMOPYRAZOLIDINUM BROMIDE

To a solution of N-allyl-N,N-dimethylamine-benzimide (3.0 g., 0.015 mole) in chloroform (25 ml.) was added bromine (2.4 g., 0.015 mole) in chloroform (25 ml.), dropwise over 15 minutes. The solvent was removed, in vacuo, to give a yellow oil which solidified on triturating with a little hexane. The solid was crystallised from 2-propanol to give 1,1-dimethyl-2-benzoyl-4-bromopyrazolidinium bromide (4.1 g., 76%) as white microcrystals, m.p. 200-202°, decomp. (Found: C, 39.53; H, 4.50; Br, 44.01%. \( \text{C}_{12}\text{H}_{16}\text{Br}_2\text{N}_2\text{O} \) requires: C, 39.56; H, 4.40; Br, 43.96%); \( \nu_{\text{max.}} \) 3010 s, 2990 s, 2910, 1625 (C=O), 1445 s, 1370, 1320, 1300, 1205, 1135, 700 s cm.\(^{-1}\).

1,1-DIMETHYL-2-BENZOYL-4-BROMOPYRAZOL-3-ENIUM BROMIDE

To a solution of N,N-dimethyl-N-propargylamine-benzimide (4.0 g., 0.02 mole) in chloroform (25 ml.) was added bromine (3.2 g., 0.02 mole) in chloroform (25 ml.), dropwise over 30 minutes. The solvent was removed, in vacuo, to give a semicrystalline solid which was crystallised from 2-propanol to give 1,1-dimethyl-2-benzoyl-4-bromopyrazol-3-enium bromide (4.2 g., 58%) as white microcrystals, m.p. 173-174°, decomp. (inserted at 165°) (Found: C, 39.99; H, 3.93; Br, 44.28%. \( \text{C}_{12}\text{H}_{14}\text{BrN}_2\text{O} \) requires: C, 39.78; H, 3.87; Br, 44.20%); \( \nu_{\text{max.}} \) 2910, 1625 (C=O), 1450 s, 1340, 1200 s, 1160, 815 s, 780 s, 690 s cm.\(^{-1}\).
N-ALLYL-N,N-DIMETHYLAMINE-N-OXIDE

N-Allyl-N,N-dimethylamine (25 g., 0.29 mole) was added drop-wise to 15% hydrogen peroxide solution (100 ml.). When the flask had cooled to room temperature, a small piece of platinum foil was introduced to decompose the excess peroxide. After standing overnight, the water was removed, in vacuo, to leave a clear oil. The oxide is a hygroscopic material readily soluble in water and is usually purified by sublimation. This procedure was not deemed necessary and the oxide was used in the crude state for the next reaction.

2,2-DIMETHYL-4-BROMOISOXAZOLINIUM BROMIDE

N-Allyl-N,N-dimethylamine-N-oxide from the previous experiment was taken into chloroform (25 ml.) and treated with a 10% solution of bromine in chloroform until the red colour persisted; the solvent was removed, in vacuo, and the semi-crystalline mass was dissolved in 2-propanol. Treatment of the solution with ether gave a white, amorphous precipitate which was crystallised from 2-propanol to give 2,2-dimethyl-4-bromoisoaxazolinium bromide (2.1 g., 3% based on N-allyl-N,N-dimethylamine) as white, hygroscopic needles, m.p. 143-144 decomp. (inserted at 135°) (Found: C, 23.11; H, 4.20; Br, 61.25%. C₅H₁₁Br₂NO requires: C, 22.99; H, 4.21; Br, 61.30%); ν max. 3000, 1470, 1445, 1420, 1270, 1255, 940, 785, 735 cm⁻¹.
ATTEMPTED REACTION BETWEEN 1,1-DIMETHYL-2-BENZOYL-4-BROMOPYRAZOL-3-ENIUM BROMIDE AND POTASSIUM THIOCYANATE

A solution of 1,1-dimethyl-2-benzoyl-4-bromopyrazolidinium bromide (1.0 g., 0.0027 mole) and potassium thiocyanate (1.0 g., 0.01 mole) in 95% ethanol was refluxed for 24 hours. The solvent was removed, in vacuo, and the resulting solid crystallised to yield starting material, m.p. and mixed m.p. 200-202° decamp., the infra-red spectra were identical. The reaction was also attempted in absolute ethanol and in 2-propanol, but without success.

HYDROLYSIS OF 1,1-DIMETHYL-2-BENZOYL-4-BROMOPYRAZOL-3-ENIUM BROMIDE

1,1-Dimethyl-2-benzoyl-4-bromopyrazol-3-enium bromide (1.0 g., 0.0027 mole) was refluxed overnight with 2 M hydrochloric acid (25 ml.). On cooling, benzoic acid (0.2 g., 75%) was deposited, m.p. and mixed m.p. 121-122° (lit., (80), 121.5°). The remaining solution was evaporated to dryness and the off-white solid dissolved in a little water and filtered. The water was removed from the filtrate, in vacuo, to leave an off-white solid which could not be crystallised satisfactorily. ¹H n.m.r. D₂O indicated that the solid was 1,1-dimethylhydrazinium chloride; 3.54, 3.65 δ (doublet), c.f. 3.52, 3.61 δ (doublet) for 1,1-dimethylhydrazine in hydrochloric acid.

HYDROGENOLYSIS OF 1,1-DIMETHYL-2-BENZOYL-4-BROMOPYRAZOL-3-ENIUM BROMIDE

A solution of 1,1-dimethyl-2-benzoyl-4-bromopyrazol-3-enium bromide (2.0 g., 0.0055 mole) in 95% ethanol (25 ml.) containing a
5% palladium/barium sulphate catalyst (0.2 g.) was stirred under hydrogen at atmospheric pressure. After six hours, 270 ml. (at S.T.P.) (0.012 mole) had been taken up. The catalyst was filtered off and the solvent removed, in vacuo, to leave a red oil which could not be crystallised. The oil was dissolved in 95% ethanol (25 ml.) and a saturated solution of picric acid in 95% ethanol (25 ml.) was added. After standing for two weeks, yellow prisms of a single picrate, either (127a) or (127b) (1.7 g., 67%) were deposited. Crystallisation from 2-butanol gave yellow microcrystals, m.p. 184-185° (Found: C, 47.98; H, 4.49; N, 15.66%. C₁₈H₂₁N₂O₉ requires: C, 47.89; H, 4.65; N, 15.52%); ν\text{max.} 3290, 3150, 1695 (C=O), 1635, 1555, 1360 s, 1330, 1320 sh, 1305, 1285, 1260, 1070, 910 s, 710 cm\textsuperscript{-1}.

HYDROGENOLYSIS OF 1,1-DIMETHYL-2-BENZOYL-4-BROMOPYRAZOLIDINUM BROMIDE

A solution of 1,1-dimethyl-2-benzoyl-4-bromopyrazolidinium bromide (2.0 g., 0.0055 mole) in 95% ethanol (25 ml.) containing a 5% palladium/barium sulphate catalyst (0.2 g.) was stirred under hydrogen at atmospheric pressure. After six hours, 140 ml. (at S.T.P.), (0.006 mole) had been taken up. The catalyst was filtered off and a saturated solution of picric acid in 95% ethanol (25 ml.) was added. On standing, yellow prisms of the picrate (127a) or (127b) (1.8 g., 70%) m.p. and mixed m.p. 184-185°. Mass Spectrum m/e 229 (Picric acid), 205 ((127)-H₂O), 190 (-CH₃), 160 (-NHMe₂).
SECTION 3

1,1-DIMETHYL-2-THIOBENZOYLHYDRAZINE

This was prepared according to the method of Jensen (81) and crystallised from chloroform/ether as off-white needles, m.p. 107-108° (lit. (81), m.p. 108-109°); νₘₐₓ 1460, 1310, 1260, 1240, 1200, 1165, 760, 690, 675 cm⁻¹.

REACTION OF 1,1-DIMETHYL-2-THIOBENZOYLHYDRAZINE WITH ALLYL BROMIDE

A solution of 1,1-dimethyl-2-thiobenzoylhydrazine (0.5 g., 0.003 mole) and allyl bromide (0.5 g., 0.004 mole) in toluene (5 ml.) was stirred for two hours when 1,1-dimethyl-2-thiobenzoylhydrazinium bromide slowly separated as a yellow amorphous powder (0.4 g., 47%) m.p. 192-196°. An analytical sample crystallised from 2-propanol as yellow leaflets, m.p. 192-194° (Found: C, 41.72; H, 5.13%. C₁₈H₁₃BrN₂S requires: C, 41.38; H, 4.98%); νₘₐₓ 3050, 2810 sh, 2750 br, 2675 sh, 1515, 1440, 1325, 1310, 1295, 1175, 825 s, 755 s, 725 s, 680 s cm⁻¹. A sample of 1,1-dimethyl-2-thiobenzoylhydrazinium bromide was prepared from hydro-bromic acid and 1,1-dimethyl-2-thiobenzoylhydrazine, m.p. and mixed m.p. 193-194°.

A sample of the salt was dissolved in 10% sodium hydroxide and extracted with chloroform. After drying with anhydrous sodium carbonate, the chloroform was removed, in vacuo, to leave 1,1-dimethyl-2-thiobenzoylhydrazine, m.p. and mixed m.p. 107-108°.
ATTEMPT TO PREPARE TRIMETHYLAMINE-THIOBENZIMIDE

To a solution of potassium t-butoxide (11.2 g., 0.1 mole) in t-butanol (200 ml.) was added 1,1,1-trimethylhydrazinium iodide (10.1 g., 0.05 mole) and carboxymethylthiobenzoate (10.6 g., 0.05 mole). The mixture was refluxed for 24 hours when the solvent was removed, in vacuo. The resulting solid was extracted with chloroform (3 x 50 ml.) and the extract was dried over anhydrous sodium carbonate. The chloroform was removed, in vacuo, to leave an intractable gum which could not be characterised.

1,1-DIMETHYL-2-(2,4-DINITROPHENYL)HYDRAZINE

1-Chloro-2,4-dinitrobenzene (4.0 g., 0.02 mole) and 1,1-dimethylhydrazine (2.4 g., 0.04 mole) were stirred in ethanol (50 ml.) overnight. Water (25 ml.) was added to the solution to precipitate a red oil which solidified on standing. Crystallisation from 2-propanol gave 1,1-dimethyl-2-(2,4-dinitrophenyl)hydrazine (3.1 g., 69%) as orange-yellow needles, m.p. 110-120°C (lit.(83), 109°C); ν max. 3300 (N-H), 1620, 1585, 1480, 1355, 1330, 1305, 1270, 1130 cm. -1.

ATTEMPTED PREPARATION OF 1-(2,4-DINITROPHENYL)-2,2,2-TRIMETHYLHYDRAZINUM p-TOLUENESULPHONATE

A solution of 1,1-dimethyl-2-(2,4-dinitrophenyl)hydrazine (2.2 g., 0.01 mole) and methyl p-toluenesulphonate (3.7 g., 0.02 mole) in anhydrous 2-propanol, was refluxed overnight in the presence of
anhydrous potassium carbonate. Thin-layer chromatography (2-propanol) indicated that no reaction had taken place. The mixture was refluxed for a further two days but no reaction could be detected by thin-layer chromatography.

REACTION BETWEEN 1,1-DIMETHYL-2-FORMYLHYDRAZINE AND DIMETHYLACETYLENEDICARBOXYLATE

To a solution of 1,1-dimethyl-2-formylhydrazine prepared by the method of Hinman and Fulton (84) (8.8 g., 0.1 mole) in methanol (50 ml.) was added dimethyl acetylenedicarboxylate (14.2 g., 0.1 mole). After a short time the reaction turned black and smelled strongly of pyridine. The mixture was boiled with decolourising charcoal and on filtering gave a violet solution; this was treated with concentrated hydrochloric acid to give a reddish solution which was extracted with chloroform (3 x 20 ml.). The aqueous solution was treated with saturated sodium carbonate solution when the violet colour returned; this solution was extracted with chloroform (3 x 20 ml.) to give a brown solution. After drying with anhydrous sodium carbonate the chloroform from the base extraction was removed in vacuo to leave a recalcitrant black tar which could not be separated or identified.

SECTION 4

BENZAMIDODIMETHYLSULPHONIUM BROMIDE

Freshly prepared N-bromobenzamide (85) (10.0 g., 0.05 mole) was dissolved in acetone (50 ml.) and cooled to -23° in a bath of
melting carbon tetrachloride. To this solution was added dimethyl sulphide (3.1 g., 0.05 mole) in carbon tetrachloride (50 ml.), drop-wise so that the temperature did not rise above -15°C. After the addition was complete, the orange solution was diluted with light petroleum (b.p. 30-60°) to give a yellow, semicrystalline solid which was crystallised from 2-propanol to give benzamidodimethylsulphonium bromide (6.4 g., 48%) as off-white needles, m.p. 124-125° decomp. (inserted at 115°) (Found: C, 41.68; H, 4.75; Br, 30.64%; C9H12BrNOS requires: C, 41.24; H, 4.69; Br, 30.52%); ν max. 2900, 2715, 2640, 1675 (C=O), 1405 s, 1410, 1260, 1100 s, 990, 980, 725, 690 cm. -1.

REACTION OF BENZAMIDODIMETHYLSULPHONIUM BROMIDE WITH BASE

Benzamidodimethylsulphonium bromide (2.6 g., 0.01 mole) was added to a 10% solution of sodium hydroxide (25 ml.). After standing for 15 minutes a white precipitate of benzamide (1.2 g., 100%) appeared, m.p. and mixed m.p. 128-129° (lit. (86), m.p. 129°).

p-BROMOPHENACYLTRIETHYLAMMONIUM BROMIDE

A solution of α,p-dibromoacetophenone (2.8 g., 0.001 mole) and triethylamine (1.1 g., 0.001 mole) in benzene (20 ml.) was stirred overnight to give p-bromophenacyltriethylammonium bromide (2.9 g., 72%) as off-white needles. Crystallisation from water and twice from 2-propanol gave white needles, m.p. 194-195° decomp. (inserted at 180°) (Found: C, 44.39; H, 5.59; Br, 42.07%. C14H21BrNO requires: C, 44.35;
H, 5.54; Br, 42.22%); $\nu_{\text{max.}}$ 1690 (C=O), 1580, 1475, 1410, 1225, 1070, 1005, 815 cm.$^{-1}$.

**REACTION OF p-BROMOPHENACYLTRIETHYLAMMONIUM BROMIDE WITH BASE**

p-Bromophenacyltriethylammonium bromide (2.0 g., 0.0005 mole) was dissolved in 50% sodium hydroxide solution (25 ml.) and the mixture stirred for 15 minutes when the solution was extracted with chloroform (3 x 10 ml.). The extract was dried with anhydrous sodium sulphate and the solvent was removed in vacuo to leave an oil which solidified on triturating with a little light petroleum (b.p. 30–60°). The solid was crystallised from ethanol to give p-bromophenacyl alcohol (0.42 g., 42%) as colourless plates, m.p. 135–136°, mixed$^{(87)}$ m.p. 136–137° (lit.$^{(87)}$, m.p. 136.6°); $\nu_{\text{max.}}$ 1575, 1540, 1250 br, 1115, 1000, 830, 805, 730 cm.$^{-1}$. 
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