Base Catalysed Rearrangements involving Ylide Intermediates. Part 16.[1] The Preparation and Thermal Rearrangement of Allylammonioamidates

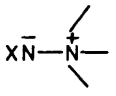
Kan Chantrapromma, W. David Ollis,* and Ian O. Sutherland
Department of Chemistry, The University, Sheffield S3 7HF

The ammonioamidates (7) and (11) undergo [1,2] rearrangement (R^3 = CH_2Ph) and competing [1,2] and [3,2] rearrangements (R^3 = allyl). The rates of the [1,2] and [3,2] rearrangements of the cinnamyl ammonioamidates (11a), (11b), (11d), and (11g) show similar dependence on the nature of the substituent X. The rate of the [1,3] rearrangement of the reaction products (14b), (14d), and (14g) is relatively insensitive to substituent effects, suggesting that the rates of ammonioamidate rearrangements are largely controlled by conjugation between the group X and the $\bar{N}CO$ system. The [1,2] and [3,2] rearrangements of the cinnamylammonioamidate (11d) show moderate and similar dependence upon solvent polarity suggesting that the transition state for both reactions has considerable dipolar character. The apparent intramolecularity of the [1,2] and [3,2] rearrangements of the cinnamylammonioamidate (11e) as estimated by isotopic mixing methods is decreased by isotopic scrambling in the ylide due to radical recombination to give ylide (11l) in addition to products (13l) and (14l). If allowance is made for this effect the [3,2] rearrangement appears to be largely, or even entirely, intramolecular and the [1,2] rearrangement shows intermolecularity comparable with that found for the rearrangements of analogous ammonium ylides under similar reaction conditions.

The hydrazinium ylides (1) in which the group X is strongly electron-withdrawing (X = RCO, RSO_2, CN, NO_2) are a particularly stable group of ylides which had been studied rather extensively before the investigation described in this paper. The ammonioamidates (1; X = COR) are the best known compounds of this type and their structure, as represented[2] by the mesomeric system (2), is closely analogous to that of the acyl-stabilised ammonium ylides (3) which have been discussed in earlier parts in this series.[3] It was, therefore, of interest to study the sigmatropic rearrangements of ammonioamidates (2) in which the group R^2 might participate in [1,2] (R^2 = benzyl) and [3,2] (R^2 = allyl) rearrangements. It had been shown that the ylides (2) could undergo three general types of reaction, cleavage of the $\overset{+}{N}-\overset{-}{N}$ bond,[4,5] elimination if the group R^2 contains a β-hydrogen substituent,[6] and rearrangement; the latter type of reaction has commonly been reported for systems having R^2 = benzyl or allyl.[7,8]

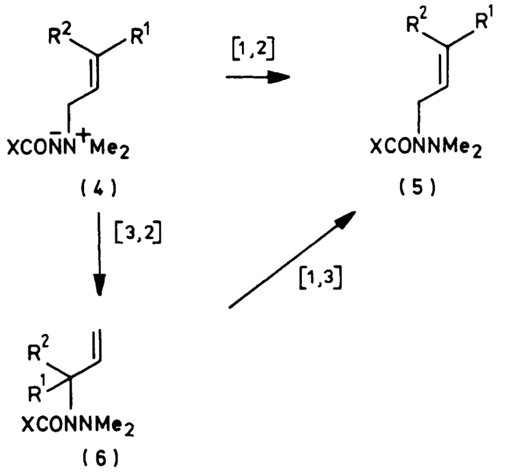
The rearrangements of allylic systems (2; R^2 = allyl) had been reported[9,10] to proceed by the [1,2] pathway (4) ⟶ (5) rather than by the [3,2] pathway (4) ⟶ (6), in striking contrast with other rearrangements of allylic ylides, for example (3; R^2 = allyl), in which the [3,2] pathway predominated. The [1,2] rearrangement had been reported, in some cases, to give rise to CIDNP[9,11,12] under appropriate reaction conditions, suggesting a radical pair mechanism, and it had been shown[9] in other cases that these [1,2] products (5) arose directly from the ylide (4) and not by [1,3] rearrangement (6) ⟶ (5) of an initial [3,2] rearrangement product. The contrast between these results for the allylic ammonioamidates (2) and the closely related[13] allylic ammonium ylides (3) prompted us to investigate further the reactions of the ammonioamidate systems.[14]

The oxopyrazolidinium ylide (7a) had been reported[11] to react by the homolytic pathway (7a) ⟶ (8a) ⟶ (9a), because the benzyl radical component of the radical pair (8a) could be trapped by added toluene-α-thiol or bromotrichloromethane. These systems were accordingly selected for our initial investigation; the oxopyrazolidinium salts (10b—d) † were prepared and the stable ylides (7b—d) † were obtained from these salts by treatment with methanolic sodium methoxide.



(1)

(2) X = N
(3) X = CR^3



Scheme 1. Sigmatropic rearrangements of allylammonioamidates

The ylides (7b—d) rearranged smoothly when heated in benzene at 80 °C to give the product(s) (9). In the case of the ylide (7b) the products of [1,2] and [3,2] rearrangements are not distinguishable but the ylide (7c) gave the [1,2] product (9c) and the [3,2] product (9e) in 18 and 82% yields respectively. The ylide (7d) gave a single product readily identified (n.m.r. spectrum) as the product (9f) of a [3,2] rearrangement. The products (9e) and (9f) were, as expected, converted totally by [1,3] rearrangement into (9c) and (9d) when heated

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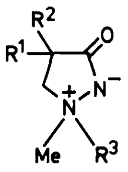
† The n.m.r. spectra of the salts (10) and the corresponding ylides (7) showed that each consisted of a pair of diastereoisomers which could not be separated.

Table 1. Competing [3,2] and [1,2] sigmatropic rearrangements of allylammonioamidates (11)

Ylide	X	R^1	R^2	Solvent[a]	Time (h)[a]	Product Yield (%)[b] [1,2]	Product Yield (%)[b] [3,2]
(11a)	Ph	H	Ph	Benzene	72	88	12
(11b)	Me	H	Ph	Toluene	48	80	20
(11c)	Me	Me	Me	Xylene	2	80	9
(11d)	OEt	H	Ph	Benzene	6	45	55
(11e)	OEt	Me	Me	Toluene	1.5	67	22
(11g)	MeNH	H	Ph	Benzene	1	40	60
(11h)	MeNH	Me	Me	Toluene	1.5	72	28
(11l)	PhNH	Ph	H	Benzene	8	23	68

[a] Reaction carried out at boiling point of solvent. [b] Based upon isolated products and consistent with n.m.r. spectrum of crude reaction products.



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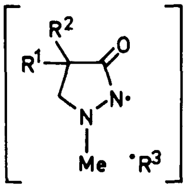

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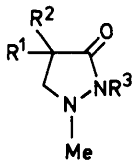

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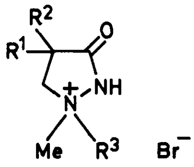
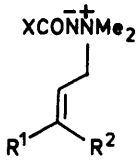


(10)

In (7)—(10): a, $R^1 = R^2 = Me$, $R^3 = CH_2Ph$; b, R^1 and R^2 = H and Me, $R^3 = CH_2CH{=}CH_2$; c, R^1 and R^2 = H and Me, $R^3 = CH_2CH{=}CHPh$; d, R^1 and R^2 = H and Me, $R^3 = CH_2CH{=}CMe_2$ In (9): e, R^1 and R^2 = H and Me, $R^3 = CHPhCH{=}CH_2$; f, R^1 = H, R^2 = Me, $R^3 = CMe_2CH{=}CH_2$



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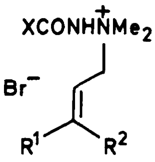

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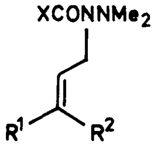

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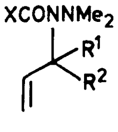

(14)

In (11)—(14): a, X = Ph, R^1 = Ph, R^2 = H; b, X = CH_3, R^1 = Ph, R^2 = H; c, X = CH_3, $R^1 = R^2$ = Me; d, X = OEt, R^1 = Ph, R^2 = H; e, X = OEt, $R^1 = R^2$ = Me; f, X = OEt, $R^1 = R^2$ = H; g, X = NHMe, R^1 = Ph, R^2 = H; h, X = NHMe, $R^1 = R^2$ = Me; i, X = NHMe, $R^1 = R^2$ = H; j, X = H, R^1 = Ph, R^2 = H; k, X = H, $R^1 = R^2$ = Me; l, X = NHPh, R^1 = Ph, R^2 = H

at 138 °C. These results appeared to be in conflict with the earlier work,[9,10] but the oxopyrazolidinium system (7) is restricted to a transoid arrangement of the $^-O{-}C{=}N{-}N^+$ grouping whereas acyclic ammonium ylides are known to adopt a cisoid arrangement of the analogous $^-O{-}C{=}C{-}N^+$ grouping.[15] We therefore extended our investigation to the acyclic allylic ammonioamidates (11), derivable from reaction of the salts (12) with aqueous sodium hydroxide.

The ylides (11a—i) rearranged when heated in benzene, toluene, or xylene to give products (13) and (14) that were readily identified by their n.m.r. spectra (Experimental section). For the cases (11; $R^1 = R^2$ = H) the products of [1,2] and [3,2] rearrangement could not be distinguished, but for the cases (11; R^1 = Ph, R^2 = H) and (11; $R^1 = R^2$ = Me) the yields of the two different products are summarised in Table 1. In contrast with earlier reports,[9,10] in all cases both reaction products could be isolated. This qualitative investigation suggested that the rates of [1,2] and [3,2] rearrangement depended upon the substituent X (see 11) in a different manner and the cinnamylammonioamidates were investigated in more detail. The rates of the competing [1,2] and [3,2] rearrangements of these ylides (11a), (11b), (11d), and (11g) are reported in Table 2, and it can be seen that both reactions are sensitive to changes in the group X. In general, the order of reactivity of the ylides (11) is X = Ph, Me < EtO < MeNH which is in accord with the expected stabilisation of the negatively charged fragment $XCO\bar{N}$ of the ylide structure by conjugation.* The [3,2] rearrangement is rather more sensitive than the [1,2] rearrangement. By analogy with other rearrangements of ylides [1] the [1,2] reaction is expected to involve an intermediate radical pair (15) and the [3,2] rearrangement the pericyclic transition state (16). Presumably the conjugation

Table 2. Rates[a] of [1,2] and [3,2] rearrangements of cinnamylammonioamidates (11) at 79 °C and of [1,3] rearrangements of (1-phenylallyl)hydrazines (14) at 150 °C

Compd.	X	$k_{[1,2]}$[b] ($s^{-1} \times 10^6$)	$k_{[3,2]}$[b] ($s^{-1} \times 10^6$)	Compd.	$k_{[1,3]}$[c] ($s^{-1} \times 10^6$)
(11a)	Ph	2.26	0.33	(14a)	
(11b)	Me	1.66	0.64	(14b)	31.5
(11d)	OEt	18.7	13.0	(14d)	13.8
(11g)	MeNH	980	1 580	(14g)	144

[a] First order rate constants measured by n.m.r. analysis of reactant and product signals. [b] In methyl cyanide at 70 °C. [c] Neat at 150 °C. First order rate constants for [1,3] rearrangement of (14d) at 150 °C: 16.1 × 10^{-6} s^{-1} in dimethylformamide and 4.81 × 10^{-6} s^{-1} in nonane.

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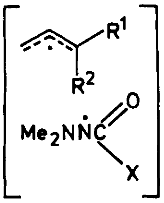
* A useful, but perhaps over simple, analogy is provided by the conjugation energy of the $\ddot{N}COX$ system as indicated by rotational barriers about the N−COX bond of amides.[16]



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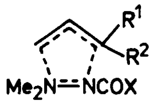

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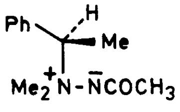
Table 3. Solvent effects on rates [a] of [1,2] and [3,2] rearrangements of cinnamylammonioamidate (11d) at 79 °C

Solvent	E_T value [b]	$k_{[1,2]}$ ($s^{-1} \times 10^6$)	$k_{[3,2]}$ ($s^{-1} \times 10^6$)
CCl_4	32.5	127	232
C_6H_6	34.5	104	133
Dioxan	36.0	45	51
$MeCO_2Et$ [c]	38.1	47	58
MeCN	46.0	19	13

[a] First-order rate constants. [b] As defined in ref. 19. [c] At 76.5 °C.



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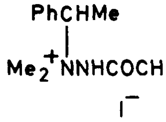

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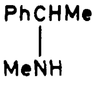

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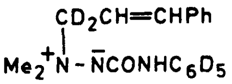

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$Me_2NNHCONHC_6D_5$

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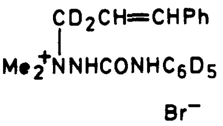

(22)

in the developing hydrazyl radical component $Me_2N\dot{N}COX$ of (15) bears a closer resemblance to that in the $XCO\bar{N}$ fragment of the ylide (11) than does that of the pericyclic transition state (16).

The sensitivity of the pericyclic transition state of the [3,3] rearrangement to substituent effects has been widely noted and exploited,[17] and there is also a number of cases [18] where rather similar substituent effects have been observed for the [1,3] rearrangement, for which a radical pair mechanism may be expected other than in unusual stereochemical situations. In view of this similarity in substituent effects in the [1,2] and [3,2] rearrangements it was also of interest to investigate solvent effects and the rearrangement (11d) ⟶ (13d) + (14d) was examined in a range of solvents. The rates of both the [1,2] and [3,2] rearrangements (Table 3) show limited sensitivity to changes in the solvent parameter E_T,[19] indicating similarity of charge separation * in the ylide (11), the transition state for formation of the radical pair (15) and the pericyclic transition state (16).

The alternative interpretation of the similarity of solvent and substituent effects in competing [1,2] and [3,2] rearrangements would be that both reactions involve either radical pair or concerted pathways. This consideration prompted us to examine the rearrangements of the ammonioamidate systems using the same criteria that had proved useful in our investigation [1,21] of the Stevens [1,2] rearrangement of acyl-stabilised ammonium ylides. The stereochemical test, using a migrating phenylethyl substituent, could not be applied because suitable ammonioamidate systems, for example (17), undergo thermal elimination to give styrene and the corresponding hydrazine rather than a [1,2] rearrangement. Thus, the (*R*,*S*)-salt (18), prepared from the secondary amine (19) (see Experimental section) reacted with aqueous sodium hydroxide to give the (*R*,*S*)-ylide [*cf.* (17)] which at 120 °C gave styrene and *N*-acetyl-*N*′,*N*′-dimethylhydrazine with no detectable rearrangement product. Since the stereoselectivity of the rearrangement could not be examined readily, we undertook an investigation of the intermolecularity of the reaction following an analogous procedure to that used in other investigations of sigmatropic rearrangements.[1,21,22]

The crystalline ammonioamidate (11l) was selected for this study since the preparation of the heptadeuterio-derivative (20) could be achieved readily from [$^2H_5$]phenyl semicarbazide (21). The hydrazine derivative (21) reacted readily with [1,1-$^2H_2$]cinnamyl bromide to give the salt (22) which was converted into the [$^2H_7$]ammonioamidate (20). A 1 : 1 mixture of the [$^2H_0$]- and [$^2H_7$]-ammonioamidates was rearranged under a variety of reaction conditions (Table 4), the [1,2] and [3,2] rearrangement products were separated and their isotopic composition {[$^2H_0$], [$^2H_2$], [$^2H_5$] and [$^2H_7$]} was determined by mass spectrometry. The interpretation of the results in the terms of apparent intramolecularity of the competing [1,2] and [3,2] rearrangements in a range of solvents of varying viscosity is presented in Table 4. The apparently significant intermolecularity of the [3,2] rearrangement in solvents such as butanol and methyl cyanide was surprising, since it had been expected that this reaction mode would involve a pericyclic transition state [13,23] rather than a radical pair intermediate. However, one obvious interpretation of these results is that the observed 'mixing' occurs by radical recombination from the free radical state (see Scheme 2) to give the starting ylide in addition to the products of [1,2] and [3,2] rearrangement. This possibility was checked by determining the isotopic composition of the ylide after partial rearrangement in methyl cyanide at 80 °C. The isotopic composition of the ylide could not be determined directly by mass spectrometry, due to its thermal sensitivity, but it could be determined with reasonable accuracy by rearrangement in glycerol at 80 °C, since under these conditions the [1,2] and [3,2] products are formed with only 3 and <1% isotopic scrambling † respectively. The [1,2] and [3,2] rearrangement products from the partly rearranged ylide were found to have been formed with 18 and 22% apparent intramolecularity representing *ca.* 80% scrambling in the original partly rearranged ylide. Thus, the high level of isotope scrambling in the [3,2] rearrangement product formed by rearrangement in methyl cyanide may be accounted for by intermolecular radical recombination to give the starting ylide rather than a [3,2] rearrangement involving

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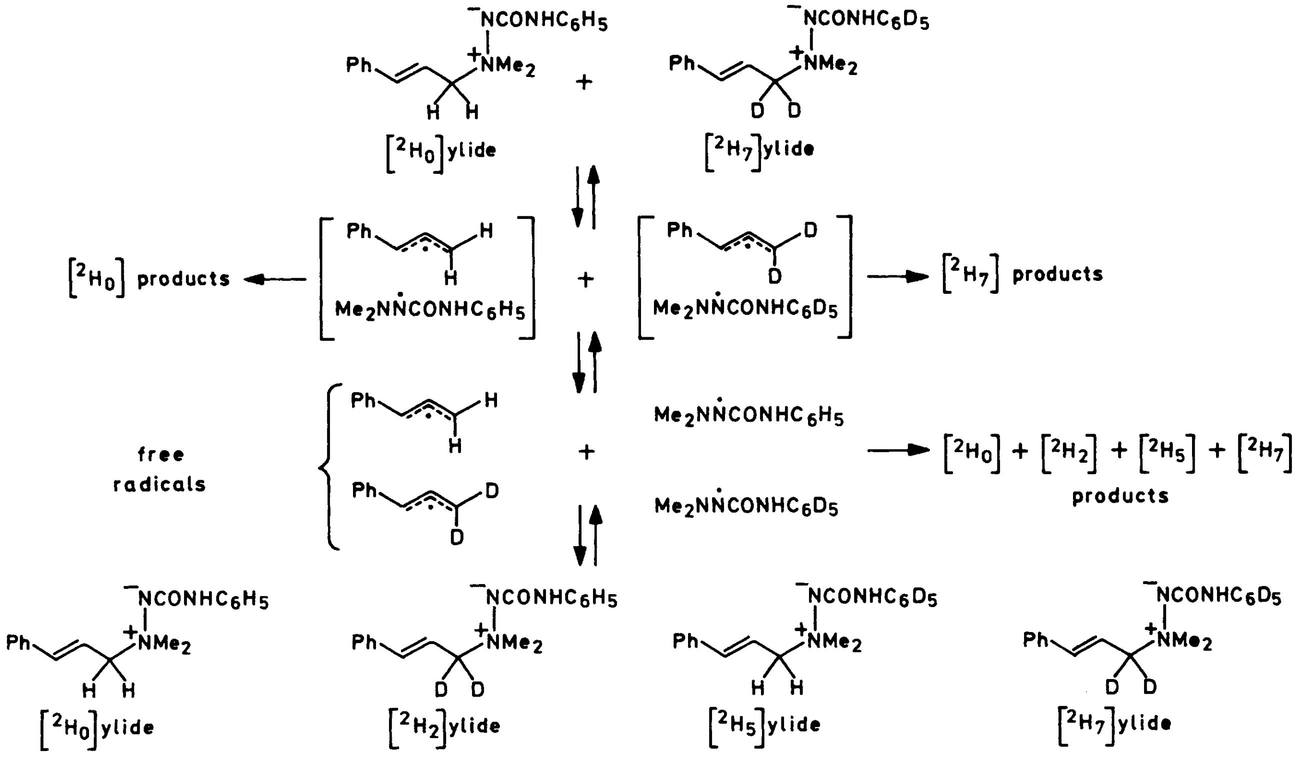
* For an excellent example of the use of solvent effects to determine reaction mechanism of a possibly pericyclic process see ref. 20.

† The term 'isotopic scrambling' is used to summarise intermolecular free radical recombination to give equal amounts of [$^2H_0$], [$^2H_2$], [$^2H_5$], and [$^2H_7$] products (see Scheme 2).

Table 4. Apparent intramolecularity[a] of the [1,2] and [3,2] rearrangements of the cinnamylammonioamidate (11l) under various reaction conditions

Solvent	Temp. (°C)	Time (h)	Solvent viscosity (c.P.)	Product ratio [3,2]/[1,2]	Apparent intramolecularity (%) [1,2]	[3,2]
Glycerol	80	48	31.9	2.0	97	>99
Ethylene glycol	55	168	5.95		97	>99
Ethylene glycol	80	24	3.03	1.25	82	95
Butanol	80	18	0.76	1.29	45	80
Methyl cyanide	80	12	0.22	0.79	5	22
Methyl cyanide/Glycerol[b]	80				18[b]	22[b]
Methyl cyanide[c]	80				20[c]	42[c]

[a] Reaction carried out using a 1 : 1 mixture of [$^2H_0$] (11l) and [$^2H_7$] (20) ylide (1 mmol of each) in 5 ml of solvent. For a reaction product consisting of z% [$^2H_5$] and z% [$^2H_2$] products intermolecularity = $4z$% and intramolecularity = $(100 - 4z)$%. [b] Ylide partially rearranged in methyl cyanide and recovered ylide then rearranged in glycerol, the extent of isotopic scrambling indicates *ca.* 80% isotopic scrambling in the ylide during the initial partial rearrangement in methyl cyanide. [c] Partial rearrangement only, recovered ylide rearranged in glycerol.

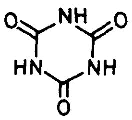


Scheme 2. Isotopic scrambling during [1,2] and [3,2] rearrangements of [$^2H_0$]- and [$^2H_7$]-[cinnamyl(dimethyl)ammonio]phenylureides

radical intermediates. The precise interpretation of the results given in Table 4 is, therefore, rather difficult; however, if it is assumed that the [3,2] rearrangement is totally intramolecular, then the [1,2] rearrangement involves intermolecularity to an extent that is comparable with the intermolecularity observed[1] during the [1,2] rearrangement of analogous ammonium ylides (3) [up to 23% for the ylide (3; R^1 = Ph, R^2 = PhCHMe, R^3 = H) at 60 °C in methanol].

The [1,2] rearrangement of *N*-benzylammonioamidates has been reported[7] and in accord with these reports the rearrangement of the *N*-benzylammonioamidate (23a) gave only the product (25a). The rearrangement of the methylcarbamoyl stabilised ammonioamidate (23b) also gives largely the product (25b) of a [1,2] rearrangement, but there is formed, in addition, a small amount (18%) of the dibenzyl derivative (26). The latter product is presumably formed by a combination of [1,2] rearrangement and an intermolecular nucleophilic displacement involving the anion (27) and the ylide (23b).

The *N*-formylammonioamidates (11j) and (11k) did not undergo [3,2] and [1,2] rearrangement. The reaction products consisted of an oil identified as *N*,*N*-dimethylcinnamylamine (from 11j) and *N*,*N*-dimethyl(3,3-dimethylallyl)amine from (11k) together with a small quantity of a crystalline product identified as cyanuric acid (28). A similar result was obtained from the *N*-benzyl-*N*-formylammonioamidate (23c). These ammonioamidates evidently undergo thermolysis of the $\overset{+}{N}-\overset{-}{N}$ bond to give HCO$\ddot{N}$ which rearranges and trimerises[4] to give the product (28). Similar fragmentation has been reported for ammonium ylides under certain conditions, particularly those unable to undergo [1,2] or [3,2] rearrange-



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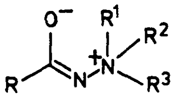

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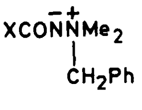
ment, and is most common for ammonioamidates (29) in which the ylide adopts a cisoid conformation and the groups R^1, R^2, and R^3 are unable to migrate readily.[5] The reaction is formally similar to the Curtius, Hofmann, Schmidt, and Lössen rearrangements.[24]

The [1,3] rearrangement of the 1-phenylallylhydrazines (14; R^1 = Ph, R^2 = H) took place at reaction temperatures significantly higher than those required for the [1,2] and [3,2] rearrangements of the corresponding cinnamylammonioamidates (11). This is in accord with earlier work [9] in which it was shown that the formation of the [1,2] rearrangement product does not involve consecutive [3,2] and [1,3] rearrangements. The [1,3] rearrangement with geometrically reasonable s,r geometry is not a symmetry allowed process [23,25] and it is probable that the [1,3] rearrangement (14; R^1 = Ph, R^2 = H) ⟶ (13; R^1 = Ph, R^2 = H) involves a radical pair intermediate (15; R^1 = Ph, R^2 = H) similar to that involved in the [1,2] rearrangement of the ylide. It was, therefore, of interest to determine whether the formation of this radical pair from the hydrazine derivatives (13; R^1 = Ph, R^2 = H) showed sensitivity to solvent and substituent effects similar to that shown by the formation of the radical pair from the ylide. The results (Table 2) of a brief investigation of these effects show that the [1,3] rearrangement is not sensitive to either substituent or solvent effects.

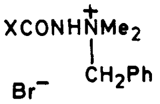
We conclude from the investigation reported in this paper, that the sigmatropic rearrangement reactions of ammonioamidates resemble those of the ammonium ylides. However, in a number of cases for allylic systems the [1,2] rearrangement, involving a radical mechanism, competes significantly with the [3,2] rearrangement. The allylic ammonioamidates are readily isolated, in contrast with allylic ammonium ylides which rearrange at low temperatures.[13] This increased stability of the ammonioamidates is consistent with the presence of an additional hetero-atom in the anionic system and the effects of substituents upon the rates of rearrangement are in accord with this view. The ammonioamidate system undergoes homolysis to give a radical pair which, in contrast with the radical pair from ammonium ylides,[1] undergoes recombination to give the original ylide in addition to rearrangement products. Nevertheless, in solvents of high viscosity (glycerol at 80 °C and ethylene glycol at 55 °C) radical pair recombination is fast compared with diffusion from the solvent cage and may be essentially intramolecular. However, in solvents of low viscosity (methyl cyanide at 80 °C and butanol at 80 °C) the [1,2] rearrangement shows considerable intermolecularity and the [3,2] rearrangement shows apparent intermolecularity as a result of free radical recombination to give the original ammonioamidate. These conclusions are in accord with the observation of CIDNP in reactions of allylic ammonioamidates carried out under rather extreme conditions.[9,12]

The similar response of competing [1,2] and [3,2] rearrangement modes to changes of solvent and substituents indicates that the transition states for both processes are rather similar, although that for [1,2] rearrangement more closely resembles the starting ylide. This is not inconsistent with the belief that the [1,2] rearrangement involves a radical pair mechanism and that the [3,2] rearrangement involves a concerted mechanism since the transition state for each process may formally be derived from an interacting radical pair. In contrast, the rates of the [1,3] rearrangement of the 1-phenylallylhydrazines (14; R^1 = Ph, R^2 = H) are rather insensitive to substituent and solvent effects and in this case the transition state for the formation of a radical pair, similar to that involved in the [1,2] rearrangement, must resemble the acylhydrazine system.



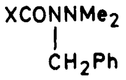
$\mathrm{XCO\overset{-}{N}\underset{CH_2Ph}{\overset{+}{N}}Me_2}$

(23)



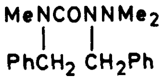
$\mathrm{XCONH\underset{CH_2Ph}{\overset{+}{N}}Me_2 \quad Br^-}$

(24)



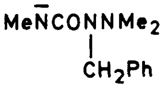
$\mathrm{XCO\underset{CH_2Ph}{N}NMe_2}$

(25)



$\mathrm{Me\underset{PhCH_2}{N}CO\underset{CH_2Ph}{N}NMe_2}$

(26)



$\mathrm{Me\overset{-}{N}CO\underset{CH_2Ph}{N}NMe_2}$

(27)

In (23)—(25): a, X = OEt; b, X = MeNH; c, X = H

Experimental

General Methods.—See Part 1 of this series.[13] N.m.r. spectra were recorded using a Varian HA100 spectrometer and chemical shifts are given in p.p.m. (δ) relative to an internal $SiMe_4$ standard. Ether refers to diethyl ether.

Quaternary Salts (10) *and* (12).—The following procedure is typical; the other quaternary salts listed were prepared by a similar method from the appropriate hydrazine derivative and cinnamyl, 3,3-dimethylallyl, allyl, or benzyl bromide.

1-*Cinnamyl*-1,4-*dimethyl*-3-*oxopyrazolidinium bromide* (10c). A solution of cinnamyl bromide (5.91 g) in methyl cyanide (10 ml) was added dropwise to a stirred solution of 1,4-dimethylpyrazolidin-3-one [26] (3.42 g) in methyl cyanide (10 ml). After 1 h the solid which separated was collected and crystallised from ethanol–ether to give the *salt* (10c) (8.70 g, 96%) as a mixture of diastereoisomers, m.p. 174—175 °C (Found: C, 54.0; H, 6.4; Br, 25.6; N, 9.0. $C_{14}BrN_2O$ requires C, 54.0; H, 6.1; Br, 25.7; N, 9.0%); $\nu_{max.}$ (KBr) 3 440, 1 735, and 1 650 cm^{-1}; δ[$(CD_3)_2CO$ + D_2O] 7.66—7.30 (m, 5 aryl H), 7.13 (d, *J* 16 Hz, PhC*H*=CH), 6.59 (m, $\overset{+}{N}CH_2CH$=CH), 5.06—4.54 (m, C*H*CH_3 + $\overset{+}{N}CH_2$CH=CH), 3.80 (s, $\overset{+}{N}Me$), 4.20—3.10 (m, CH_2), and 1.30 and 1.28 (d, *J* 7 Hz, CHCH_3 of two diastereoisomers).

1,4-*Dimethyl*-1-(3,3-*dimethylallyl*)-3-*oxopyrazolidinium bromide* (10d). This was obtained as a mixture of diastereoisomers (86%), m.p. 145—147 °C (Found: C, 45.5; H, 7.4; Br, 30.45; N, 10.8. $C_{10}H_{19}BrN_2O$ requires C, 45.6; H, 7.2; Br, 30.4; N, 10.65%); $\nu_{max.}$ (KBr) 3 440, 1 740, and 1 675 cm^{-1}; δ[$(CD_3)_3CO$ + D_2O] 5.50 (t, *J* 6 Hz, CH_2CH=CMe_2), 4.87—4.40 (m, $\overset{+}{N}CH_2$CH=CMe_2 + C*H*CH_3), 4.07—3.14 (m, CH_2), 3.68 and 3.66 (s, $\overset{+}{N}Me$ of two diastereoisomers), 1.85 (s, C=CMe_2), and 1.27 and 1.25 (d, *J* 7 Hz, CHCH_3 of two diastereoisomers).

1-*Allyl*-1,4-*dimethyl*-3-*oxopyrazolidinium bromide* (10b). This was obtained as a mixture of diastereoisomers (90%), m.p. 139—141 °C (Found: C, 40.8; H, 6.2; Br, 33.9; N, 12.1. $C_8H_{15}BrN_2O$ requires C, 40.85; H, 6.4; Br, 34.05; N, 11.9%); $\nu_{max.}$ (Nujol) 3 430, and 1 735 cm^{-1}; δ[$(CD_3)_2CO$ + D_2O] 6.30—5.70 (m, CH=CH_2), 4.96—4.50 (m, $\overset{+}{N}CH_2$CH=CH_2 + CHCH_3), 4.10—3.00 (m, CH_2), 3.71 and 3.68 (s, $\overset{+}{N}Me$ of two diastereoisomers), and 1.31 and 1.29 (d, *J* 7 Hz, CHCH_3 of two diastereoisomers).

1-*Benzoyl*-2-*cinnamyl*-2,2-*dimethylhydrazinium bromide*

(12a). This was obtained (87%) as crystals, m.p. 159—160 °C (Found: C, 59.85; H, 5.6; Br, 22.1; N, 7.8. $C_{18}H_{21}BrN_2O$ requires C, 59.8; H, 5.8; Br, 22.1; N, 7.8%); $\nu_{max.}$ (KBr) 3 420, 3 110, 1 700, 1 650, and 1 600 cm^{-1}; $\delta[(CD_3)_2CO + D_2O]$ 7.98—7.30 (m, 10 aryl H), ABX_2 system, δ_A 7.10, δ_B 6.57, δ_X 5.08 [J_{AB} 16, J_{BX} 7.5 Hz, $\overset{+}{N}C(H_X)_2CH_B{=}CH_A$], and 3.98 (s, $\overset{+}{N}Me_2$).

1-*Acetyl*-2-*cinnamyl*-2,2-*dimethylhydrazinium bromide* (12b). This was obtained (83%) as crystals, m.p. 122—123 °C (Found: C, 52.0; H, 6.4; Br, 26.45; N, 9.4. $C_{13}H_{19}BrN_2O$ requires C, 52.1; H, 6.35; Br, 26.7; N, 9.4%); $\nu_{max.}$ (KBr) 3 120, 1 712, and 1 700 cm^{-1}; $\delta[(CD_3)_2CO + D_2O]$ 7.32 (m, 5 aryl H), ABX_2 system, δ_A 7.02, δ_B 6.28, δ_X 5.02 [J_{AB} 15, J_{BX} 7 Hz, $\overset{+}{N}C(H_X)_2CH_B{=}CH_A$], 3.81 (s, $\overset{+}{N}Me_2$), and 2.18 (s, $COCH_3$).

1-*Acetyl*-2-(3,3-*dimethylallyl*)-2,2-*dimethylhydrazinium bromide* (12c). This was obtained (88%) as hygroscopic plates (Found: C, 42.8; H, 7.7; Br, 31.6; N, 11.4. $C_9H_{19}BrN_2O$ requires C, 43.0; H, 7.6; Br, 31.9; N, 11.15%); $\nu_{max.}$ (KBr) 3 120 and 1 705 cm^{-1}; $\delta[(CD_3)_2CO + D_2O]$ AX_2 system, δ_A 5.46, δ_X 4.72 [J_{AX} 8.0 Hz, $\overset{+}{N}C(H_X)_2CH_A$], 3.70 (s, $\overset{+}{N}Me_2$), 2.09 (s, $COCH_3$), 1.89 (s, C=CMe), and 1.83 (s, C=CMe).

1-*Cinnamyl*-2-*ethoxycarbonyl*-1,1-*dimethylhydrazinium bromide* (12d). This was obtained (93%) as crystals, m.p. 142—143 °C (Found: C, 51.05; H, 6.2; Br, 24.15; N, 8.35. $C_{14}H_{21}BrN_2O_2$ requires C, 51.1; H, 6.4; Br, 24.3; N, 8.5%); $\nu_{max.}$ (KBr) 3 085, 1 735, and 1 655 cm^{-1}; $\delta[(CD_3)_2CO + D_2O]$ 7.70—7.30 (m, 5 aryl H), ABX_2 system, δ_A 7.08, δ_B 6.52, δ_X 4.90 [J_{AB} 15.5, J_{BX} 5.5 Hz, $\overset{+}{N}C(H_X)_2CH_B{=}CH_A$], A_2X_3 system, δ_A 4.08, δ_X 1.24 [J_{AX} 7 Hz, $OC(H_A)_2C(H_X)_3$], and 3.80 (s, $\overset{+}{N}Me_2$).

2-*Ethoxycarbonyl*-1,1-*dimethyl*-1(3,3-*dimethylallyl*)*hydrazinium bromide* (12e). This was obtained (80%) as crystals, m.p. 91—93 °C (Found: C, 42.5; H, 7.6; Br, 28.35; N, 10.2. $C_{10}H_{21}BrN_2O_2$ requires C, 42.7; H, 7.5; Br, 28.5; N, 10.0%); $\nu_{max.}$ (KBr) 3 445—3 395, 1 740, and 1 665 cm^{-1}; $\delta[(CD_3)_2CO + D_2O]$ AX_2 system, δ_A 5.49, δ_X 4.70 [J_{AX} 8.0 Hz, $\overset{+}{N}C(H_X)_2CH_A$], A_2X_3 system, δ_A 4.26, δ_X 1.27 [J_{AX} 7.5 Hz, $OC(H_A)_2C(H_X)_3$], 3.71 (s, $\overset{+}{N}Me_2$), 1.90 (s, C=CMe), and 1.84 (s, C=CMe).

1-*Allyl*-2-*ethoxycarbonyl*-1,1-*dimethylhydrazinium bromide* (12f). This was obtained (85%) as very hygroscopic crystals (Found: C, 37.6; H, 7.0; Br, 32.1; N, 11.3. $C_8H_{17}BrN_2O_2$ requires, C, 37.9; H, 6.7; Br, 31.8; N, 11.1%); $\nu_{max.}$ (Nujol) 3 400, 1 740, and 1 630 cm^{-1}; $\delta[(CD_3)_2CO + D_2O]$ $ABCX_2$ system, δ_A 6.14, δ_B 5.76, δ_C 5.74, δ_X 4.72 [J_{AB} 17, J_{AC} 9, J_{AX} 6.5 Hz, $C(H_X)_2CH_A{=}CH_BH_C$], A_2X_3 system, δ_A 4.20, δ_X 1.28 [J_{AX} 7 Hz, $OC(H_A)_2C(H_X)_3$], and 3.74 (s, $\overset{+}{N}Me_2$).

1-*Benzyl*-2-*ethoxycarbonyl*-1,1-*dimethylhydrazinium bromide* (24a). This was obtained (91%) as crystals, m.p. 115—116 °C (Found: C, 47.6; H, 6.5; Br, 26.4; N, 9.2. $C_{12}H_{19}BrN_2O_2$ requires C, 47.5; H, 6.3; Br, 26.4; N, 9.2%); $\nu_{max.}$ (KBr) 3 100 and 1 730 cm^{-1}; $\delta[(CD_3)_2CO + D_2O]$ 7.70—7.40 (m, 5 aryl H), 5.31 (s, CH_2Ph), A_2X_3 systems, δ_A 4.29, δ_X 1.29 [J_{AX} 7 Hz, $OC(H_A)_2C(H_X)_3$], and 3.77 (s, $\overset{+}{N}Me_2$).

1-*Cinnamyl*-1,1-*dimethyl*-2-*methylcarbamoylhydrazinium bromide* (12g). This was obtained (86%) as plates, m.p. 130—131 °C (Found: C, 50.0; H, 6.55; Br, 25.65; N, 13.5. $C_{13}H_{20}BrN_3O$ requires C, 49.7; H, 6.4; Br, 25.5; N, 13.4%); $\nu_{max.}$ (KBr) 3 270, 3 140, and 1 710 cm^{-1}; $\delta[(CD_3)_2CO + D_2O]$ 7.76—7.30 (m, 5 aryl H), ABX_2 system, δ_A 7.08, δ_B 6.50, δ_X 4.86 [J_{AB} 15.5, J_{BX} 7.5 Hz, $\overset{+}{N}C(H_X)_2CH_B{=}CH_A$], 3.73 (s, $\overset{+}{N}Me_2$), and 2.72 (s, NMe).

1,1-*Dimethyl*-1-(3,3-*dimethylallyl*)-2-*methylcarbamoylhydrazinium bromide* (12h). This was obtained (80%) as an oil; δ, AX_2 system, δ_A 5.48, δ_X 4.64 [J_{AX} 8 Hz, $\overset{+}{N}C(H_X)_2CH_A$], 3.64 (s, $\overset{+}{N}Me_2$), 2.74 (s, NMe), 1.91 (s, C=CMe), and 1.85 (s, C=CMe).

1-*Allyl*-1,1-*dimethyl*-2-*methylcarbamoylhydrazinium bromide* (12i). This was obtained (84%) as crystals, m.p. 124—125 °C (Found: C, 35.4; H, 6.9; Br, 33.7; N, 17.9. $C_7H_{16}BrN_3O$ requires C, 35.3; H, 6.7; Br, 33.6; N, 17.65%); $\nu_{max.}$ (KBr) 3 260, 3 150, and 1 710 cm^{-1}; $\delta[(CD_3)_2CO + D_2O]$, $ABCX_2$ system, δ_A 6.16, δ_B 5.80, δ_C 5.66, δ_X 4.72 [J_{AB} 16, J_{AC} 9, J_{AX} 7 Hz, $\overset{+}{N}C(H_X)_2CH_A{=}CH_BH_C$], 3.70 (s, $\overset{+}{N}Me_2$), and 2.72 (s, NMe).

1-*Cinnamyl*-2-*formyl*-1,1-*dimethylhydrazinium bromide* (12j). This was obtained (91%) as crystals, m.p. 130—132 °C (Found: C, 50.5; H, 6.0; Br, 28.3; N, 9.6. $C_{12}H_{17}BrN_2O$ requires C, 50.5; H, 6.0; Br, 28.1; N, 9.8%); $\nu_{max.}$ (KBr) 1 705 cm^{-1}; $\delta[(CD_3)_2CO + D_2O]$ 8.19 (s, NCHO), 7.60—7.27 (m, 5 aryl H), ABX_2 system, δ_A 7.04, δ_B 6.46, δ_X 4.84 [J_{AB} 15.5, J_{BX} 7.5 Hz, $\overset{+}{N}C(H_X)_2CH_B{=}CH_A$], and 3.74 (s, $\overset{+}{N}Me_2$).

1-*Benzyl*-1,1-*dimethyl*-2-*methylcarbamoylhydrazinium bromide* (24b). This was obtained (85%) as crystals, m.p. 101—103 °C (Found: C, 45.7; H, 6.2; Br, 27.9; N, 14.8. $C_{11}H_{18}BrN_3O$ requires C, 45.8; H, 6.25; Br, 27.8; N, 14.6%), $\nu_{max.}$ (Nujol) 3 230, 3 150, and 1 710 cm^{-1}; $\delta[(CD_3)_2CO + D_2O]$ 7.70—7.46 (m, 5 aryl H), 5.29 (s, $\overset{+}{N}CH_2$), 3.68 (s, $\overset{+}{N}Me_2$), and 2.75 (s, NMe).

2-*Formyl*-1,1-*dimethyl*-1-(3,3-*dimethylallyl*)*hydrazinium bromide* (12k). This was obtained (87%) as hygroscopic needles, m.p. 87—88 °C (Found: C, 39.2; H, 7.1; Br, 32.9; N, 11.6. $C_8H_{17}BrN_2O.\frac{1}{2}H_2O$ requires C, 39.2; H, 7.35; Br, 32.7; N, 11.4%); $\nu_{max.}$ (Nujol) 3 450 and 1 710 cm^{-1}; $\delta[(CD_3)_2CO + D_2O]$ 8.30 (s, NCHO), AX_2 system, δ_A 5.58, δ_X 4.81 [J_{AX} 8 Hz, $\overset{+}{N}C(H_X)_2CH_A$], 3.81 (s, $\overset{+}{N}Me_2$), and 1.92 (s, CMe_2).

1-*Benzyl*-2-*formyl*-1,1-*dimethylhydrazinium bromide* (24c). This was obtained (93%) as crystals, m.p. 117—118 °C (Found: C, 46.35; H, 5.8; Br, 30.9; N, 10.7. $C_{10}H_{15}BrN_2O$ requires C, 46.3; H, 5.8; Br, 30.9; N, 10.8%); $\nu_{max.}$ 1 700 cm^{-1}; $\delta[(CD_3)_2CO + D_2O]$ 8.29 (s, NCHO), 7.70—7.47 (m, 5 aryl H), 5.36 (s, $\overset{+}{N}CH_2$), and 3.82 (s, $\overset{+}{N}Me_2$).

1-*Cinnamyl*-1,1-*dimethyl*-2-*phenylcarbamoylhydrazinium bromide* (12l). This was obtained (90%) as crystals, m.p. 121—122 °C (Found: C, 57.2; H, 5.9; Br, 21.2; N, 11.4. $C_{18}H_{22}BrN_3O$ requires C, 57.4; H, 5.9; Br, 21.2; N, 11.2%); $\nu_{max.}$ 3 260, 3 200, 3 120, 1 722, and 1 605 cm^{-1}; $\delta[(CD_3)_2CO]$ 7.70—7.16 (m, 10 aryl H), ABX_2 system, δ_A 7.10, δ_B 6.66, δ_X 4.90 [J_{AB} 16, J_{BX} 8 Hz, $\overset{+}{N}C(H_X)_2CH_B{=}CH_A$], and 3.83 (s, $\overset{+}{N}Me_2$).

1-[1,1-$^2H_2$]*Cinnamyl*-1,1-*dimethyl*-2-([$^2H_5$]*phenylcarbamoyl*)-*hydrazinium bromide* (22). This was obtained† (88%) as crystals, m.p. 122 °C (Found: C, 56.3; H *, 6.0; Br, 20.9; N, 11.0. $C_{18}H_{15}D_7BrN_3O$ requires C, 56.4; H *, 5.8; Br, 20.9; N, 11.0%), $\delta(CD_3OD)$ 7.60—7.24 (m, 5 aryl H), AB system, δ_A 7.01, δ_B 6.43 (J_{AB} 16 Hz, $\overset{+}{N}CD_2CH_B{=}CH_A$), and 3.67 (s, $\overset{+}{N}Me_2$).

Ammonioamidates (7) and (11). ‡—The following procedures are typical.

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† For preparation of [1,1-$^2H_2$]cinnamyl bromide see ref. 27.

* For this and other deuteriated compounds the value for H refers to the combined D and H content estimated as H.

‡ These compounds are systematically named as ammonio-amidides and -ureides.

Method A. A slight excess of saturated methanolic sodium methoxide was slowly added to a solution of the quaternary salt (10 mmol) in methanol (25 ml). The mixture was kept at 0 °C for 12 h, the solvent evaporated, the residual solid extracted with dichloromethane, and the extract evaporated to give the ylide.

Method B. A solution of the salt (10 mmol) in water (10 ml) was treated with a slight excess of 10% aqueous sodium hydroxide. The solution was kept at 0 °C for 12 h, extracted with dichloromethane, and the extract dried and evaporated to give the ylide.

1-*Cinnamyl*-1,4-*dimethyl*-3-*oxopyrazolidin*-1-*ium*-2-*ide*) (7c). This was prepared by method A as a hygroscopic white solid (86%) (Found: M^+, 230.1415. $C_{14}H_{18}N_2O$ requires *M*, 230.1415); $\nu_{max.}$ 1 605 cm^{-1}; δ 7.42—7.23 (m, 5 aryl H), 6.79 and 6.76 (d, *J* 16 Hz, CH=C*H*Ph of two diastereoisomers), 6.56—6.14 (m, $\overset{+}{N}$CH$_2$C*H*=CH), 4.20—3.73 (m, $\overset{+}{N}$C*H*$_2$-CH=CH and C*H*CH$_3$), 3.19 and 3.13 (s, $\overset{+}{N}$Me of two diastereoisomers), 3.10—2.70 (m, CH$_2$), and 1.27 and 1.25 (d, *J* 7 Hz, CHC*H*$_3$ of two diastereoisomers).

1,4-*Dimethyl*-1-(3,3-*dimethylallyl*)-3-*oxopyrazolidin*-1-*ium*-2-*ide* (7d). This was prepared by method A as a hygroscopic white solid (87%) (Found: M^+, 182.1424. $C_{10}H_{18}N_2O$ requires *M*, 182.1419); $\nu_{max.}$ 1 605 cm^{-1}; δ 5.45br (m, CH$_2$-C*H*CMe$_2$), 4.20—3.78 (m, $\overset{+}{N}$C*H*$_2$CH=CMe$_2$ + C*H*CH$_3$), 3.04—2.70 (m, CH$_2$), 3.11 and 3.06 (s, $\overset{+}{N}$Me of two diastereoisomers), 1.84 (s, C=CCH$_3$), 1.77 (s, C=CCH$_3$), and 1.27 and 1.24 (d, *J* 7 Hz, CHC*H*$_3$ of two diastereoisomers).

1-*Allyl*-1,4-*dimethyl*-3-*oxopyrazolidin*-1-*ium*-2-*ide* (7b). This was prepared by method A as a white solid (92%) (Found: M^+, 154.1109. $C_8H_{14}N_2O$ requires *M*, 154.1106); $\nu_{max.}$ 1 605 cm^{-1}; δ 6.20—5.85 (m, CH$_2$C*H*=CH$_2$), 5.66—5.40 (CH=C*H*$_2$), 4.28—3.70 (m, $\overset{+}{N}$C*H*$_2$CH=CH$_2$), 3.47—2.76 (m, CH$_2$), 3.15 and 3.09 (s, $\overset{+}{N}$Me of two diastereoisomers), and 1.25 and 1.23 (d, *J* 7 Hz, CHC*H*$_3$ of two diastereoisomers).

N-[*Cinnamyl*(*dimethyl*)*ammonio*]*benzamidide* (11a). This was prepared by method B (93%); recrystallisation from dichloromethane–hexane gave crystals, m.p. 106—107 °C (Found: C, 77.3; H, 7.4; N, 10.3. $C_{10}H_{20}N_2O$ requires C, 77.1; H, 7.1; N, 10.0%); $\nu_{max.}$ 1 595 cm^{-1}; δ 8.10—7.94 (m, 2 aryl H), 7.46—7.20 (m, 8 aryl H), ABX$_2$ system, δ$_A$ 6.73, δ$_B$ 6.35, δ$_X$ 4.50 [J_{AB} 16, J_{BX} 7 Hz, $\overset{+}{N}C(H_X)_2CH_B{=}CH_A$], and 3.35 (s, $\overset{+}{N}$Me$_2$).

N-[*Cinnamyl*(*dimethyl*)*ammonio*]*acetamidide* (11b). This was prepared by method B (82%) as a hygroscopic, crystalline solid (Found: M^+, 218.1423. $C_{13}H_{18}N_2O$ requires *M*, 218.1419); $\nu_{max.}$ 1 580 cm^{-1}; δ 7.35 (m, 5 aryl H), ABX$_2$ system, δ$_A$ 6.82, δ$_B$ 6.28, δ$_X$ 4.85 [J_{AB} 15, J_{BX} 7 Hz,] $\overset{+}{N}C(H_X)_2$-$CH_B{=}CH_A$, 3.65 (s, $\overset{+}{N}$Me$_2$), and 2.11 (s, COCH$_3$).

N-[3,3-*Dimethylallyl*(*dimethyl*)*ammonio*]*acetamidide* (11c). This was prepared by method B (84%) as a hygroscopic solid (Found: M^+, 170.1420. $C_9H_{18}N_2O$ requires *M*, 170.1419); $\nu_{max.}$ 1 575 cm^{-1}; δ, AX$_2$ system, δ$_A$ 5.38, δ$_X$ 4.32 [J_{AX} 8 Hz, $\overset{+}{N}C(H_X)_2CH_A$], 3.19 (s, $\overset{+}{N}$Me$_2$), 1.82 (s, C=CMe$_2$), and 1.79 (s, COCH$_3$).

N-[*Cinnamyl*(*dimethyl*)*ammonio*]*ethoxyformamidide* (11d). This was prepared by method B (89%) as an oil (Found: M^+, 248.1525. $C_{14}H_{20}N_2O_2$ requires *M*, 248.1525); $\nu_{max.}$ 1 640 cm^{-1}; δ 7.40—7.24 (m, 5 aryl H), ABX$_2$ system, δ$_A$ 6.72, δ$_B$ 6.32, δ$_X$ 4.37 [J_{AB} 15.5, J_{BX} 7.5 Hz, $\overset{+}{N}C(H_X)_2CH_B{=}CH_A$], A$_2X_3$ system, δ$_A$ 3.99, δ$_X$ 1.23 [J_{AX} 7.0 Hz, $OC(H_A)_2C(H_X)_3$], and 3.26 (s, $\overset{+}{N}$Me$_2$).

N-[3,3-*Dimethylallyl*(*dimethyl*)*ammonio*]*ethoxyformamidide* (11e). This was prepared by method B (90%) as an oil (Found: M^+, 200.1516. $C_{10}H_{20}N_2O_2$ requires *M*, 200.1524); $\nu_{max.}$ 1 640 cm^{-1}; δ, AX$_2$ system, δ$_A$ 5.40, δ$_X$ 4.22 [J_{AX} 8.0 Hz, $\overset{+}{N}C(H_X)_2CH_A$], A$_2X_3$ system, δ$_A$ 3.96, δ$_X$ 1.20 [J_{AX} 7.0 Hz, $OC(H_A)_2C(H_X)_3$], 3.18 (s, $\overset{+}{N}$Me$_2$), 1.82 (s, C=CMe), and 1.77 (s, C=CMe).

N-[*Allyl*(*dimethyl*)*ammonio*]*ethoxyformamidide* (11f). This was prepared by method B (87%) as an oil (Found: M^+, 172.1212. $C_8H_{16}N_2O_2$ requires *M*, 172.1212); $\nu_{max.}$ 1 640 cm^{-1}; δ AMNX$_2$ system, δ$_A$ 6.05, δ$_M$ 5.52, δ$_N$ 5.46, δ$_X$ 4.22 [J_{AM} 11, J_{AN} 16, J_{AX} 7 Hz, $\overset{+}{N}C(H_X)_2CH_A{=}CH_MH_N$], A$_2X_3$ system, δ$_A$ 3.96, δ$_X$ 1.20 [J_{AX} 7 Hz, $OC(H_A)_2C(H_X)_3$], and 3.22 (s, $\overset{+}{N}$Me$_2$).

N-[*Benzyl*(*dimethyl*)*ammonio*]*ethoxyformamidide* (23a). This was prepared by method B (94%); purification by recrystallisation from dichloromethane–hexane gave hygroscopic crystals, m.p. 118—119 °C (Found: C, 64.65; H, 8.1; N, 12.8. $C_{12}H_8N_2O_2$ requires C, 64.9; H, 8.1; N, 12.6%); $\nu_{max.}$ 1 640 cm^{-1}; δ 7.39 (m, 5 aryl H), 4.29 (s, $\overset{+}{N}$CH$_2$), A$_2$X$_3$ system, δ$_A$ 4.03, δ$_X$ 1.26 [J_{AX} 7 Hz, $OC(H_A)_2C(H_X)_3$], and 3.18 (s, $\overset{+}{N}$Me$_2$).

N-[*Cinnamyl*(*dimethyl*)*ammonio*]*methylureide* (11g). This was prepared by method B (82%); recrystallisation from dichloromethane–hexane gave plates, m.p. 122—123 °C (Found: C, 67.2; H, 8.0; N, 18.0. $C_{13}H_{19}N_3O$ requires C, 67.0; H, 8.15; N, 18.0%); $\nu_{max.}$ 1 590 cm^{-1}; δ 7.44—7.28 (m, 5 aryl H), ABX$_2$ system, δ$_A$ 6.73, δ$_B$ 6.34, δ$_X$ 4.46 [J_{AB} 16.0, J_{BX} 7.0 Hz, $\overset{+}{N}C(H_X)_2CH_B{=}CH_A$], 3.28 (s, $\overset{+}{N}$Me$_2$), and 2.70 (d, *J* 5.0 Hz, NH*Me*).

N-[3,3-*Dimethylallyl*(*dimethyl*)*ammonio*]*methylureide* (11h). This was prepared by method B (76%) as hygroscopic crystals (Found: C, 55.4; H, 10.2; N, 21.5%. M^+, 185.1526. $C_9H_{19}N_3O\cdot0.5H_2O$ requires C, 55.6; H, 10.4; N, 21.6%. $C_9H_{19}N_3O$ requires *M*, 185.1528); $\nu_{max.}$ 1 590 cm^{-1}; δ, AX$_2$ system, δ$_A$ 5.40, δ$_X$ 4.30 [J_{AX} 8.0 Hz, $\overset{+}{N}C(H_X)_2CH_A$], 3.19 (s, $\overset{+}{N}$Me$_2$), 2.66 (d, *J* 5.0 Hz, NH*Me*), 1.81 (s, C=CMe), and 1.76 (s, C=CMe).

N-[*Allyl*(*dimethyl*)*ammonio*]*methylureide* (11i). This was prepared by method B (70%) as hygroscopic crystals (Found: C, 53.6; H, 9.8; N, 27.0. $C_7H_{15}N_3O$ requires C, 53.5; H, 9.55; N, 26.8%); $\nu_{max.}$ 1 580 cm^{-1}; δ, AMNX$_2$ system, δ$_A$ 6.06, δ$_M$ 5.54, δ$_N$ 5.40, δ$_X$ 4.32 [J_{AM} 9, J_{AN} 18, J_{AX} 7 Hz, $\overset{+}{N}C(H_X)_2CH_A{=}CH_MH_N$], 3.28 (s, $\overset{+}{N}$Me$_2$), and 2.66 (s, NH*Me*).

N-[*Benzyl*(*dimethyl*)*ammonio*]*methylureide* (23b). This was prepared by method B (87%) as hygroscopic crystals, m.p. 137—139 °C (Found: C, 63.5; H, 8.5; N, 20.5. $C_{11}H_{17}N_3O$ requires C, 63.8; H, 8.2; N, 20.3%); $\nu_{max.}$ 1 590 cm^{-1}; δ 7.40 (m, 5 aryl H), 5.91 (s, $\overset{+}{N}$CH$_2$), 3.22 (s, $\overset{+}{N}$Me$_2$), and 2.72 (d, *J* 5 Hz, NHMe).

N-[*Cinnamyl*(*dimethyl*)*ammonio*]*formamidide* (11j). This was prepared by method B as an oil (80%) (Found: M^+, 204.1275. $C_8H_{16}N_2O$ requires *M*, 204.1263); $\nu_{max.}$ 1 602 cm^{-1}; δ 7.73 (s, NCHO), 7.60—7.25 (m, 5 aryl H), ABX$_2$ system, δ$_A$ 7.76, δ$_B$ 6.33, δ$_X$ 4.43 [J_{AB} 16, J_{BX} 7 Hz, $\overset{+}{N}C(H_X)_2CH_B{=}CH_A$], and 3.32 (s, $\overset{+}{N}$Me$_2$).

N-[3,3-*Dimethylallyl*(*dimethyl*)*ammonio*]*formamidide* (11k). This was prepared by method B (80%) as an oil (Found: *M*, 156.1259. $C_8H_{16}N_2O$ requires *M*, 156.1263); $\nu_{max.}$ 1 600 cm^{-1}; δ 7.70 (s, NCHO), AX$_2$ system, δ$_A$ 5.46, δ$_X$ 4.34 [J_{AX} 7.5 Hz, $\overset{+}{N}C(H_X)_2CH_A$], 3.28 (s, $\overset{+}{N}$Me$_2$), 1.77 (s, C=CMe), and 1.70 (s, C=CMe).

N-[*Benzyl(dimethyl)ammonio*]*formamidide* (23c). This was prepared by method B (87%); recrystallisation from dichloromethane-hexane gave hygroscopic needles (Found: C, 67.3; H, 7.8; N, 15.95. $C_{10}H_{14}N_2O$ requires C, 67.4; H, 7.9; N, 15.7%); $\nu_{max.}$ 1 600 cm^{-1}; δ 7.75 (d, NCHO), 7.42 (m, 5 aryl H), 4.91 (s, $\overset{+}{N}CH_2$), and 3.26 (s, $\overset{+}{N}Me_2$).

N-[*Cinnamyl(dimethyl)ammonio*]*phenylureide* (11l). This was prepared by method B (91%) as crystals, m.p. 138—139 °C (Found: C, 73.0; H, 7.2; N, 14.5. $C_{18}H_{21}N_3O$ requires C, 73.2; H, 7.1; N, 14.2%); $\nu_{max.}$ 1 620 cm^{-1}; δ 7.46—6.72 (m, 10 aryl H), ABX$_2$ system, δ_A 6.70, δ_B 6.32, δ_X 4.42 [J_{AB} 16, J_{BX} 8 Hz, $\overset{+}{N}C(H_X)_2CH_B{=}CH_A$], and 3.28 (s, $\overset{+}{N}Me_2$).

N-{[1,1-$^2H_2$]*Cinnamyl(dimethyl)ammonio*}[$^2H_5$]*phenylureide* (20). This was prepared by method B (92%) as crystals, m.p. 139 °C (Found: C, 71.4; H*, 7.15; N, 13.7. $C_{18}H_{14}D_7N_3O$ requires C, 71.5; H *, 6.95; N, 13.9%); δ 7.50—7.20 (m, 5 aryl *H*), AB system, δ_A 6.70, δ_B 6.29 (J_{AB} 16 Hz, $\overset{+}{N}CD_2CH_B{=}CH_A$), and 3.27 (s, $\overset{+}{N}Me_2$).

Thermal Rearrangements of Ammonioamidates.—The ammonioamidate (7), (11), or (23) was heated under reflux in dry benzene, toluene, or xylene until t.l.c. examination of the reaction products indicated that the reaction was complete. The solvent was evaporated and reaction products separated by t.l.c. (light petroleum–ethyl acetate). Details of reaction products are given below and summarised in Table 1.

1-*Cinnamyl*-1,4-*dimethyl*-3-*oxopyrazolidin*-1-*ium*-2-*ide* (7c). This substance when heated (benzene, 6 h) gave two products. (i) 2-*Cinnamyl*-1,4-*dimethylpyrazolidin*-3-*one* (9c) (18%) was obtained as a yellow oil (Found: M^+, 230.1415. $C_{14}H_{18}N_2O$ requires M, 230.1419); $\nu_{max.}$ 1 680 cm^{-1}; δ 7.40—7.14 (m, 5 aryl H), ABXY system, δ_A, 6.56, δ_B 6.12, δ_X and δ_Y 4.40—3.90 (J_{AB} 16, J_{BX} 6, J_{BY} 6 Hz, $CH_XH_YCH_B{=}CH_APh$), 3.44—3.16 (m, C*H*CH$_3$), 3.00—2.74 (m, CH$_2$), 2.58 (s, NMe), and 1.19 (d, *J* 6 Hz, CHC*H*$_3$).

(ii) 1,4-*Dimethyl*-2-(1-*phenylallyl*)*pyrazolidin*-3-*one* (9e) (82%) was obtained as a yellow oil (Found: M^+, 230.1415. $C_{14}H_{18}N_2O$ requires M, 230.1419); $\nu_{max.}$ 1 695 cm^{-1}; diastereoisomer A, δ 7.45—7.20 (m, 5 aryl H), ABCD system, δ_A 6.32, δ_B 5.70, δ_C 5.26, δ_D 5.22 (J_{AB} 7, J_{AC} 10.5, J_{AD} 16.5 Hz, $CH_B{-}CH_A{=}CH_CH_D$), 3.30—2.80 (m, C*H*$_2$ + C*H*CH$_3$), 2.18 (s, NMe), and 1.14 (d, *J* 6 Hz, CHC*H*$_3$); diastereoisomer B, δ 7.45—7.20 (m, 5 aryl H), ABCD system, δ_A 6.27, δ_B 5.62, δ_C 5.26, δ_D 5.22 (J_{AB} 7, J_{AC} 10.5, J_{AD} 16.5 Hz, $CH_B{-}CH_A{=}CH_CH_D$), 3.30—2.80 (m, C*H*$_2$ + C*H*CH$_3$), 2.59 (s, NMe), and 1.10 (d, *J* 6 Hz, CHC*H*$_3$). The pyrazolidinone (9e) was heated at 138 °C for 6 h under N$_2$; the n.m.r. spectrum of the product was identical with that of the pyrazolidinone (9c).

1,4-*Dimethyl*-1-(3,3-*dimethylallyl*)-3-*oxopyrazolidin*-1-*ium*-2-*ide* (7d). This substance when heated (benzene 1 h) gave a single product identified as 1,4-*dimethyl*-2-(1,1-*dimethylallyl*)-*pyrazolidin*-3-*one* (9f) (Found: M^+, 182.1424. $C_{10}H_{18}N_2O$ requires M, 182.1419); $\nu_{max.}$ 1 680 cm^{-1}; δ, ABX system, δ_A 5.08, δ_B 5.02, δ_X 6.13 (J_{AX} 17, J_{BX} 10.5 Hz, $CH_X{=}CH_AH_B$), 3.22—2.92 (m, C*H*$_2$ + C*H*CH$_3$), 2.58 (s, NMe), 1.48 (s, C=CMe$_2$), and 1.07 (d, *J* 6 Hz, CHC*H*$_3$). The pyrazolidinone (9f) (100 mg) was heated at 138 °C for 24 h under N$_2$. The product was separated by t.l.c. to give the starting pyrazolidinone (9f) (50 mg) and 1,4-*dimethyl*-2-(3,3-*dimethylallyl*)*pyrazolidin*-3-*one* (9d) (50 mg) as a pale yellow oil; $\nu_{max.}$ 1 675 cm^{-1}; δ, AX$_2$ system, δ_A 5.16, δ_X 4.01 [J_{AX} 6 Hz, $C(H_X)_2{-}CH_A$], 3.50—3.10 (m, C*H*CH$_3$), 3.00—2.70 (m, CH$_2$), 2.55 (s, NMe), 1.69 (s, C=CMe$_2$), and 1.18 (d, *J* 6 Hz, CHC*H*$_3$). The *methiodide* was obtained as needles, m.p. 136—137 °C (Found: C, 40.6; H, 6.45; I, 39.1; N, 8.4. $C_{11}H_{21}IN_2O$ requires C, 40.7; H, 6.5; I, 39.1; N, 8.6%); $\nu_{max.}$ (Nujol) 1 730 cm^{-1}; δ[(CD$_3$)$_2$CO + D$_2$O] AX$_2$ system, δ_A 5.35, δ_X 4.49 [J_{AX} 7 Hz, $C(H_X)_2CH_A$], 4.93 (dd, *J* 8, 11 Hz, $\overset{+}{N}C\mathit{H}HCH$), 4.15 (t, *J* 11 Hz, $\overset{+}{N}CH\mathit{H}CH$), 3.88 (s, $\overset{+}{N}Me$), 3.81 (s, $\overset{+}{N}Me$), 3.80—3.35 (m, C*H*CH$_3$), 1.80 (s, C=CMe), 1.74 (s, C=CMe), and 1.35 (d, *J* 7 Hz, CHC*H*$_3$).

1-*Allyl*-1,4-*dimethyl*-3-*oxopyrazolidin*-1-*ium*-2-*ide* (7b). This substance when heated (benzene, 6 h) gave 2-*allyl*-1,4-*dimethylpyrazolidin*-3-*one* (9b) (100%) as a pale yellow oil (Found: M^+, 154. $C_8H_{14}N_2O$ requires M, 154); $\nu_{max.}$ 1 680 cm^{-1}; δ, AMNXY system, δ_A 5.75, δ_M 5.29, δ_N 5.15, δ_X 4.06, δ_Y 3.90 (J_{AM} 17, J_{AN} 9.5, J_{MX} 6.5, J_{NX} 6.5, J_{XY} *ca*. 15 Hz, $CH_XH_YCH_A{=}CH_MH_N$), 3.37 (m, C*H*CH$_3$), 2.85 (m, CH$_2$), 2.56 (s, NMe), and 1.19 (d, *J* 6 Hz, CHC*H*$_3$). The *methiodide* was obtained as needles, m.p. 171—172 °C (Found: C, 36.3; H, 5.9; I, 43.2; N, 9.2. $C_9H_{17}IN_2O$ requires C, 36.5; H, 5.7; I, 42.9; N, 9.5%); $\nu_{max.}$ 1 730 cm^{-1}; δ[(CD$_3$)$_2$CO + D$_2$O] AMNXY system, δ_A 6.00, δ_M 5.55, δ_N 5.28, δ_X *ca*. 4.55, δ_Y *ca*. 4.55 (J_{AM} 16.5, J_{AN} 9.5, J_{AX} 5.5, J_{AY} 5.5 Hz, $CH_XH_YCH_A{=}CH_MH_N$), ABMX$_3$ system, δ_A 4.98, δ_B 4.22, δ_M 3.58, δ_X 1.38 [J_{AB} 11, J_{AM} 8, J_{BM} 11, J_{MX} 7 Hz, $\overset{+}{N}CH_AH_BCH_MC(H_X)_3$], 3.91 (s, $\overset{+}{N}Me$), and 3.85 (s, $\overset{+}{N}Me$).

N-[*Cinnamyl(dimethyl)ammonio*]*benzamidide* (11a). This substance when heated (benzene, 72 h) gave two products. (i) 1-*Benzoyl*-1-*cinnamyl*-2,2-*dimethylhydrazine* (13a) (88%) was obtained as a yellow oil (Found: M^+, 280.1563. $C_{18}H_{20}N_2O$ requires M, 280.1576); $\nu_{max.}$ 1 630 cm^{-1}; δ 7.61—7.10 (m, 10 aryl H), ABX$_2$ system, δ_A 6.63, δ_B 6.38, δ_X 4.27 [J_{AB} 16, J_{BX} 5 Hz, $NC(H_X)_2CH_B{=}CH_A$], and 2.55 (s, NMe$_2$).

(ii) 1-*Benzoyl*-2,2-*dimethyl*-1-(1-*phenylallyl*)*hydrazine* (14a) (12%) was obtained as a yellow oil (Found: M^+, 280.1574. $C_{18}H_{20}N_2O$ requires M, 280.1576); $\nu_{max.}$ 1 640 cm^{-1}; δ 7.60—7.15 (m, 10 aryl H), AXYZ system, δ_A 6.62, δ_X 5.31, δ_Y 5.29, δ_Z 5.13 (J_{AX} 10, J_{AY} 7.5, J_{AZ} 17 Hz, $CH_YCH_A{=}CH_XH_Z$), 2.80br (s, NMe), and 2.55br (s, NMe). This product (14a) was heated under reflux in xylene for 1 h, after which the solvent was evaporated to give a residual oil with an n.m.r. spectrum identical with that of the cinnamylhydrazine (13a).

N-[*Cinnamyl(dimethyl)ammonio*]*acetamidide* (11b). This substance when heated (toluene, 48 h) gave two products. (i) 1-*Acetyl*-1-*cinnamyl*-2,2-*dimethylhydrazine* (13b) (80%) was obtained as a pale yellow oil (Found: M^+, 218.1426, $C_{13}H_{18}N_2O$ requires M, 218.1419); $\nu_{max.}$ 1 640 cm^{-1}; δ 7.36—7.16 (m, 5 aryl H), ABX$_2$ system, δ_A 6.52, δ_B 6.26, δ_X 4.10 [J_{AB} 16.5, J_{BX} 5.5 Hz, $NC(H_X)_2CH_A{=}CH_B$], 2.50 (s, NMe$_2$), and 2.22 (s, COCH$_3$).

(ii) 1-*Acetyl*-2,2-*dimethyl*-1-(1-*phenylallyl*)*hydrazine* (14b) (20%) was obtained as crystals, m.p. 70—72 °C (Found: M^+, 218.1426. $C_{13}H_{18}N_2O$ requires M, 218.1419); $\nu_{max.}$ 1 650 cm^{-1}; δ 7.30—7.20 (m, 5 aryl H), AXYZ system, δ_A 6.60, δ_X 5.25, δ_Y 5.20, δ_Z 5.04 (J_{AX} 9, J_{AY} 16, J_{AZ} 7 Hz, $NCH_ZCH_A{=}CH_XH_Y$), 2.57 (s, NMe$_2$), and 2.14 (s, COCH$_3$). This product (14b) was heated at 150 °C under N$_2$ for 24 h; the n.m.r. spectrum indicated that after this time the product consisted of the cinnamylhydrazine (13b) contaminated with a small quantity of the (1-phenylallyl)hydrazine (14b).

N-[3,3-*Dimethylallyl(dimethyl)ammonio*]*acetamidide* (11c). This substance when heated (xylene, 2 h) gave two products. (i) 1-*Acetyl*-1-(3,3-*dimethylallyl*)-2,2-*dimethylhydrazine* (13c) (80%) was obtained as a yellow oil (Found: M^+, 170.1418. $C_9H_{18}N_2O$ requires M, 170.1419); $\nu_{max.}$ 1 640 cm^{-1}; δ, AX$_2$

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* For this and other deuteriated compounds the value for H refers to the combined D and H content estimated as H.

system, δ_A 5.20, δ_X 3.93 [J_{AX} 6 Hz, $CH_AC(H_X)_2N$], 2.48 (s, NMe_2), 2.11 (s, $COCH_3$), and 1.68 (s, C=CMe$_2$).

(ii) 1-*Acetyl*-1-(1,1-*dimethylallyl*)-2,2-*dimethylhydrazine* (14c) (9%) was obtained as a yellow oil (Found: M^+, 170.1418. $C_9H_{18}N_2O$ requires *M*, 170.1419); δ, AXY system, δ_A 6.14, δ_X 5.04, δ_Y 4.98 (J_{AX} 10, J_{AY} 17 Hz, CH_A=CH_XH_Y), 2.75 (s, NMe_2), 1.98 (s, $COCH_3$), and 1.41 (s, CMe_2).

N-[*Cinnamyl*(1,1-*dimethyl*)*ammonio*]*ethoxyformamidide* (11d). This substance when heated (benzene, 6 h) gave two products. (i) 2-*Cinnamyl*-2-*ethoxycarbonyl*-1,1-*dimethylhydrazine* (13d) (45%) was obtained as a yellow oil (Found: M^+, 248.1518. $C_{14}H_{20}N_2O_2$ requires *M*, 248.1525); $\nu_{max.}$ 1 690 cm^{-1}; δ 7.40—7.15 (m, 5 aryl H), ABX_2 system, δ_A 6.52, δ_B 6.18, δ_X 4.25 [J_{AB} 16, J_{BX} 6 Hz, $NC(H_X)_2CH_B$=CH_A], A_2X_3 system, δ_A, 4.05, δ_X 1.24 [J_{AX} 7 Hz, $OC(H_A)_2C(H_X)_3$], and 2.64 (s, NMe_2).

(ii) 2-*Ethoxycarbonyl*-1,1-*dimethyl*-2-(1-*phenylallyl*)*hydrazine* (14d) (55%) was obtained as a yellow oil (Found: M^+, 248.1518. $C_{14}H_{20}N_2O_2$ requires *M*, 248.1525); $\nu_{max.}$ 1 690 cm^{-1}; δ 7.50—7.20 (m, 5 aryl H), AMXY system, δ_A 6.42, δ_M 5.60, δ_X 5.22, δ_Y 5.19 (J_{AM} 8, J_{AX} 9.5, J_{AY} 17 Hz, CH_MCH_A=CH_XH_Y), A_2X_3 system, δ_A 4.20, δ_X 1.27 [J_{AX} 7 Hz, $OC(H_A)_2C(H_X)_3$], 2.68br (s, NMe), and 2.40br (s, NMe).

N-[3,3-*Dimethylallyl*(*dimethyl*)*ammonio*]*ethoxyformamidide* (11e). This substance when heated (toluene, 1.5 h) gave two products. (*i*) 2-*Ethoxycarbonyl*-1,1-*dimethyl*-2-(3,3-*dimethylallyl*)*hydrazine* (13e) (67%) was obtained as a pale yellow oil (Found: M^+, 200.1522. $C_{10}H_{20}N_2O_2$ requires *M*, 200.1525); $\nu_{max.}$ 1 690 cm^{-1}; δ, AX_2 system, δ_A 5.27, δ_X 3.90 [J_{AX} 7 Hz, $NC(H_X)_2CH_A$], A_2X_3 system, δ_A 4.16, δ_X 1.26 [J_{AX} 7 Hz, $OC(H_A)_2C(H_X)_3$], 2.64 (s, NMe_2), and 1.70 (s, C=CMe$_2$).

(ii) 2-*Ethoxycarbonyl*-1,1-*dimethyl*-2-(1,1-*dimethylallyl*)-*hydrazine* (14e) (22%) was obtained as an oil (Found: M^+, 200.1522. $C_{10}H_{20}N_2O_2$ requires *M*, 200.1525); $\nu_{max.}$ 1 690 cm^{-1}; δ, AXY system, δ_A 6.02, δ_X 4.99, δ_Y 4.85 (J_{AX} 10, J_{AY} 17, J_{XY} 1.5 Hz, CH_A=CH_XH_Y), A_2X_3 system, δ_A 4.13, δ_X 1.25 [J_{AX} 7 Hz, $OC(H_A)_2C(H_X)_3$], 2.64 (s, NMe_2), and 1.38 (s, CMe_2).

N-[*Allyl*(*dimethyl*)*ammonio*]*ethoxyformamidide*. (11f). This substance when heated (toluene, 1.5 h) gave 2-*allyl*-2-*ethoxycarbonyl*)-1,1-*dimethylhydrazine* (13f) (*ca.* 100%) as an oil (Found: M^+, 172.1215. $C_8H_{16}N_2O_2$ requires *M*, 172.1212); $\nu_{max.}$ 1 720 cm^{-1}; δ, $AMNX_2$ system, δ_A 5.88, δ_M 5.16, δ_N 5.08, δ_X 3.89 [J_{AM} 17, J_{AN} 9.5, J_{AX} 6, J_{MN} 1.5, J_{MX} 1.5, J_{NX} 1.5 Hz, $NC(H_X)_2CH_A$=CH_MH_N], A_2X_3 system, δ_A 4.16, δ_X 1.26 [J_{AX} 7 Hz, $OC(H_A)_2C(H_X)_3$], and 2.65 (s, NMe_2).

N-[*Benzyl*(*dimethyl*)*ammonio*]*ethoxyformamidide* (23a). This substance when heated (xylene, 12 h) gave 2-*benzyl*-2-*ethoxycarbonyl*-1,1-*dimethylhydrazine* (25a) as an oil (Found: M^+, 222.1373. $C_{12}H_{18}N_2O_2$ requires *M*, 222.1368); $\nu_{max.}$ 1 695 cm^{-1}; δ 7.30 (m, 5 aryl H), A_2X_3 system, δ_A 4.22, δ_X 1.32 [J_{AX} 7 Hz, $OC(H_A)_2C(H_X)_3$], 4.27 (s, C*H*$_2$Ph), and 2.60 (s, NMe_2).

N-[*Cinnamyl*(*dimethyl*)*ammonio*]*methylureide* (11g). This substance when heated (benzene, 1 h) gave two products. (i) 2-*Cinnamyl*-1,1-*dimethyl*-2-*methylcarbamoylhydrazine* (13g) (40%) was obtained as crystals, m.p. 104—106 °C (Found: C, 66.8; H, 8.3; N, 18.2%; M^+, 233.1539. $C_{13}H_{19}N_3O$ requires C, 67.0; H, 8.15; N, 18.0%; *M*, 233.1528); $\nu_{max.}$ 3 420 and 1 650 cm^{-1}; δ 7.36—7.15 (m, 5 aryl H), ABX_2 system, δ_A 6.55, δ_B 6.35, δ_X 4.15 [J_{AB} 16, J_{BX} 7 Hz, $NC(H_X)_2CH_B$=CH_A], 7.18 (d, *J* 5 Hz, NH*Me*), and 2.50 (s, NMe_2).

(ii) 1,1-*Dimethyl*-2-(*methylcarbamoyl*)-2-(1-*phenylallyl*)-*hydrazine* (14g) (60%) was obtained as crystals, m.p. 80—90 °C (Found: C, 66.8; H, 8.2; N, 18.05%; M^+, 233.1537. $C_{13}H_{19}N_3O$ requires C, 67.0; H, 8.15; N, 18.0%; *M*, 233.1528); $\nu_{max.}$ 3 425 and 1 660 cm^{-1}; δ 7.48—7.20 (m, 5 aryl H), AXYZ system, δ_A 6.60, δ_X 5.24, δ_Y 5.14, δ_Z 4.92 (J_{AX} 10, J_{AY} 15.5, J_{AZ} 7.5 Hz, NCH_ZCH_A=CH_XH_Y), 2.77 (d, *J* 5 Hz, NH*Me*), and 2.54 (s, NMe_2). This product (14g) was heated at 138 °C for 24 h under N_2 to give a product having m.p. and n.m.r. spectrum identical with those of the cinnamylhydrazine (13g).

N-[3,3-*Dimethylallyl*(*dimethyl*)*ammonio*]*methylureide* (11h). This substance when heated (toluene, 1.5 h) gave two products. (i) 1,1-*Dimethyl*-2-(3,3-*dimethylallyl*)-2-(*methylcarbamoyl*)-*hydrazine* (13h) (72%) was obtained as a yellow oil (Found: M^+, 185.1526. $C_9H_{19}N_3O$ requires *M*, 185.1528); $\nu_{max.}$ 3 420 and 1 645 cm^{-1}; δ, AX_2 system, δ_A 5.28, δ_X 3.95 [J_{AX} 7 Hz, $NC(H_X)_2CH_A$], 2.80 (d, *J* 5 Hz, NH*Me*), 2.48 (s, NMe_2), and 1.72 (s, C=CMe$_2$).

(ii) 1,1-*Dimethyl*-2-(1,1-*dimethylallyl*)-2-(*methylcarbamoyl*)-*hydrazine* (14h) (28%) was obtained as a yellow oil (Found: M^+, 185.1532. $C_9H_{19}N_3O$ requires *M*, 185.1528); $\nu_{max.}$ 3 430 and 1 645 cm^{-1}; δ, AXY system, δ_A 6.20, δ_X 5.08, δ_Y 5.00 (J_{AX} 18, J_{AY} 10 Hz, CH_A=CH_XH_Y), 2.80 (s, NH*Me* + NMe_2), and 2.52 (s, CMe_2).

N-[*Allyl*(*dimethyl*)*ammonio*]*methylureide* (11i). This substance when heated (toluene, 1.5 h) gave 2-*allyl*-1,1-*dimethyl*-2-(*methylcarbamoyl*)*hydrazine* (13i) (95%) as a pale yellow oil (Found: M^+, 157.1213. $C_7H_{15}N_3O$ requires *M*, 157.1215); $\nu_{max.}$ 3 420 and 1 650 cm^{-1}; δ, $AMNX_2$ system, δ_A 5.95, δ_M 5.18, δ_N 5.04, δ_X 3.94 [J_{AM} 17.5, J_{AN} 10, J_{AX} 5.5, J_{MN} 1.5, J_{MX} 1.5, J_{NX} 1.5 Hz, $NC(H_X)_2CH_A$=CH_MH_N], 2.78 (d, *J* 5 Hz, NH*Me*), and 2.46 (s, NMe_2).

N-[*Benzyl*(*dimethyl*)*ammonio*]*methylureide* (23b). This substance when heated (toluene, 48 h), gave two products. (i) 2-*Benzyl*-1,1-*dimethyl*-2-(*methylcarbamoyl*)*hydrazine* (25b) (64%) was obtained as a yellow oil (Found: M^+, 207.1374. $C_{11}H_{17}N_3O$ requires *M*, 207.1372); $\nu_{max.}$ 3 420 and 1 650 cm^{-1}; δ 7.40—7.15 (m, 5-aryl H), 4.58 (s, NCH_2), 2.84 (d, *J* 5 Hz, NH*Me*), and 2.40 (s, NMe_2).

(ii) 2-*Benzyl*-1,1-*dimethyl*-2-(*benzylmethylcarbamoyl*)*hydrazine* (26) (18%) was obtained as crystals, m.p. 76 °C after crystallisation from light petroleum (Found: C, 73.0; H, 7.5; N, 14.4%; M^+, 297.1846. $C_{18}H_{23}N_3O$ requires C, 72.2; H, 7.75; N, 14.1%; *M*, 297.1841); $\nu_{max.}$ 1 640 cm^{-1}; δ 7.35—7.20 (m, 10 aryl H), 4.49 (s, NCH_2), 4.38 (s, NCH_2), 2.84 (s, NMe), and 2.44 (s, NMe_2).

N-[*Cinnamyl*)*dimethyl*)*ammonio*]*phenylureide* (11l). This substance when heated (benzene) gave two products. (i) 2-*Cinnamyl*-1,1-*dimethyl*-2-(*phenylcarbamoyl*)*hydrazine* (13l) (23%) was obtained as crystals, m.p. 134—135 °C after crystallisation from chloroform–light petroleum (Found: C, 73.4; H, 7.4; N, 14.5. $C_{18}H_{21}N_3O$ requires C, 73.2; H, 7.1; N, 14.2%); $\nu_{max.}$ 3 360 and 1 673 cm^{-1}; δ 7.57—6.85 (m, 10 aryl H), ABX_2 system, δ_A 6.56, δ_B 6.39, δ_X 4.17 [J_{AB} 16, J_{BX} 16, J_{BX} 6 Hz, $NC(H_X)_2CH_B$=CH_A], and 2.57 (s, NMe_2).

(ii) 1,1-*Dimethyl*-2-(1-*phenylallyl*)-2-(*phenylcarbamoyl*)-*hydrazine* (14l) (68%) was obtained as crystals, m.p. 75–76 °C, after crystallisation from chloroform–light petroleum (Found: C, 73.2; H, 7.1; N, 14.2. $C_{18}H_{21}N_3O$ requires C, 73.2; H, 7.1; N, 14.2%); $\nu_{max.}$ 3 360 and 1 680 cm^{-1}; δ 7.54—6.78 (m, 10 aryl H), AXYZ system, δ_A 6.58, δ_X 5.24, δ_Y 5.17, δ_Z 4.96 (J_{AX} 10, J_{AY} 18, J_{AZ} 8 Hz, NCH_ZCH_A=CH_XH_Y), and 2.59 (s, NMe_2). The rearrangement of a 1 : 1 mixture of the [$^2H_0$]ylide (11l) and the [$^2H_7$]ylide (20) was carried out under the conditions summarised in Table 4. The reaction mixture, in each case, was diluted with ether (75 ml) and water (25 ml), the organic layer was evaporated, and the residue was dissolved in hydrochloric acid (M; 25 ml). The resulting solution was washed with ether, made basic (2.5M-NaOH), and the products (13) and (14) extracted into ether. The product mixture was separated by t.l.c. (ether–light petroleum, 1 : 4) and the isotopic composition of each product determined by mass spectrometry.

In a further experiment the ylide was recovered as a crystalline product after partial rearrangement in methyl cyanide at 80 °C. The recovered ylide was rearranged in glycerol at

80 °C and the isotopic composition of the products (13) and (14) determined by mass spectrometry.

Measurement of the Rates of Thermal Rearrangements.—The ylide was heated, either neat or in solution, in the vapour of an appropriate boiling solvent. Samples were removed at measured intervals and the composition of the sample determined from the intensities of appropriate signals in its n.m.r. spectrum. The value of the first order rate constant for the formation of the combined products was obtained in the usual way and rate constants for the formation of individual products were obtained from product ratios. The results of these kinetic studies are summarised in Tables 2 and 3.

Thermal Reaction of Dimethylammonioformamidides (11j), (11k), *and* (23c).—A solution of each ylide (*ca.* 2 g) in benzene (15 ml) was heated under reflux for 12 h. The precipitated white solid was collected and recrystallised from water to give a low yield of cyanuric acid (28), m.p. >360 °C (Found: C, 28.2; H, 2.55; N, 33.6. Calc. for $C_3H_3N_3O_3$: C, 27.9; H, 2.3; N, 32.55%); $\nu_{max.}$ (KBr) 3 100, 1 780, 1 750, and 1 725 cm^{-1}. The benzene solution was evaporated to give the appropriate *N,N*-dimethylallylamine as a yellow oil which could be characterised as its methiodide derivative. Cinnamyltrimethylammonium iodide was obtained as needles, m.p. 181—183 °C (Found: C, 47.5; H, 5.9; I, 41.9; N, 4.7. $C_{12}H_{18}IN$ requires C, 47.5; H, 5.9; I, 41.9; N, 4.6%); $\delta[(CD_3)_2CO + D_2O]$ 7.18—7.30 (m, 5 aryl H), ABX_2 system, δ_A 7.14, δ_B 6.58, δ_X 4.34 [J_{AB} 16, J_{BX} 8 Hz, $\overset{+}{N}C(H_X)_2CH_B{=}CH_A$], and 3.31 (s, $\overset{+}{N}Me_3$). (3,3-Dimethylallyl)trimethylammonium iodide had m.p. 169—170 °C (Found: C, 37.8; H, 7.0; I, 50.0; N, 5.65. $C_8H_{18}IN$ requires C, 37.65; H, 7.1; I, 49.8; N, 5.5%); $\delta[(CD_3)_2CO + D_2O]$ AX_2 system, δ_A 5.58, δ_X 4.19 [J_{AX} 8 Hz $\overset{+}{N}C(H_X)_2CH_A$], 3.28 (s, $\overset{+}{N}Me_3$), and 1.90 (s, $C{=}CMe_2$).

N-*Nitroso*-N-(1-*phenylethyl)methylamine*.—Hydrochloric acid (3.60 g; 11M) was added dropwise to stirred *N*-(1-phenylethyl)methylamine (19) (13.50 g) at 5—10 °C. The resulting mixture was stirred and maintained at 70—75 °C and a saturated aqueous solution of sodium nitrite (6.9 g) was added with further additions of hydrochloric acid (2M) to maintain the acidity of the solution. After a further 3 h at 70—75 °C the reaction mixture was cooled, extracted with ether (3 × 50 ml), and the combined extracts dried and concentrated. The residual yellow oil was distilled to give the nitrosamine (14.8 g, 90%) as a pale yellow liquid, b.p. 95—96 °C at 0.02 mmHg (Found: C, 65.9; H, 7.4; N, 16.9. $C_9H_{12}N_2O$ requires C, 65.85; H, 7.3; N, 17.1%); δ 7.40—7.05 (m, 5 aryl H), AX_3 system, δ_A 7.76, δ_X 1.82 [J_{AX} 7 Hz, $CH_AC(H_X)_3$], and 7.87 (s, NMe).

2-*Acetyl*-1-*methyl*-1-(1′-*phenylethyl)hydrazine*.—A suspension of lithium aluminium hydride (3.0 g) in dry ether (200 ml) was added dropwise to a stirred solution of the nitrosamine (13.0 g) in dry ether (50 ml). The resulting suspension was heated under reflux for 4 h, cooled, and hydrolysed by the dropwise addition of wet ether followed by water. The solution was made basic (30% aqueous NaOH) and the product extracted with ether; the extract was dried and evaporated and the residual oil distilled to give *N*-methyl-*N*-(1-phenylethyl)hydrazine as a colourless oil, b.p. 81—82 °C at 0.2 mmHg (9.90 g, 91%); δ 2.70 (m, 5 aryl H), AX_3 system, δ_A 3.36, δ_X 1.40 [J_{AX} 7 Hz, $CH_AC(H_X)_3$], 3.45br (s, NH_2), and 2.41 (s, NMe). Acetic anhydride (3.06 g) was added dropwise to a cooled and stirred solution of the hydrazine (3.0 g) in benzene (15 ml). The mixture was stirred at room temperature for 12 h and the solvent evaporated; the residue was then crystallised from light petroleum to give the *acetylhydrazine* (2.8 g, 73%), m.p. 72—75 °C (Found: C, 68.2; H, 8.3; N, 14.5. $C_{11}H_{16}N_2O$ requires C, 68.3; H, 8.3; N, 14.6%); $\nu_{max.}$ 3 300, 1 670, and 1 600 cm^{-1}; δ 7.30 (m, 5 aryl H), AX_3 system, δ_A 3.94, δ_X 1.38 [J_{AX} 7 Hz, $CH_AC(H_X)_3$], 3.67br (s, NH), 2.52 and 2.40 (2 × s, $COCH_3$ of two conformers), and 2.09 and 1.83 (2 × s, NMe of two conformers).

2-*Acetyl*-1,1-*dimethyl*-1-(1-*phenylethyl)hydrazinium Iodide* (18).—A mixture of the acetyl hydrazine (3.0 g) and methyl iodide (10 g) in methanol (10 ml) was stirred at room temperature for one week. The reaction mixture was concentrated and the product precipitated by the addition of ether. The product was recrystallised from methanol–ether to give the *salt* (18) (3.50 g, 67%), m.p. 120—122 °C (Found: C, 43.4; H, 5.8; I, 38.0; N, 8.5. $C_{12}H_{19}IN_2O$ requires C, 43.1; H, 5.7; I, 38.0; N, 8.4%), $\nu_{max.}$ (Nujol) 3 124 and 1 700 cm^{-1}; $\delta[(CD_3)_2CO + D_2O)]$ 7.76—7.46 (m, 5 aryl H), AX_3 system, δ_A 5.83, δ_X 1.93 [J_{AX} 7 Hz, $CH_AC(H_X)_3$], 3.72 and 3.56 (2 × s, $\overset{+}{N}Me_2$), and 2.19 (s, $COCH_3$).

N-[*Dimethyl*(1-*phenylethyl)ammonio]acetamidide* (17).—Aqueous sodium hydroxide (5 ml; 20%) was added to a solution of the salt (18) (1.2 g) in water (5 ml). The solution was left at room temperature for 6 h, extracted with methylene chloride, and the extracts dried and evaporated to give the ylide (17) (0.6 g, 80%) as a colourless hygroscopic solid (Found: M^+, 206. $C_{12}H_{18}N_2O$ requires *M*, 206); $\nu_{max.}$ 1 570 cm^{-1}; δ 7.60—7.30 (m, 5 aryl H), AX_3 system, δ_A 5.95, δ_X 1.71 [J_{AX} 7 Hz, $CH_AC(H_X)_3$], 3.25 and 3.02 (2 × s, $\overset{+}{N}Me_2$), and 1.84 (s, $COCH_3$). The ylide (100 mg) was heated at 140—145 °C at 0.02 mmHg for 30 min and the volatile products collected in a trap cooled by liquid nitrogen. The residual oil was identified as 2-acetyl-1,1-dimethylhydrazine (30 mg, 66%) and the liquid in the trap was identified as styrene.

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