# Base Catalysed Rearrangements involving Ylide Intermediates. Part 1. The Rearrangements of Diallyl- and Allylpropynyl-ammonium Cations

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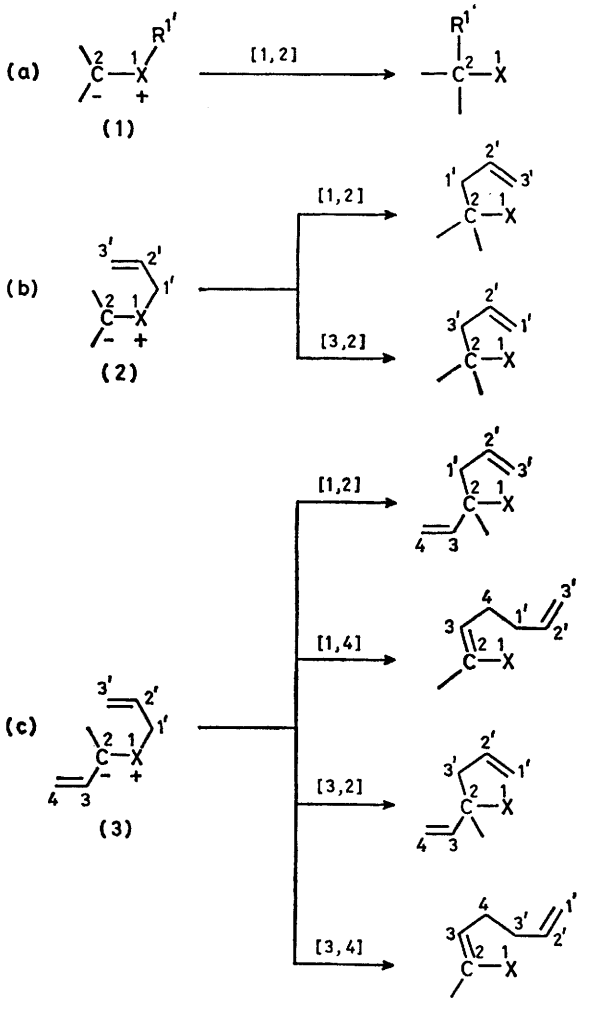
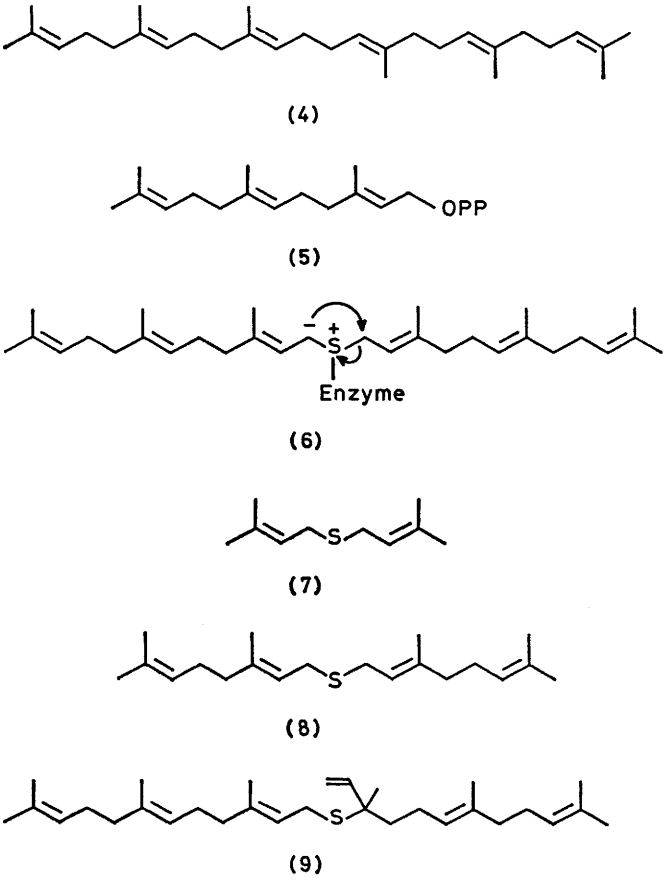
The base catalysed rearrangements of diallylammonium cations and allylpropynylammonium cations are described. In most cases, the major product arises by a symmetry-allowed [3,2] sigmatropic rearrangement of the intermediate ylide. The minor products can be regarded as being derived by homolysis of the ylide into a radical pair followed by recombination.

THE structural relations associated with the thermal transformation of ylide precursors [1-6] into neutral products may be conveniently summarised by Scheme 1. It must be emphasised that Scheme 1 indicates only the structural opportunities for intramolecular rearrangement associated with internal neutralisation of positive and negative charges. Case (a) formally represents the well known Stevens [1,2] rearrangement [5-7] in which, for example, X = $NMe_2$ or SMe. When the anionoid and cationoid centres of the ylide residue are associated with allylic substituents then additional opportunities for intramolecular rearrangement may be recognised.[8,9] These include case (b) for which two reaction possibilities,




SCHEME 1 Possible intramolecular rearrangements of the ylides (1)—(3) without regard to geometrical and stereoelectronic requirements




[1,2] and [3,2], could be envisaged. Similarly for case (c) the number of possibilities is apparently increased to four, [1,2], [1,4], [3,2], and [3,4], provided that geometrical and stereoelectronic requirements for the four reactions are disregarded.

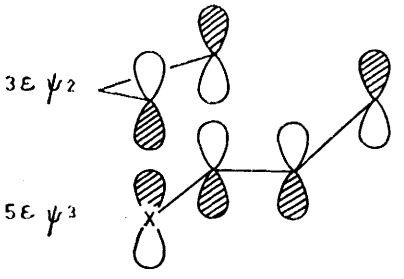
Our interest in the chemistry of ylides was initiated by our association with Professor T. S. Stevens (University of Sheffield, 1947—1966) who discovered the Stevens rearrangement in 1928.[10] In 1966, the possibility was put forward [11] that the creation of the interfarnesyl bond during the biosynthesis of squalene (4) from farnesyl

pyrophosphate (5) might conceivably involve a Stevens rearrangement (6; arrows) of an intermediate bis-farnesylsulphonium derivative of an enzyme. This ingenious suggestion [11] was discussed by one of us (W. D. O.) in 1966 [12] and model experiments for the rearrangement [*cf.* (6)] were initiated.[8] These included the study of the base catalysed transformation of sulphonium salts, derived from bis-3,3-dimethylallyl sulphide [8] (7), bisgeranyl sulphide [13] (8), and farnesyl nerolidyl sulphide (9).[14] At that time analogous and in some cases identical studies of the thermal rearrangements of bisallyl sulphonium ylides (3; X = SR) were in progress.[15] It soon became clear that the biogenetic proposal [11] (6; arrows) corresponded to the [1,2] sigmatropic rearrangement of the ylide (3; X = SR). Subsequent studies have shown that the biosynthesis of squalene (4) from farnesyl pyrophosphate (5) takes a completely different pathway [16] but at the least the suggestion [11] that a Stevens rearrangement might be involved certainly played a role in stimulating some of our current interest in ylide rearrangements. Our synthesis of squalene (4) from farnesyl nerolidyl sulphide (9) [14] must now be regarded only as an example of the application in synthesis of sulphonium ylide intermediates.[1]

At an early stage in our investigations, we compared the base catalysed rearrangements of ammonium [9] and sulphonium [17] cations associated with one and with two allyl substituents (2; X = $NMe_2$), (2; X = SR), (3; X = $NMe_2$), and (3; X = SR). This was initially necessary because by labelling the allyl residue in ammonium ylides of the type (2; X = $NMe_2$) it had apparently been shown [18] that their rearrangement followed the Stevens [1,2] pathway rather than the symmetry allowed [3,2] sigmatropic rearrangement with allylic participation. Reinvestigation [9,19] established that the rearrangement of the ammonium ylides (2; X = $NMe_2$) is entirely analogous to the rearrangement of the corresponding sulphonium ylides [17] (2; X = SR). Under normal circumstances the concerted [3,2] sigmatropic rearrangement * of ylides (2) and (3) is observed but there are interesting exceptions where other pathways (Scheme 1) supervene.[19]

As has already been emphasised, Scheme 1 is an over-simplification of transformations which could be exhibited by the ylides (1)—(3). For ylides of type (3), the four indicated rearrangements could, in principle, be associated with sixteen stereochemical possibilities.[20] These involve either suprafacial or antarafacial modes of reaction (Scheme 2) between the transition state components. Eight are symmetry allowed processes and eight are forbidden.[20] Of the eight which are symmetry allowed, the [3,2] sigmatropic process with suprafacial–suprafacial characteristics is obviously most acceptable (see upper diagram in Scheme 2). Stereochemical factors associated with the inhibition of symmetry-allowed [1,4] sigmatropic rearrangements have been recognised.[21]

In considering the thermal rearrangements of ylides, it is also useful to recognise the association of observed reaction pathways with aromatic transition states.[22] The four reaction modes associated with suprafacial–suprafacial presentation (Scheme 3) are either aromatic ([1,4] and [3,2]) or anti-aromatic ([1,2] and [3,4]) transition states. It is a question of considerable current

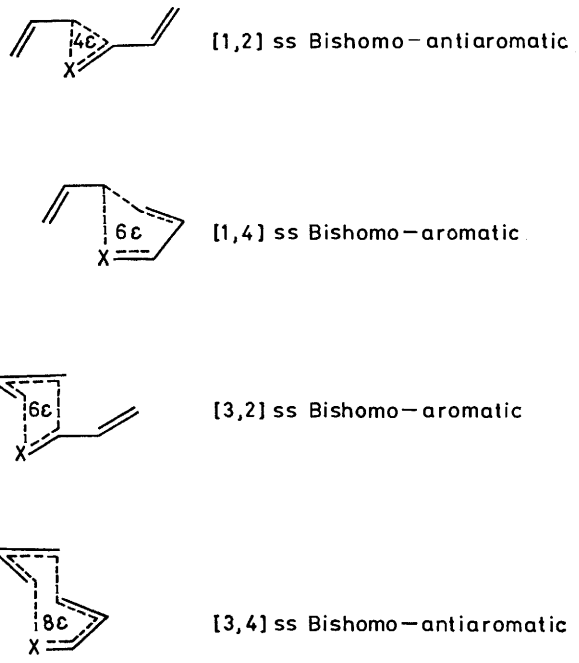



| Eight allowed transformations | | | Eight forbidden transformations | | |
|---|---|---|---|---|---|
| [1,2] | sa | as | [1,2] | ss | aa |
| [1,4] | ss | aa | [1,4] | sa | as |
| [3,2] | ss | aa | [3,2] | as | sa |
| [3,4] | sa | as | [3,4] | ss | aa |

SCHEME 2 Application of Woodward–Hoffmann rules to possible sigmatropic rearrangements of the ylide (3)

* The term ' concerted ' is usually used for rearrangements in which bond breaking and making occur simultaneously at some point in the reaction pathway. The distinction between a concerted process and one involving a radical pair is not easy to make unless the two components of the radical pair are not electronically linked at a point on the reaction pathway. To avoid this difficulty we shall use ' concerted ' as a description of rearrangements in which the two components of the radical pair interact strongly in the transition state; this corresponds to the description of the transition state for ' allowed ' sigmatropic rearrangements that was used in the original papers of Woodward and Hoffmann. The less strongly interacting radical pair that is often the transition state for ' non-allowed ' sigmatropic rearrangements will generally be referred to as a ' radical pair ' in this series of papers. It is characterised by the formation of escape products and some loss of configuration in cases where the rearranging group is chiral at the migration terminus.

interest whether the observed Stevens [1,2] rearrangement may be regarded as a *concerted-forbidden process*.[21b,23a]



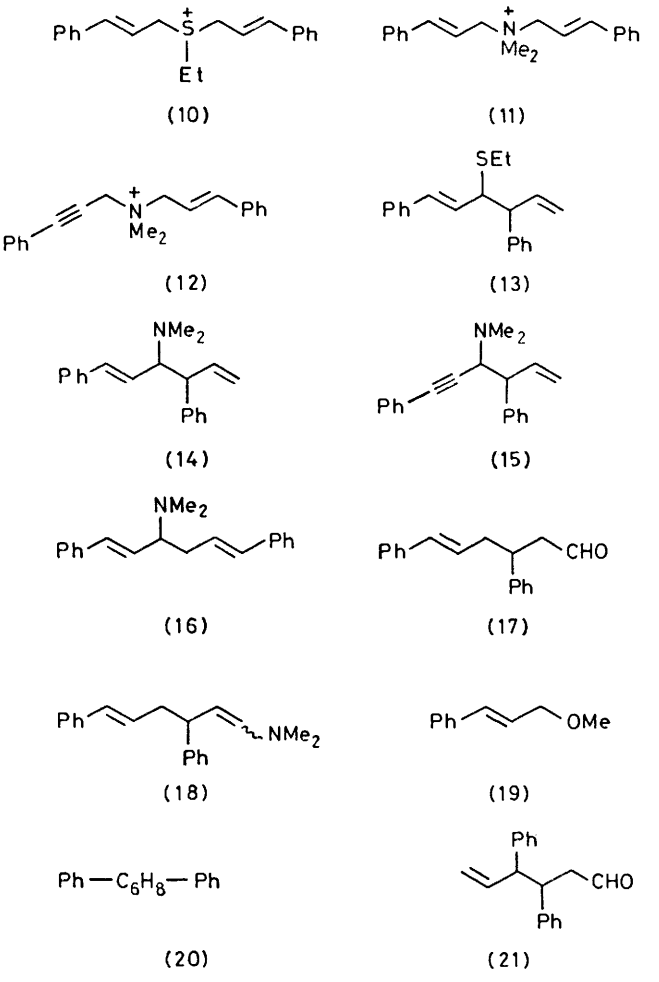

SCHEME 3 Four suprafacial–suprafacial transition states for the thermal rearrangement of the ylide (3)

*The Base Catalysed Rearrangement of Diallylammonium Cations.*—Our point of departure [9] in these studies involved a comparison of the base catalysed thermal rearrangements of the dicinnamylsulphonium cation (10) and the dicinnamylammonium cation (11). In order to determine the influence of an acetylenic bond comparative studies with the analogous 3-phenylprop-2-ynyl derivative (12) were also made.[24]

The sulphonium cation (10) underwent a [3,2] rearrangement [(10) ⟶ (13)] almost quantitatively under very mild conditions of basic catalysis using potassium carbonate in ethanol.[17] In contrast, the corresponding dicinnamylammonium cation (11) was unchanged under these conditions and the much more strongly basic reagent, sodium methoxide, was required. The reaction between the ammonium cation (11) and phenyl-lithium was first investigated by Wittig and Sommer [25] with a singularly unpromising result. The reaction gave in low yield an uncharacterised amine which by a Hofmann degradation of its methiodide yielded 1,6-diphenylhexa-1,3,5-triene. This suggested that a Stevens [1,2] rearrangement of the ylide derived from the ammonium cation (11) had occurred, but as the constitution of the amine isolated in low yield was not established, further investigation was demanded.

In contrast with these earlier results,[25] we found that the dicinnamylammonium cation (11) reacted smoothly with sodium methoxide in dimethyl sulphoxide solution at room temperature. In order to avoid the problem of separating tertiary amines and enamines, the total reaction product was treated with dilute aqueous hydrochloric acid and separated into basic and neutral fractions. The major product (yield 65%) was identified, mainly on the basis of its n.m.r. and mass spectra, as the tertiary amine (14). In fact the product (14) was shown on the basis of its n.m.r. spectrum to be a mixture of diastereoisomers (10 : 1); the major component was characterised as its picrate, m.p. 158°. Thus the preferred reaction pathway [(11) ⟶ (14); 65%] followed by the ylide derived from the ammonium cation (11) is a [3,2] sigmatropic rearrangement. This result corresponds exactly with (i) the [3,2] rearrangement [(10) ⟶ (13); 100%] shown by the sulphonium cation [17] (10) and (ii) the [3,2] rearrangement [(12) ⟶ (15); 91%] shown by the acetylenic ammonium cation [24] (12). A comparative study of the rearrangements (11) ⟶ (14) and (12) ⟶ (15) is discussed below.

The base catalysed rearrangement of the dicinnamylammonium cation (11) using sodium methoxide in dimethyl sulphoxide solution at room temperature gave




(after acid hydrolysis) the major product (14) (yield 65%), and a number of other compounds. The [1,2] Stevens rearrangement product (16) (yield 28%) was isolated and characterised as its methiodide, m.p. 149°,

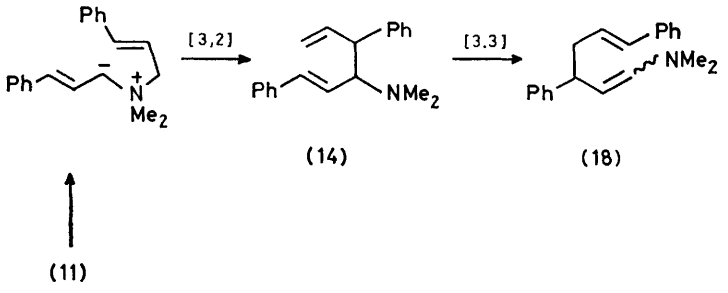
TABLE 1

Relative yields of significant products from the base catalysed rearrangement of the dicinnamylammonium cation (11)

| Conditions | Yields of products (%) (14) | (16) | (17) ≡ (18) |
|---|---|---|---|
| *ca.* 20°; 12 h (NaOMe–$Me_2SO$) | 65 | 28 | 5 |
| 80°; 1 h (NaOMe–MeOH) | 24 | 23 | 50 |
| 85°; 15 h (NaOMe–MeOH) | | 23 | 76 |

its constitution (16) was clearly indicated by its n.m.r. spectrum. The neutral fraction of the reaction product gave the crystalline aldehyde (17) (yield 5%), m.p. 77°: its constitution (17) followed from its i.r., n.m.r., and mass spectra. This aldehyde (17) was obviously formed by the acid hydrolysis of the enamine (18). This enamine (18) could, in principle, have been formed by a process (11) ⟶ (18) which corresponds to a symmetry allowed [1,4] sigmatropic rearrangement of the ylide [Scheme 1, case (c)]. This possibility is given consideration and excluded on the basis of further results (Table 1). The other minor products were cinnamyl aldehyde (17) derived from the enamine (18) is increased (5 ⟶ 76%). The most acceptable interpretation of these results is that the transformation (11) ⟶ (18) does not involve the [1,4] sigmatropic rearrangement [Scheme 1; case (c)] mentioned above. The transformation (11) ⟶ (18) could involve the sequence (11) ⟶ (14) ⟶ (18), that is a [3,2] sigmatropic rearrangement of the ylide followed by a [3,3] thermal Cope rearrangement of the hexa-1,5-diene (14) to its isomer (18) (Scheme 4). An alternative route involving a radical pair intermediate (31) is also possible. The [3,3] sigmatropic rearrangement (14) ⟶ (18) is discussed in detail in Part 4 [26] and is related to the thermal [1,3] sigmatropic rearrangement [27] which misled Millard and Stevens [18] in their interpretation of the base catalysed rearrangement of monoallylammonium cations [Scheme 1, case (b)] (see Part 2).[19]

Similarly, the base catalysed transformation of the diallylammonium cation (22) with sodium methoxide in dimethyl sulphoxide solution at room temperature gave the amine (23) (yield 50%) characterised as its picrate,



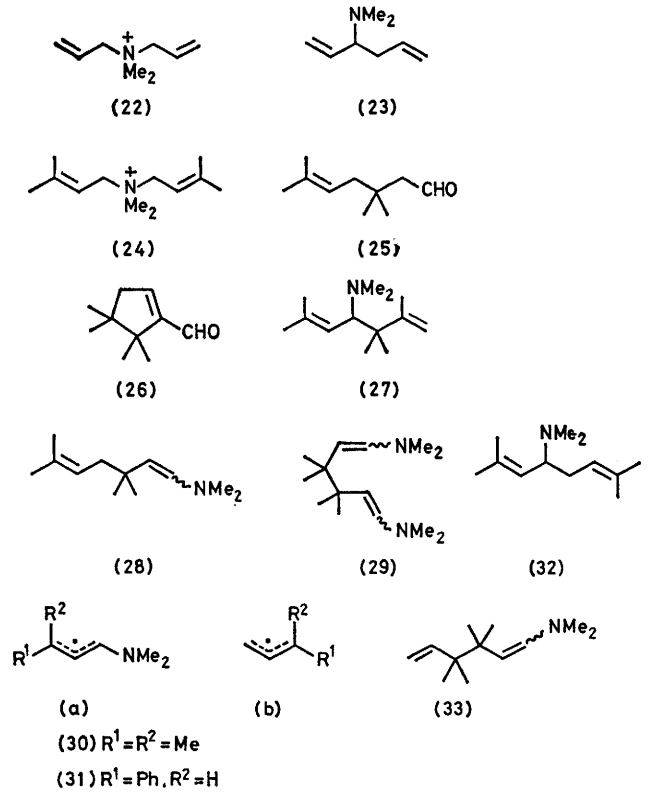

SCHEME 4

methyl ether (19) (yield *ca.* 0.2%), a mixture of hydrocarbons (20) (yield *ca.* 0.2%), and an aldehyde tentatively formulated as compound (21) (yield *ca.* 0.5%). The methyl ether (19) is presumably formed by an alternative nucleophilic displacement of the cation (11) with methoxide anion. The mixture of hydrocarbons (20) was characterised by its mass spectrum but was not investigated further. The aldehyde, whose constitution (21) is tentatively assigned, was observed only as a contaminant in the n.m.r. spectrum of the crude aldehyde (17). Thus the significant products isolated from the base catalysed rearrangement of the ammonium cation (11) using sodium methoxide in dimethyl sulphoxide at room temperature were the [3,2] rearrangement product (14), the [1,2] rearrangement product (16), and the aldehyde (17) equivalent to the enamine (18). The relative yields are given in Table 1.

Highly significant results were obtained by varying the reaction temperature and the time during the base catalysed transformation of the dicinnamylammonium cation (11) (see Table 1). The yield of the [1,2] Stevens rearrangement product (16) is approximately constant (28—23%). However, with increase in reaction temperature and time, the yield of the [3,2] rearrangement product (14) is reduced (65 ⟶ 0%) and the yield of the m.p. 70°. It is, of course, not possible on this evidence to make a decision regarding the transformation (22) ⟶ (23) in terms of either a [1,2] or [3,2] sigmatropic rearrangement but presumably the [3,2] rearrangement is the favoured pathway. In this connection, the base catalysed rearrangement of the bis-3,3-dimethylallylammonium cation (24) was examined using phenyllithium in boiling ether (10 min). Even these mild conditions and short reaction time were associated with an untidy collection of products. No basic products were isolated but mild acid hydrolysis, followed by treatment with 2,4-dinitrophenylhydrazine, gave derivatives corresponding to the aldehydes (25) and (26).

The aldehyde (25) could at first sight arise from the cation (24) during base catalysed rearrangement followed by acidic hydrolysis by a sequence corresponding with that already discussed (Scheme 1). [3,2] Sigmatropic rearrangement of the ylide derived from the cation (24) would yield the amine (27) which by a [3,3] rearrangement could, in principle, give the enamine (28) as the precursor of the isolated aldehyde (25). However, although some [3,3] Cope rearrangements are known to take place at low temperatures these involve rather special circumstances; [26,28] the transformation (27) ⟶ (28) is most unlikely in boiling ether. The alternative

route to the enamine (28) could be a further example of a dissociation–recombination process involving the radical pair (30) derived from the corresponding ylide. Leakage from the solvent cage and dimerisation of the radical




(30a) is an acceptable route to the bisenamine (29) which is a reasonable precursor of the cyclopentenecarbaldehyde (26) isolated after acid hydrolysis. Similarly, the formation in very low yield (*ca.* 0.2%) of the mixture of hydrocarbons (20) from the cation (11) could also involve dimerisation of the radical (31b) derived from the radical-pair (31).

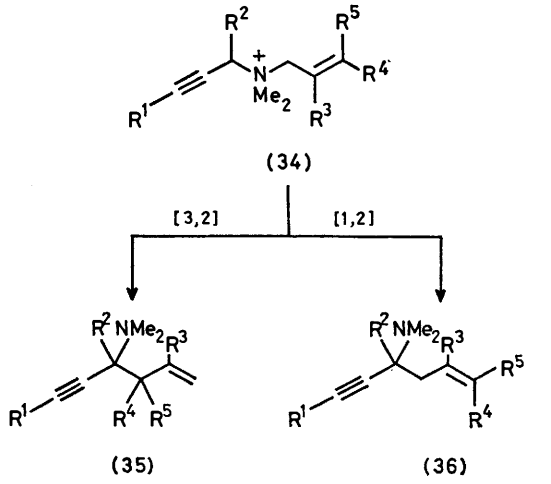
After the conclusion of these studies Rautenstrauch [29] reported a very careful study of the rearrangement of the bis-3,3-dimethylallylammonium cation (24) using sodium amide in liquid ammonia. This is clearly an ideal reagent for this rearrangement (yield 80—75%) giving the products (27), (32), and (33) in the relative proportions 72 : 16 : 12 (at −33°) and 87 : 9 : 4 (at −73°) respectively. Rautenstrauch concludes that at these low temperatures the major reaction product (27) is formed by a [3,2] sigmatropic rearrangement of the ylide whereas the isomers (32) and (33) are formed from the radical pair (30). It may be noted that in spite of a careful search the enamine (28) was not detected as a product using sodium amide in liquid ammonia whereas it is now postulated as the precursor of the isolated aldehyde (25) when phenyl-lithium is used as the basic reagent.

Babayan *et al.*[30] have claimed the isolation of an aldehyde, $C_6H_{10}O$, by boiling the diallylammonium cation (22) with aqueous alkali. This unprecedented stability of an aldehyde under these conditions has been further investigated as have other base catalysed rearrangements described by Babayan.[31] A different interpretation of these transformations is given in Part 6.[32]

*The Base Catalysed Rearrangement of Allylpropynylammonium Cations.*—Iwai and Hiroaka [33] have reported that the allylpropynylammonium cation (34a) is rearranged by boiling aqueous sodium hydroxide giving the amine (35a) (yield 22%). Reinvestigation [24] has shown that the transformation (34a) ⟶ (35a) may be achieved in much higher yield (85%) using sodium methoxide in dimethyl sulphoxide solution at room temperature. This result does not, however, discriminate between product formation from the ylide by either a [1,2] or a [3,2] rearrangement. Further studies have been carried out to answer this question. The high overall yields in this series also encouraged us to examine substituent effects upon the relative yields of the products (35) and (36) determined by competition between [1,2] and [3,2] rearrangements. The results are summarised in Table 2; they have been reported in a

TABLE 2

Yields of products (35) and (36) from base catalysed rearrangements (sodium methoxide–dimethyl sulphoxide) of the allylpropynyl cations (34)



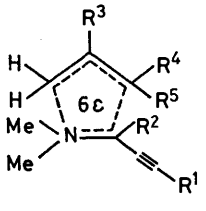

| | R¹ | R² | R³ | R⁴ | R⁵ | Yields of products (%) (35) | (36) |
|---|---|---|---|---|---|---|---|
| (a) | Ph | H | H | H | H | 85 | *a* |
| (b) | Ph | H | Me | H | H | 86 | *a* |
| (c) | Ph | H | Ph | H | H | 55 | *a* |
| (d) | Ph | H | H | Me(H) [b] | H(Me) [b] | 96 (1 : 1) [c] | Trace |
| (e) | Ph | H | H | Ph | H | 91 (6 : 1) [c] | 7 |
| (f) | Ph | H | H | H | Ph | 85 (1 : 9) [c] | |
| (g) | Ph | H | H | Me | Me | 83 | 12 |
| (h) | H | H | H | Ph | H | 99 [d] | |
| (j) | H | Ph | H | Me | Me | 70 | 22 |

[a] The products (35) and (36) from [3,2] and [1,2] rearrangements are identical. [b] The precursor (34) was a mixture of *trans*- and *cis*-crotyl derivatives (*trans* : *cis* *ca.* 4 : 1). [c] The product ratios for mixtures of diastereoisomers (35) were determined by n.m.r. analysis. [d] Only a single diastereoisomer was detectable.

preliminary form.[24] It has been shown that the base catalysed rearrangements of the allylpropynyl cations (34) take completely different courses in aprotic solvents (sodium methoxide–dimethyl sulphoxide) (Table 2) as compared with protic solvents (aqueous sodium hydroxide) (see Part 6).[32] Another interesting development from this study is that it has been shown that the products (35) formed by the [3,2] sigmatropic rearrangement undergo a novel thermal transformation leading eventually to substituted biphenyls (see Part 5).[24,34]

For the cases (a)—(c) of Table 2 it is not possible to distinguish between [3,2] and [1,2] rearrangement because the products from both pathways are structurally identical. However, on the basis of the other results [Table 2; cases (d)—(j)], it seems most likely that the major pathway in all cases (a)—(j) is the [3,2] sigmatropic rearrangement. The base catalysed rearrangement of the allylpropynyl cations (34) is certainly a concerted process involving a bishomo-aromatic six-electron transition state (37) which corresponds to that discussed (Scheme 3) for the corresponding rearrangement of diallylammonium ylides (3). In three cases (34e, g, and j) the products from [1,2] Stevens rearrangements have been isolated; their formation may be associated either with a ' concerted–forbidden ' process or by a dissociation–recombination mechanism involving the radical pair (38).

The relatively lower yield of product (35c) (55%) from the cation (34c) ($R^3$ = Ph), as compared with the yields of products from cations (34a) ($R^3$ = H) and (34b) ($R^3$ = Me), is due to its slower rate of rearrangement. This is presumably due to a steric inhibition of the reaction due to the larger steric demands in the transition state (37) when $R^3$ = Ph as compared with $R^3$ = H or Me. The base catalysed rearrangements in the allylpropynyl series (34) are much cleaner than the rearrangement in the bisallyl series [*e.g.* (11)]. This may well be due in the allylpropynyl series (34) to a relative increase in the stabilisation of the ylide intermediate and a relative decrease of steric interactions in the transition state (37). This decrease in steric interaction is directly attributable to the smaller size of a phenylethynyl group as compared with a styryl group but other factors could be involved.

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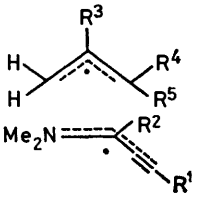
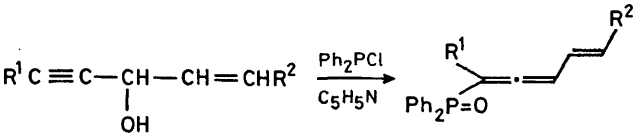



(38)

A final comment on the results given in Table 2 concerns the increase in the yield of the [1,2] Stevens rearrangement product (36) as the number of substituents $R^2$, $R^4$, and $R^5$ is increased. This substituent effect may be interpreted in terms of steric destabilisation of the transition state (37) and stabilisation by the substituents of the radical pair (38). Substituent effects associated with stabilisation of the transition state in a concerted–forbidden process are also possible.[26] There could therefore be an increase in the activation energy associated with the $[_\pi 2_s + _\sigma 2_s + _\omega 2_s]$ [3,2] rearrangement and a decrease in the activation energy of the $[_\sigma 2_s + _\omega 2_s]$ [1,2] rearrangement. These suggestions are based upon the assumption that enthalpy of activation is dominant so that with increased substitution the [1,2] rearrangement (34) ⟶ (36) can compete more effectively with the [3,2] rearrangement (34) ⟶ (35). The sensitivity of the rate of [3,2] sigmatropic rearrangements to steric effects is well established.[35]

It will be noticed that the observed products from base catalysed rearrangements of the allylpropynyl cations (34) do not include a [3,2] sigmatropic rearrangement involving participation by the acetylenic triple bond. This result is in accord with our view [36] that concerted anionic [3,2] sigmatropic rearrangement involving triple bonds is a relatively unlikely process. However, a case of a [3,2] sigmatropic rearrangement (39) ⟶ (40) has




(39) (40)

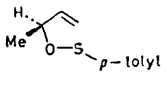
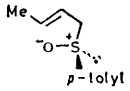
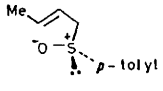
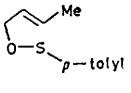
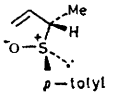
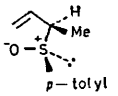
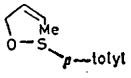
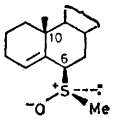
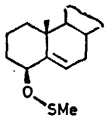
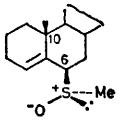
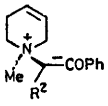
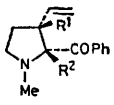
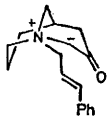
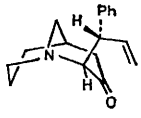
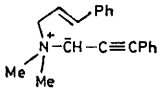
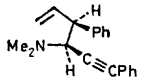
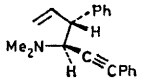
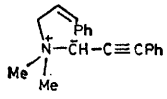
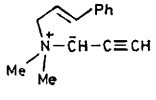
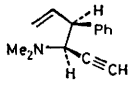
been reported [37] which apparently involves participation by the acetylenic triple bond rather than the ethylenic double bond.

*Stereochemistry of* [3,2] *Anionic Sigmatropic Rearrangements*.—The rearrangements of the isomeric *cis*- and *trans*-cinnamyl derivatives (34e and f) gave high yields (96 and 91%, respectively) of the products (35e and f) as mixtures of diastereoisomers. However, a striking contrast in the ratio of diastereoisomers was observed: (34e) ⟶ (35e); ratio 6 : 1 and (34f) ⟶ (35f); ratio 1 : 9. The relative configurations of the diastereoisomers (35) have not been established, but it is possible to compare the stereochemical characteristics of this [3,2] rearrangement (34) ⟶ (35) with other [3,2] sigmatropic rearrangements which exhibit stereoselectivity in the formation of diastereoisomeric products. This comparison with earlier investigations (Table 3) has brought to our attention some inconsistencies between published results which are briefly mentioned.

The envelope geometry (see Scheme 5) for the transition state of [3,2] anionic sigmatropic rearrangements is generally recognised.[35] This envelope geometry can be associated with two diastereoisomeric transition states (42) and (43) leading to diastereoisomeric products (44) and (45) (Scheme 5). It must be emphasised that the terms *endo* [see (42) ≡ (46)] and *exo* [see (43) ≡ (47)] refer to the configurational relation between the substituent $R^1$ and the planar three-carbon residue C(3)—C(5).

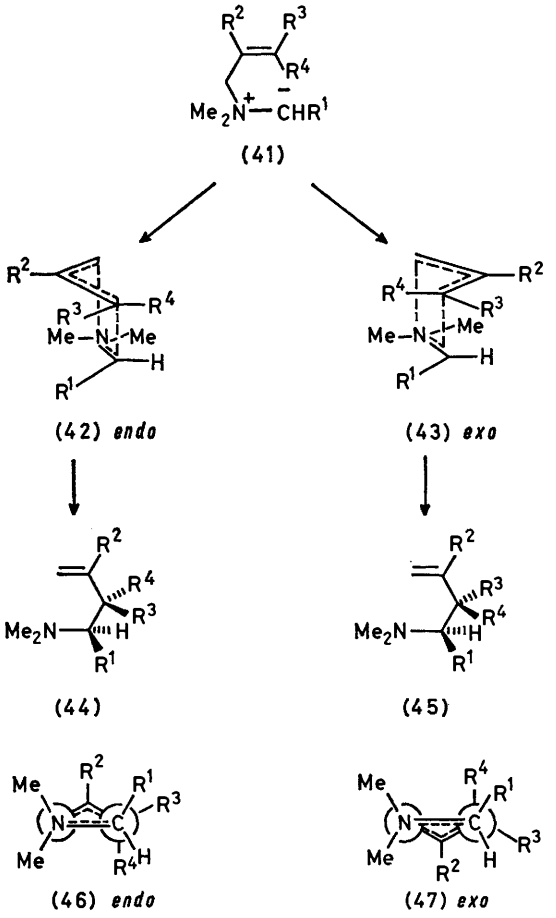
The stereoselectivity in the reactions of ammonium ylides (41) ⟶ (44) or (45) is compared (Table 3) with

TABLE 3

| Reaction | Precursor | Products † A | Products † B | Product ratio A : B | Transition states leading to A or B ‡ | Reference |
|---|---|---|---|---|---|---|
| (i) |  (48) |  (49) |  (50) | 68 32 | *endo* exo | 38a |
| (ii) |  (51) |  (52) |  (53) | 76 24 | *exo* endo | 39 |
| (iii) |  (54) | (52) | (53) | 22 78 | endo *exo* | 39 |
| (iv) |  (55) |  (56) | | 100 | *exo* | 40 |
| (v) |  (57) | (56) | | 100 | *endo* | 40 |
| (vi) |  (58) |  (59) |  (60) | 50 50<br>66 34 | *exo* endo<br>*exo* endo | 41<br>42 |
| (vii) |  (61) | (59) | (60) | 100 | *exo* | 41 |
| (viii) |  (62) |  (63) | | 100 | *endo* | 35 |
| (ix) |  (64) |  (65) | | 100 | *exo* | 43 |
| (x) |  (66) |  (67) |  (68) | 86 14 | *endo* exo | This paper (Table 2) |
| (xi) |  (69) | (67) | (68) | 10 90 | exo *endo* | This paper (Table 2) |
| (xii) |  (70) |  (71) | | 100 | *endo* | This paper (Table 2) |

† The relative configurations given for the pairs of diastereoisomers are those recorded in the literature. The relative configurations (52), (53), (59), and (60) are based upon the selection of an energetically preferred transition state and may require revision.
‡ The preferred transition states are italicised. The decisions recorded in the Table are those given in the original publications.

similar stereoselectivities exhibited in analogous [3,2] sigmatropic rearrangements. Related [3,2] sigmatropic rearrangements involving transfer of chirality are known:[38] some cannot lead to diastereoisomeric products.[38a-c,e] The reactions which have been examined (Table 3), and are relevant to our results, include thermal interconversions between sulphenates and sulphoxides [(i)—(v)], Wittig rearrangements [(vi) and (vii)], and rearrangements involving ammonium ylide intermediates [(viii)—(xii)]. The results summarised in Table 3 also




SCHEME 5

refer to the favoured transition states {*endo* [*cf.* (42) and (46)] or *exo* [*cf.* (43) and (47)]} which have been selected to account for the diastereoisomers formed in major yield. The favoured transition state selected by the authors is italicised in Table 3.

Reaction (i) [38a] is particularly useful because this is the one example where the relation has been firmly established between the chirality of the precursor, (*S*)-α-methylallyl toluene-*p*-sulphenate (48) and the major product, (—)-(*S*)-*trans*-crotyl *p*-tolyl sulphoxide (49). This transfer of chirality from carbon to sulphur in this case and in other similar [3,2] sigmatropic rearrangements has been interpreted, in general geometrical terms, as involving an energetically favoured transition state of the *endo*-type [*cf.* (42) ≡ (46)]. We do not understand, therefore, the statement [39] that the observation that optically active sulphenate (48) rearranges to give optically active sulphoxide (49) 'with at least 37% stereoselectivity can also be explained in terms of preferred *exo*-transition states.' We reaffirm our view that the experimental facts for the rearrangement (48) ⟶ (49) require the geometrical consequences of the *endo*-transition state [*cf.* (42) ≡ (46)]. This opinion helps to remove another difficulty. It has been claimed [39] that the major products from the rearrangements of the sulphenates (51) and (54) are the sulphoxides (52) and (53) respectively, formed in each case by an assumed *exo*-transition state. If the *endo*-transition state for these reactions is assumed to be more favourable, by analogy with the proved stereochemistry [38a] of the reaction (48) ⟶ (49), it is necessary to reassign product stereochemistry in terms of the major *endo*-reaction pathways (51) ⟶ (53) and (54) ⟶ (52).

*exo*-Transition states have also been postulated [41,42] as being associated with the favoured pathway to diastereoisomeric products for the Wittig rearrangements (vi) and (vii). However, these suggestions are not to be regarded as well based since they invoke 'an assumed topography for diastereoisomeric transition states' and a comparison of 'secondary (non-bonding interaction) forces.' [38a] This encouragement [38a] to be cautious in the interpretation of product ratios cannot be easily ignored. Furthermore, the deduction [42] of the relative configurations (59) and (60) rests upon an interpretation [42] of the difference between two vicinal coupling constants (6 and 8 Hz) in diastereoisomeric tetrasubstituted ethanes.[43]

The product ratios associated with the rearrangements (viii)—(xii) of ammonium ylides clearly demonstrate the need for a cautious approach in the interpretation of stereoselective discrimination in the formation of diastereoisomers. The relative configuration of the rearrangement product (63) is well established [35] and this requires that the rearrangement [viii; (62) ⟶ (63)] proceeds exclusively by an *endo*-transition state.[35] On the other hand, the rearrangement [ix; (64) ⟶ (65)] is believed to proceed exclusively by an *exo*-transition state.[44] The origins of the apparent *endo*-stereospecificity (with respect to the COPh group and the allylic residue) in reaction (viii) is under further investigation but it may be noted that secondary orbital interactions between the carbonyl group and allylic residue may well play a determinative role in directing the steric course of the reaction (viii). The thermal isomerisations (iv) and (v) of the steroidal sulphoxides (55) and (57) show a stereospecific transformation to the same sulphenate (56).[40] Thus one reaction (55) ⟶ (56) involves an exclusively *exo*-transition state process and the other (57) ⟶ (56) involves an exclusively *endo*-transition state: these stereospecificities are certainly directed by the steric interaction between the methyl group of the axial 6β-methylsulphinyl group and the axial 10-methyl group [see (55) and (57)].

Reactions (x) and (xi) of the *trans*-cinnamyl ylide (66) and the *cis*-cinnamyl ylide (69) show a striking contrast

in their product ratios: these are (67) : (68) = 86 : 14 and (67) : (68) = 10 : 90. These results support the view that both reactions (x) and (xi) involve transition states of the same type but they do not immediately indicate whether both reactions proceed by *endo*- or *exo*-transition states [*cf.* reactions (ii) and (iii), and (vi) and (vii)]. This decision is not easily made from consideration of the *endo*- and *exo*-transition states (Scheme 5) for the *trans*-cinnamyl ylide (66), but for the *cis*-cinnamyl ylide (69) the distinction between the two transition states appears to be much clearer. For the *cis*-cinnamyl series (Scheme 5; $R^1$ = PhC≡C, $R^2$ = $R^3$ = H, $R^4$ = Ph), comparison of the non-bonding interactions between $R^1$ and $R^4$ indicates that the *endo*-transition state (42) is less sterically hindered than the *exo*-transition state (43). This conclusion must also be extended to the *trans*-cinnamyl series (Scheme 5; $R^1$ = PhC≡C, $R^2$ = $R^4$ = H, $R^3$ = Ph) where again the *endo*-transition state is presumably also energetically favoured. It must be emphasised that decisions between *endo*- and *exo*-transition-states (42) and (43) must be regarded as tentative.

The proposal that the reactions (x) and (xi) involve *endo*-transition states is apparently well based but further work is necessary. This view is obviously supported by the observation that the stereoselectivity (86 : 14) of reaction (x) is increased to (100 : 0) for reaction (xii). This is an interesting trend when the only structural difference between (66) and (70) is the replacement of the PhC≡C group by the smaller HC≡C group.

## EXPERIMENTAL

Unless otherwise stated, i.r. spectra were measured in chloroform, u.v. spectra in ethanol, and 60 and 100 MHz $^1$H n.m.r. spectra in deuteriochloroform (tetramethylsilane as internal reference). Only significant bands from these spectra are quoted. Mass spectra were determined using A.E.I. M.S.9 and M.S.12 high resolution mass spectrometers. M.p.s were determined using a Kofler hot-stage apparatus and are uncorrected. Extracts were dried with either anhydrous magnesium sulphate or sodium sulphate. Evaporation refers to evaporation under diminished pressure.

Separations by column chromatography were carried out using Hopkin and Williams MFC grade silica. Merck Kieselgel G and Reeve Angel Silica CT were used for preparative thick layer and thin layer chromatography. Products were located by examination under u.v. illumination or by spraying with 5% ceric sulphate in 2N-sulphuric acid followed by heating.

When substances are stated to be identical, their identity has been established by comparison of m.p. and mixed m.p.s and where appropriate comparison of i.r., n.m.r., and mass spectra and their behaviour on thin layer chromatography.

NN-*Dimethylcinnamylamine*.—Cinnamyl bromide (19.7 g) [45] in ether (100 ml) was added to a stirred solution of dimethylamine (18 g) in ether (200 ml) at 0°. After 12 h the solution was filtered and evaporation of the filtrate gave a residue which was distilled, b.p. 120° at 10 mmHg, yielding NN-*dimethylcinnamylamine* (15 g, 93%); τ 2.55—2.90 (m, 5 aromatic H), $ABX_2$ system, $\tau_A$ 3.47, $\tau_B$ 3.84, $\tau_X$ 7.00 [$J_{AB}$ 16.5, $J_{BX}$ 6 Hz, $CH_A$=$CH_B$–C($H_X$)$_2$], and 7.80 (s, $NMe_2$). It was characterised as the hydrochloride giving needles, m.p. 190° (lit.,[43] 189—191°) from methanol–ether.

*Dicinnamyldimethylammonium Bromide* (11).—*NN*-Dimethylcinnamylamine (20 g) in ether (150 ml) was added to a solution of cinnamyl bromide (25 g) in ether (150 ml). After 12 h the precipitate was collected and crystallisation from propan-2-ol gave *dicinnamyldimethylammonium bromide* (33 g, 73%) as thick prisms, m.p. 180° (lit.,[25] 177.5—178°); τ ($CF_3CO_2H$) 2.3—2.7 (m, 10 aromatic H), $ABX_2$ system, $\tau_A$ 2.98, $\tau_B$ 3.66, $\tau_X$ 5.88 [$J_{AB}$ 16, $J_{BX}$ 7.5 Hz, two $CH_A$=$CH_B$–C($H_X$)$_2$], and 6.84 (s, $NMe_2$).

*Base Catalysed Rearrangement of Dicinnamyldimethylammonium Bromide* (11). *Formation of* 3,6-*Diphenylhex*-5-*enal* (17), *Cinnamyl Methyl Ether* (19), 3-*Dimethylamino*-1,6-*diphenylhexa*-1,5-*diene* (16), *and* 3-*Dimethylamino*-1,4-*diphenylhexa*-1,5-*diene* (14).—(A). Dicinnamyldimethylammonium bromide (17.9 g) in dimethyl sulphoxide (25 ml) was added to a solution prepared from sodium hydride (2.4 g), methanol (3 ml), and dimethyl sulphoxide (25 ml). After 24 h at room temperature, the mixture was poured into water and extracted with ether (2 × 100 ml). The ethereal extracts were extracted with 2N-hydrochloric acid (3 × 50 ml) giving an ethereal neutral fraction (i) and an aqueous acidic fraction (ii).

Fraction (i) was dried and evaporated giving an oil (800 mg, 6%) which was separated by preparative t.l.c. (silica gel, benzene) into fraction (a), a mixture of hydrocarbons (0.25 g) (Found: $M^+$, 234. Calc. for $C_{18}H_{18}$: *M*, 234); fraction (b), a mixture of aldehydes, homogeneous on t.l.c. (0.6 g), and fraction (c). Crystallisation of fraction (b) from hexane gave 3,6-*diphenylhex*-5-*enal* (17) as prisms, m.p. 77° (Found: C, 86.4; H, 7.2. $C_{18}H_{18}O$ requires C, 86.8; H, 7.0%); $\nu_{max.}$ 1 720 and 970 cm$^{-1}$; n.m.r.: $AL_2MN_2XY$ system, $\tau_A$ 0.35, $\tau_Y$ 3.58, $\tau_X$ 3.95, $\tau_M$ 6.60, $\tau_L$ 7.24, $\tau_N$ 7.44 [$J_{AL}$ 2, $J_{LM}$ 7, $J_{MN}$ 7, $J_{NX}$ 7, $J_{XY}$ 16 Hz, $-CH_Y$=$CH_X$–C($H_N$)$_2$–$CH_M$–C($H_L$)$_2$$CH_A$=O], and τ 2.69br (s, 10 aromatic *H*) (Found: $M^+$, 250. $C_{18}H_{18}O$ requires *M*, 250), *m/e* 206 (*M* − $CH_3CHO$) and 117 (PhCH=$CH^+$–$CH_2$). The n.m.r. spectrum of the crude aldehyde fraction (b) shows, in addition to the signals due to 3,6-diphenylhex-5-enal (17), extra signals at τ 0.60 (t), 3.8—4.2 (m), 4.7—5.3 (m), 6.3—6.5 (m), and 7.1—7.6 (m) attributed to the isomer 3,4-*diphenylhex*-5-*enal* (21). Fraction (c) yielded *cinnamyl methyl ether* (19) (0.05 g); τ 2.5—2.9 (m, 5 aromatic H), $ABX_2$ system, $\tau_A$ 3.48, $\tau_B$ 3.80, $\tau_X$ 6.05 [$J_{AB}$ 16, $J_{AX}$ 6 Hz, $-CH_A$=$CH_B$–C($H_X$)$_2$–], and 6.74 (s, OMe); $M^+$ 148.

Fraction (ii) was neutralised with 5N-sodium hydroxide solution and extracted with ether (2 × 100 ml). The extracts were dried and evaporated giving an oil (12.9 g, 93%) which was separated into fractions (d) and (e) by preparative t.l.c.

(d), 3-*Dimethylamino*-1,4-*diphenylhexa*-1,5-*diene* (14), was obtained as a yellow oil (65%); τ 2.90 (s, 10 aromatic H), ABMNXYZ system, $\tau_A$ 3.88, $\tau_X$ 3.80, $\tau_B$ 4.08, $\tau_Y$ 4.94, $\tau_Z$ 4.98, $\tau_N$ 6.47, $\tau_M$ 6.71 ($J_{AB}$ 15, $J_{BM}$ 8, $J_{MN}$ 9, $J_{NX}$ 9, $J_{XY}$ 11, $J_{XZ}$ 17, $J_{YZ}$ 2 Hz, $-CH_A$=$CH_B$–$CH_M$–$CH_N$–$CH_X$=$CH_YH_Z$), and 7.72 (s, $NMe_2$). A second diastereoisomer (14), τ 7.52 ($NMe_2$), was also present in minor amount (ratio 10 : 1) (Found: $M^+$, 277. $C_{20}H_{23}N$ requires *M*, 277), *m/e* 160 (*M* − PhCH=CH–$CH_2$). The amine (14) was characterised as the *picrate*, yellow prisms, m.p. 158°, from benzene (Found: C, 61.7; H, 4.9; N, 11.0. $C_{26}H_{26}N_4O_7$ requires C, 61.7; H, 5.1; N, 11.1%).

(e), 3-*Dimethylamino*-1,6-*diphenylhexa*-1,5-*diene* (16), was obtained as a yellow oil (28%), τ 2.5—2.9 (m, 10 aromatic H), ABMN$_2$XY system, $\tau_A$, $\tau_Y$, 3.56 and 3.58, $\tau_B$,$\tau_X$ 3.6—4.0, $\tau_M$ 6.99, $\tau_N$ 7.3—7.6 [$J_{AB}$ 15, $J_{BM}$ 7, $J_{MN}$ 5, $J_{NX}$ 7, $J_{XY}$ 15 Hz, $-CH_A{=}CH_B{-}CH_M{-}C(H_N)_2{-}CH_X{=}CH_Y-$], and 7.71 (s, $NMe_2$) (Found: $M^+$, 277. $C_{20}H_{23}N$ requires $M$, 277), $m/e$ 160 ($M$ − PhCH=CH−$CH_2$). The amine (16) was characterised as its *methiodide*, prisms, m.p. 149°, from methanol–ether (Found: C, 60.3; H, 6.1; N, 3.6. $C_{21}H_{26}IN$ requires C, 60.2; H, 6.2; N, 3.3%).

(B). Dicinnamyldimethylammonium bromide (11) (3.6 g) in methanol (20 ml) was added to a solution of sodium methoxide prepared from sodium (12 g) and methanol (100 ml) and the mixture was heated (1 h at 80°). The mixture was worked up as before giving 3,6-diphenylhex-5-enal (17) (1.25 g, 50%), and a mixture (1.3 g, 47%) of 3-dimethylamino-1,4-diphenylhexa-1,5-diene (14) (24%) and 3-dimethylamino-1,6-diphenylhexa-1,5-diene (16) (23%).

(C). When experiment (B) was repeated, maintaining the reaction mixture at 85° for 15 h, the products were the aldehyde (17) (1.88 g, 76%) and the amine (16) (0.62 g, 23%).

NN-*Dimethylallylamine*.[46]—Allylamine (25 ml) was added dropwise with cooling to formic acid (51.2 g, 90%) followed by the addition of formaldehyde (45 ml, 37%). The mixture was heated (12 h) at 100° then concentrated hydrochloric acid (50 ml) was added and the volatile material was removed by evaporation. The residue was basified with aqueous 5N-sodium hydroxide and the oil was separated, dried (KOH), and distilled in contact with solid potassium hydroxide. *NN*-Dimethylallylamine (13 g, 46%) was obtained as a liquid, b.p. 60—62° (lit.,[46] 63—63.5°); n.m.r.: ABMX$_2$ system, $\tau_M$ 3.8—4.5, $\tau_A$, $\tau_B$ 4.7—5.1, $\tau_X$ 7.15 [$J_{MX}$ 6 Hz, $CH_AH_B{=}CH_M{-}C(H_X)_2-$] and 7.83 (s, $NMe_2$).

NN-*Diallyldimethylammonium Bromide*[47] (22).—*NN*-Dimethylallylamine (8.5 g) and allyl bromide (11.2 g) were boiled (12 h) in anhydrous ether (50 ml). The precipitate was collected and washed with ether (3 × 15 ml) giving NN-*diallyldimethylammonium bromide* (22) (15 g, 73%), m.p. 99° (sealed capillary) (previously reported[47] as an oil). The salt was extremely hygroscopic and was not analysed; n.m.r. ($D_2O$): ABMX$_2$ system, $\tau_A$, $\tau_B$, $\tau_M$ 3.8—4.5, $\tau_X$ 6.08 [$J_{MX}$ 6 Hz, $CH_AH_B{=}CH_M{-}C(H_X)_2$] and 6.97 (s, $\overset{+}{N}Me_2$).

*Base Catalysed Rearrangement of* NN-*Diallyldimethylammonium Bromide* (22). *Formation of* 3-*Dimethylamino-hexa*-1,5-*diene* (23).—*NN*-Diallyldimethylammonium bromide (8.2 g) in dimethyl sulphoxide (5 ml) was added to a solution prepared from sodium hydride (2.4 g), dimethyl sulphoxide (25 ml), and methanol (5 ml). After 12 h at room temperature the mixture was diluted with water and extracted with ether (3 × 75 ml). The basic products were extracted into 2N-hydrochloric acid (3 × 100 ml), neutralised with 10N-sodium hydroxide and re-extracted with ether (2 × 100 ml). Evaporation yielded 3-*dimethylamino-hexa*-1,5-*diene* (23) (2.5 g, 50%) as a pale yellow oil; τ 3.9—5.2 (m, 6 vinylic H), 7.1—7.9 (m, 3 allylic H), and 7.85 (s, $NMe_2$). The amine (23) was characterised as its *picrate* which crystallised from benzene as yellow prisms, m.p. 70° (Found: C, 47.7; H, 5.1; N, 15.6. $C_{14}H_{18}N_4O_7$ requires C, 47.5; H, 5.1; N, 15.8%).

NN-*Dimethyl*-3,3-*dimethylallylamine*.[48]—Anhydrous dimethylamine (250 ml) was slowly distilled into a stirred mixture of isoprene (247 g) and finely divided sodium (1 g) at 0°. After 18 h the solution was filtered and distillation gave *NN*-dimethyl-3,3-dimethylallylamine (290 g, 72%), b.p. 117—120° (lit.,[48] 113—115°); n.m.r.: AX$_2$ system, $\tau_A$ 4.75, $\tau_X$ 7.18 [$J_{AX}$ 7 Hz, $H_A$ shows additional long range coupling, $J$ 1.7 Hz, to the methyl groups, $=CH_A{-}C(H_X)_2$], 7.83 (s, $NMe_2$), and 8.27 and 8.37 (s, two vinylic Me).

NN-*Dimethylbis*-(3,3-*dimethylallyl*)*ammonium Chloride* (24).—3,3-Dimethylallyl chloride[49] (10.4 g) and *NN*-dimethyl-3,3-dimethylallylamine (10.3 g) in benzene (200 ml) were heated under reflux for 20 h. The hygroscopic precipitate was collected, washed with anhydrous ether and NN-*dimethylbis*-(3,3-*dimethylallyl*)*ammonium chloride* (24) (20 g, 97%) was obtained, m.p. 115° (lit.,[50] 111°), n.m.r. ($CF_3CO_2H$): AX$_2$ system, $\tau_A$ 4.57, $\tau_X$ 6.14 [$J_{AX}$ 8 Hz, two $\overset{+}{N}CH_A{-}C(H_X)_2$], 7.05 (s, $\overset{+}{N}Me_2$), and 8.07 and 8.15 (s, 4 vinylic Me).

*Base Catalysed Rearrangement of* NN-*Dimethylbis*-(3,3-*dimethylallyl*)*ammonium Chloride* (24). *Formation of* 3,3,7-*Trimethylhept*-5-*enal* (25) *and* 4,4,5,5-*Tetramethylcyclopent*-1-*enecarbaldehyde* (26).—*NN*-Dimethylbis-(3,3-dimethylallyl)ammonium chloride (9.6 g) suspended in ether (50 ml) was added to a standardised solution of phenyl-lithium (2 equiv.) in ether (500 ml). The mixture was heated under reflux for 10 min, cooled, diluted with water, and the ethereal layer was separated and shaken with 2N-sulphuric acid (2 × 50 ml). Evaporation of the ethereal solution yielded an oil (740 mg) which was dissolved in ethanol (5 ml) and added to an acidic solution of 2,4-dinitrophenylhydrazine. The mixture was heated at 80° for 10 min. The precipitate was collected and fractional crystallisation from ethanol gave two 2,4-dinitrophenylhydrazones: (i) 550 mg and (ii) 100 mg. Dinitrophenylhydrazone (i) crystallised from methanol giving 3,3,7-*trimethylhept*-5-*enal* 2,4-*dinitrophenylhydrazone* as dark orange needles, m.p. 91° (Found: C, 57.1; H, 6.6; N, 17.0. $C_{16}H_{22}N_4O_4$ requires C, 57.5; H, 6.6; N, 16.8%); τ −1.03br (s, NH), AMX system, $\tau_A$ 0.94, $\tau_M$ 1.72, $\tau_X$ 2.08 ($J_{AM}$ 2.5, $J_{MX}$ 9.5 Hz, 3′-, 5′-, and 6′-H), AX$_2$ system, $\tau_A$ 2.38, $\tau_X$ 7.67 [$J_{AX}$ 6 Hz, $-C(H_X)_2{-}CH_A{=}N$], AX$_2$ system, $\tau_A$ 4.74, $\tau_X$ 8.00 [$J_{AX}$ 7.5 Hz, $=CH_A{-}C(H_X)_2-$], τ 8.23 and 8.37 (s, two vinylic Me), and 9.00 (s, two aliphatic Me).

Dinitrophenylhydrazone (ii) crystallised from ethanol giving 4,4,5,5-*tetramethylcyclopent*-1-*enecarbaldehyde* 2,4-*dinitrophenylhydrazone* as red plates, m.p. 208° (Found: C, 57.6; H, 6.0; N, 16.9. $C_{16}H_{20}N_4O_4$ requires C, 57.8; H, 6.0; N, 16.9%); τ −1.18br (s, NH), AMX system, $\tau_A$ 0.88, $\tau_M$ 1.65, $\tau_X$ 2.17 ($J_{AM}$ 9.5, $J_{MX}$ 2.5 Hz, 3′, 5′-, and 6′-H), 2.13 (s, CH=N), AX$_2$ system, $\tau_A$ 3.77, $\tau_X$ 7.72 [$J_{AX}$ 7 Hz, $=CH_A{-}C(H_X)_2-$], 8.00 (s) and 9.00 (s, 4 aliphatic Me).

NN-*Dimethyl*-(3-*phenylprop*-2-*ynyl*)*amine*.[33]— Dimethylamine hydrochloride (82 g), aqueous formaldehyde (120 ml, 37%), copper(I) chloride (2.6 g), and phenylacetylene (102 g) gave *NN*-dimethyl-(3-phenylprop-2-ynyl)amine (115 g, 72%), b.p. 69° at 0.9 mmHg (lit.,[33] 105—106° at 8 mmHg); τ 2.5—2.9 (m, 5 aromatic H), 6.61 (s, $CH_2{-}N$), and 7.71 (s, $NMe_2$).

*Allyldimethyl*-(3-*phenylprop*-2-*ynyl*)*ammonium Bromide* (34a).—*NN*-Dimethyl-(3-phenylprop-2-ynyl)amine (16.0 g) in ether (100 ml) was added to a solution of allyl bromide (12.0 g) in ether (100 ml) with ice-cooling. After 12 h the ether was decanted and the gummy salt was dissolved in water and shaken with ether (2 × 50 ml). The aqueous layer was evaporated giving the *salt* (34a) as a gum (27 g, 96%); τ ($CF_3CO_2H$) 2.3—2.7 (m, 5 aromatic H), ABMX$_2$ system, $\tau_A$, $\tau_B$, $\tau_M$ 3.7—4.3, $\tau_X$ 5.87 [$J_{MX}$ 7 Hz, $CH_AH_B{=}$

$CH_M$–$C(H_X)_2$], 5.57 (s, C≡C–$CH_2$), and 6.77 (s, $\overset{+}{N}Me_2$).

*Base Catalysed Rearrangement of Allyldimethyl-(3-phenylprop-2-ynyl)ammonium Bromide* (34a). *Formation of 3-Dimethylamino-1-phenylhex-5-en-1-yne* (35a).—Allyldimethyl-(3-phenylprop-2-ynyl)ammonium bromide (27 g) in dimethyl sulphoxide (50 ml) was added to a solution prepared from sodium hydride (2.5 g), methanol (3 ml), and dimethyl sulphoxide (50 ml). After 2 h the mixture was poured into water and extracted with ether (2 × 100 ml). The ethereal extracts were shaken with 2N-hydrochloric acid (2 × 100 ml) and the acidic layer was basified with 5N-sodium hydroxide and extracted with ether (2 × 75 ml). The ethereal solution was dried and evaporated to give a yellow oil (19.5 g) which was distilled, b.p. 134° at 0.4 mmHg (lit.,[33] 114—115° at 5 mmHg), yielding *3-dimethylamino-1-phenylhex-5-en-1-yne* (35a) (16.7 g, 85%); τ 2.5—2.9 (m, 5 aromatic H), ABM$X_2$Y system, $\tau_M$ 4.09, $\tau_B$ 4.87, $\tau_A$ 4.93, $\tau_Y$ 6.43, $\tau_X$ 7.55 [$J_{BM}$ 17, $J_{AM}$ 10, $J_{MX}$ 6.5, $J_{XY}$ 7.5 Hz, $CH_AH_B$=$CH_M$–$C(H_X)_2$–$CH_Y$], and 7.69 (s, $NMe_2$). The amine (35a) was characterised as its *picrate*, m.p. 119° (ethanol) (Found: C, 56.1; H, 4.7; N, 13.1. $C_{20}H_{20}N_4O_7$ requires C, 55.7; H, 4.9; N, 13.0%).

*Dimethyl-(2-methylallyl)-(3-phenylprop-2-ynyl)ammonium Chloride* (34b).—A solution of *NN*-dimethyl-(3-phenylprop-2-ynyl)amine (8 g) in acetonitrile (10 ml) was added to a solution of 2-methylallyl chloride (4.5 g) in acetonitrile (10 ml). After 1 h the solution was diluted with ether (200 ml) and the crystals were collected giving *dimethyl-(2-methylallyl)-(3-phenylprop-2-ynyl)ammonium chloride* (34b) (10 g), m.p. 158—160° (Found: C, 72.2; H, 8.1; N, 5.5; Cl, 14.0. $C_{15}H_{20}ClN$ requires C, 72.0; H, 8.0; N, 5.6; Cl, 14.2%); τ 2.5—2.8 (m, 5 aromatic H), 4.37 and 4.47 (two s, $\overset{+}{N}Me_2$=$CH_2$), 4.89 (s, C≡C–$CH_2$), 5.44 (s, =C–$CH_2$), 6.44 (s, $\overset{+}{N}Me_2$), and 7.93 (s, vinylic Me).

*Base Catalysed Rearrangement of Dimethyl-(2-methylallyl)-(3-phenylprop-2-ynyl)ammonium Chloride* (34b). *Formation of 3-Dimethylamino-5-methyl-1-phenylhex-5-en-1-yne* (35b).—The ammonium salt (34b) (5.0 g) was dissolved in dimethyl sulphoxide (10 ml) and treated with a solution prepared from sodium hydride (0.48 g), methanol (1 ml), and dimethyl sulphoxide (25 ml). The solution was stirred at room temperature for 24 h, poured into water, and extracted with ether. The ethereal layer was washed with water, dried, and evaporated giving *3-dimethylamino-5-methyl-1-phenylhex-5-en-1-yne* (35b) (3.6 g, 86%) as the sole product; τ 2.5—2.8 (m, 5 aromatic H), 5.14br (s, =$CH_2$), $AX_2$ system, $\tau_A$ 6.27, $\tau_X$ 7.56 [$J_{AX}$ 8 Hz, –$CH_A$–$C(H_X)_2$–], 7.69 (s, $NMe_2$), and 8.20 (t, *J* 1 Hz, vinylic Me). The amine (35b) was characterised as its *picrate*, yellow prisms from ethanol, m.p. 123—124° (Found: C, 56.9; H, 5.3; N, 12.7. $C_{21}H_{22}N_4O_7$ requires C, 57.0; H, 5.0; N, 12.7%).

*Dimethyl-(2-phenylallyl)-(3-phenylprop-2-ynyl)ammonium Bromide* (34c).—A mixture of 2-phenylallyl bromide [51] (10 g) and *NN*-dimethyl-3-phenylprop-2-ynylamine (10 g) in dry ether was left at room temperature for 3 days. The resultant precipitate of *dimethyl-(2-phenylallyl)-(3-phenylprop-2-ynyl)ammonium bromide* (34c) (19 g) was collected (Found: C, 67.3; H, 5.9; N, 3.8; Br, 22.6. $C_{20}H_{22}BrN$ requires C, 67.4; H, 6.2; N, 3.9; Br, 22.5%); τ ($CDCl_3$–$CF_3CO_2H$) 2.4—2.8 (m, 10 aromatic H), 4.09 and 4.11 (two s, $\overset{+}{N}Me_2$=$CH_2$), 5.28 (s, $CH_2$C≡C), 5.56 (s, $CH_2$C=), and 6.82 (s, $\overset{+}{N}Me_2$).

*Base Catalysed Rearrangement of Dimethyl-(2-phenylallyl)-(3-phenylprop-2-ynyl)ammonium Bromide* (34c). *Formation of 3-Dimethylamino-1,5-diphenylhex-5-en-1-yne* (35c).—A solution of the ammonium salt (34c) (3.6 g) in dimethyl sulphoxide (10 ml) was treated with a solution prepared from sodium hydride (0.24 g), methanol (0.5 ml), and dimethyl sulphoxide (25 ml). The mixture was stirred at room temperature for 24 h, poured into water, and extracted with ether. The ethereal extracts were washed with water, dried, and evaporated giving *3-dimethylamino-1,5-diphenylhex-5-en-1-yne* (35c) (1.5 g, 55%) as a pure product; τ 2.5—2.9 (m, 10 aromatic H), 4.65br and 4.78br (two s, =$CH_2$), ABX system, $\tau_A$ 7.09, $\tau_B$ 7.11, $\tau_X$ 6.38 ($J_{AX}$ 6, $J_{BX}$ 9 Hz, –$CH_X$–$CH_AH_B$–), and 7.70 (s, $NMe_2$) (Found: $M^+$, 275. $C_{20}H_{21}N$ requires *M*, 275), *m/e* 158 (PhC≡C–CH=$\overset{+}{N}$Me) and 115 (PhC≡C–$CH_2^+$). The amine (35c) was characterised as its *methiodide*, prisms from ethyl acetate–methanol, m.p. 155—156° (Found: C, 60.1; H, 6.0; N, 3.7; I, 30.5 $C_{21}H_{24}IN$ requires C, 60.4; H, 5.75; N, 3.4; I, 30.5%).

cis- *and* trans-*(But-2-enyl)dimethyl-(3-phenylprop-2-ynyl)-ammonium Bromide* (34d).—A solution of commercial *cis*- and *trans*-crotyl bromide (13.5 g) in dry benzene (50 ml) was treated with a solution of *NN*-dimethyl-(3-phenylprop-2-ynyl)amine (15.9 g) in dry benzene (50 ml). After 24 h, the resultant precipitate of a mixture of cis- and trans-*but-2-enyldimethyl-(3-phenylprop-2-ynyl)ammonium bromide* (34d) was collected (29 g, 95%) (Found: C, 61.4; H, 6.8; N, 4.6; Br, 27.3. $C_{15}H_{20}BrN$ requires C, 61.2; H, 6.8; N, 4.7; Br, 27.2%). The n.m.r. spectrum showed that it is a mixture of *trans*- and *cis*-isomers (ratio *ca.* 4 : 1): *trans*-isomer, τ 2.5—2.7 (m, 5 aromatic H), $A_2MNX_3$ system, $\tau_A$ 5.44, $\tau_M$ 4.13, $\tau_N$ 3.70, $\tau_X$ 8.18 [$J_{AM}$ 8, $J_{MN}$ 14, $J_{NX}$ 7 Hz, –$C(H_A)_2$–$CH_M$=$CH_N$–$C(H_X)_3$–], 4.98 (s, $CH_2$C≡C), and 6.51 (s, $\overset{+}{N}Me_2$). The *cis*-isomer shows peaks at τ 8.05 (*J* 7 Hz) and 4.90 (s, $CH_2$C≡C); all the other peaks are obscured by those of the *trans*-isomer.

*Base Catalysed Rearrangement of* cis- *and* trans-*But-2-enyldimethyl-(3-phenylprop-2-ynyl)ammonium Bromide* (34d). *Formation of Diastereoisomers A and B of 3-Dimethylamino-4-methyl-1-phenylhex-5-en-1-yne* (35d).—The salt (34d) (9 0 g) was dissolved in dimethyl sulphoxide (40 ml) and treated with a solution prepared from sodium hydride (0.72 g), methanol (1.5 ml), and dimethyl sulphoxide (50 ml). The mixture was stirred for 16 h poured into water and extracted with ether (3 × 100 ml). The ether extracts were washed with water and extracted with 2N-hydrochloric acid (2 × 50 ml). The ethereal layer was dried and evaporated giving a brown oil (50 mg) which was not examined further. The acidic extracts were basified with 5N-sodium hydroxide and extracted with ether (2 × 100 ml). The ethereal extracts were dried and evaporated giving a pale yellow oil (6.1 g, 96%) which was shown by n.m.r. to consist of two major components (ratio *ca.* 1 : 1). Preparative t.l.c. (silica gel–chloroform) gave fraction (a) consisting of *diastereoisomer A* of *3-dimethylamino-4-methyl-1-phenylhex-5-en-1-yne* (35d) as a pale yellow oil; τ 2.5—2.8 (m, 5 aromatic H), ABC$XM_3$Y system, $\tau_C$ 4.10, $\tau_B$ 4.92, $\tau_A$ 4.90, $\tau_X$ 6.72, $\tau_Y$ *ca.* 7.5, $\tau_M$ 8.79 {$J_{AB}$ 2, $J_{AC}$ 16, $J_{BC}$ 9, $J_{CX}$ 7, $J_{MX}$ 6.5, $J_{XY}$ 10 Hz, $CH_AH_B$=$CH_C$–$CH_X$[$C(H_M)_3$]–$CH_Y$–}, and 7.69 (s, $NMe_2$) (Found: $M^+$, 213. $C_{15}H_{19}N$ requires *M*, 213), *m/e* 158 and 115. The amine was characterised as its *methiodide*, prisms, m.p. 116—117°, from ethanol–ether (Found: C, 53.9; H, 6.3; N, 3.8; I, 35.95. $C_{16}H_{22}IN$ requires C, 54.1; H, 6.2; N, 3.9; I, 35.8%); and fraction (b) consisting of *diastereoisomer B* of *3-dimethylamino-4-methyl-1-phenylhex-5-en-1-yne* (35d) as a pale yellow oil; τ 2.5—2.8 (m, 5 aromatic H), ABC$XM_3$Y system, $\tau_C$ 4.00, $\tau_B$ 4.90, $\tau_A$ 4.87, $\tau_X$ 6.80, $\tau_Y$ *ca.* 7.5, $\tau_M$ 8.87

{$J_{AB}$ 2, $J_{BC}$ 9, $J_{AC}$ 17, $J_{CX}$ 7, $J_{MX}$ 6.5, $J_{XY}$ 10 Hz, $CH_AH_B$=$CH_C$–$CH_X$[$C(H_M)_3$]–$CH_Y$–}, and 7.61 (s, $NMe_2$) (Found: $M^+$, 213. $C_{15}H_{19}N$ requires $M$, 213), *m/e* 158 and 115. The amine was characterised as its *methiodide*, crystals, m.p. 175—178° from ethanol–ether (Found: C, 54.1; H, 6.5; N, 3.9; I, 35.7. $C_{16}H_{22}IN$ requires C, 54.1; H, 6.2; N, 3.9; I, 35.8%).

*Cinnamyldimethyl-(3-phenylprop-2-ynyl)ammonium Bromide* (34e).—A mixture of cinnamyl bromide (19.7 g) and *NN*-dimethyl-(3-phenylprop-2-ynyl)amine (15.9 g) in ether (300 ml) slowly deposited a precipitate. After 24 h, the precipitate was collected and recrystallised from acetone giving *cinnamyldimethyl-(3-phenylprop-2-ynyl)ammonium bromide* (34e) (30 g, 87%), as prisms, m.p 145—146° (Found: C, 67.0; H, 6.2; N, 3.8; Br, 22.6. $C_{20}H_{22}BrN$ requires C, 67.0; H, 6.2; N, 3.9; Br, 22.5%); τ 2.4—2.7 (m, 10 aromatic H), $ABX_2$ system, $\tau_A$ 2.83, $\tau_B$ 3.60, $\tau_X$ 5.21 [$J_{AB}$ 16, $J_{BX}$ 7 Hz, $PhCH_A{=}CH_B{-}C(H_X)_2{-}\overset{+}{N}$], 4.94 (s, $C{\equiv}C{-}CH_2$), and 6.45 (s, $\overset{+}{N}Me_2$).

*Base Catalysed Rearrangement of Cinnamyldimethyl-(3-phenylprop-2-ynyl)ammonium Bromide* (34e). *Formation of 3-Dimethylamino-1,4-diphenylhex-5-en-1-yne* (35e) *and 3-Dimethylamino-1,6-diphenylhex-5-en-1-yne* (36e).—The salt (34e) (3.56 g) in dimethyl sulphoxide (20 ml) was treated with a solution prepared from sodium hydride (0.24 g), methanol (0.5 ml), and dimethyl sulphoxide (20 ml). The mixture was stirred at room temperature for 12 h, poured into water, and extracted with ether (2 × 100 ml). The combined ethereal extracts were washed with water several times, then separated into neutral and basic fractions using 2N-hydrochloric acid and 5N-sodium hydroxide. The resultant ethereal solutions were dried and evaporated yielding a neutral fraction (47 mg) and a basic fraction (2.7 g, 98%). The neutral fraction was a complex mixture and was not examined further. The basic fraction was separated into two components by preparative t.l.c. [silica gel–(chloroform–ethyl acetate 2 : 1)].

Fraction (i) was 3-dimethylamino-1,4-diphenylhex-5-en-1-yne (35e) (91%), a pale yellow oil; τ 2.6—3.0 (m, 10 aromatic H), ABMXY system, $\tau_A$ 6.20, $\tau_B$ 6.50, $\tau_M$ 3.80, $\tau_X$ 4.90, $\tau_Y$ 4.96 [$J_{AB}$ 10, $J_{BM}$ 8, $J_{MX}$ 10, $J_{MY}$ 18, $J_{XY}$ *ca.* 1 Hz, $CH_A{-}CH_B{-}CH_M{=}CH_XH_Y$], 7.67 (s, $NMe_2$), and 7.74 (s, $NMe_2$). The two signals (τ 7.67 and 7.74) were attributed to two diastereoisomers present in the ratio *ca.* 6 : 1 (Found: $M^+$, 275. $C_{20}H_{21}N$ requires $M$, 275), *m/e* 230 ($M$ – $HNMe_2$), 158, and 115. The amine (35e) was characterised as its *picrate*, as yellow prisms, m.p. 151°, from ethanol (Found: C, 61.6; H, 5.9; N, 10.9. $C_{26}H_{24}N_4O_7$ requires C, 61.9; H, 4.7; N, 11.1%).

Fraction (ii) was *3-dimethylamino-1,6-diphenylhex-5-en-1-yne* (36e) (7%), a pale yellow oil; τ 2.4—2.7 (m, 10 aromatic H), $AB_2XY$ system, $\tau_A$ 6.36, $\tau_B$ 7.40, $\tau_X$ 3.70, $\tau_Y$ 3.50 [$J_{AB}$ 7, $J_{BX}$ 6, $J_{XY}$ 18 Hz, $CH_A{-}C(H_B)_2{-}CH_X{=}CH_Y{-}$] (Found: $M^+$, 275. $C_{20}H_{21}N$ requires $M$, 275), *m/e* 230, 158, and 115.

NN-*Dimethyl-*(cis-*cinnamyl)amine*.— *NN*-Dimethyl-(3-phenylprop-2-ynyl)amine (15.8 g) in methanol (50 ml) was partially hydrogenated (5% Pd–$BaSO_4$ catalyst; 0.6 g) until hydrogen (1 mol. equiv., 2 240 ml) had been absorbed. The solution was then filtered and evaporated and the resultant oil was distilled giving NN-*dimethyl-*(cis-*cinnamyl)-amine* as a liquid (14 g, 87%), b.p. 108—110° at 13 mmHg; τ 2.6—2.8 (m, 5 aromatic H), $ABX_2$ system, $\tau_A$ 3.41, $\tau_B$ 4.20, $\tau_X$ 6.81 [$J_{AB}$ 12, $J_{BX}$ 6, $J_{AX}$ 2 Hz, $CH_A{=}CH_B{-}C(H_X)_2{-}N$], and 7.76 (s, $NMe_2$). The amine was characterised as its *methiodide*, m.p. 121—122°, from ethanol (Found: C, 47.5; H, 6.25; N, 4.5; I, 41.6. $C_{12}H_{18}IN$ requires C, 47.5; H, 5.9; N, 4.6; I, 41.9%).

cis-*Cinnamyldimethyl-(3-phenylprop-2-ynyl)ammonium Bromide* (34f).—A solution of *NN*-dimethyl-(*cis*-cinnamyl)-amine (2 g) in acetonitrile (5 ml) was added to a solution of 3-phenylprop-2-ynyl bromide (2 g) in acetonitrile (5 ml). After the initial exothermic reaction had subsided, the salt was precipitated with dry ether giving cis-*cinnamyldimethyl-(3-phenylprop-2-ynyl)ammonium bromide* (34f) as a gum; τ 2.5—3.0 (m, 10 aromatic H), $ABX_2$ system, $\tau_A$ *ca.* 2.5—3.0, $\tau_B$ 3.92, $\tau_X$ 5.33 [$J_{AB}$ 12, $J_{BX}$ 7 Hz, $CH_A{=}CH_B{-}C(H_X)_2{-}\overset{+}{N}$], 5.03 (s, $C{\equiv}C{-}CH_2{-}\overset{+}{N}$), and 6.48 (s, $\overset{+}{N}Me_2$).

*Base Catalysed Rearrangement of* cis-*Cinnamyldimethyl-(3-phenylprop-2-ynyl)ammonium Bromide* (34f). *Formation of 3-Dimethylamino-1,4-diphenylhex-5-en-1-yne* (35f).—A solution of the salt (34f) (3 g) in dimethyl sulphoxide (15 ml) was treated with a solution prepared from sodium hydride (0.3 g), methanol (1 ml), and dimethyl sulphoxide (25 ml) at room temperature for 1 h. The solution was poured into water (500 ml), extracted with ether, washed with water, dried, evaporated, and separated by preparative t.l.c. [silica–(ethyl acetate–chloroform 3 : 1)] giving a mixture (2.1 g) of two diastereoisomers (ratio 9 : 1 by n.m.r. analysis) of *3-dimethylamino-1,4-diphenylhex-5-en-1-yne* (35f) (Found: $M^+$, 275), *m/e* 230 ($M$ – $HNMe_2$), 173 ($M$ – PhC≡CH), 158, and 115; τ 2.5—2.9 (m, 10 aromatic H), ABMXY system $\tau_M$ 3.80 $\tau_A$ 4.91 $\tau_B$ 4.95, $\tau_X$ 6.16, $\tau_Y$ 6.40 ($J_{BM}$ 10, $J_{AM}$ 18, $J_{AX}$ 8, $J_{XY}$ 9 Hz, $CH_AH_B{=}CH_M{-}CH_X{-}CH_Y{-}NMe_2$), and 7.73 (s, $NMe_2$, major diastereoisomer), and 7.67 (s, $NMe_2$, minor diastereoisomer). The *amine* (35f) was characterised as its *picrate*, m.p. 179—180° (ethanol) (Found: C, 61.6; H, 5.15; N, 11.0. $C_{26}H_{24}N_4O_7$ requires C, 61.9; H, 4.8; N, 11.1%).

*Dimethyl-(3,3-dimethylallyl)-(3-phenylprop-2-ynyl)ammonium Chloride* (34g).—*NN*-Dimethyl-(3-phenylprop-2-ynyl)amine (16 g) and 3,3-dimethylallyl chloride (22 g) were mixed in benzene (100 ml) and set aside for 48 h. The precipitate was collected and crystallisation from ethanol gave *dimethyl-(3,3-dimethylallyl)-(3-phenylprop-2-ynyl)-ammonium chloride* (34g) (20 g, 55%) as prisms, m.p. 175° (Found: C, 73.0; H, 8.3; N, 5.7. $C_{16}H_{22}ClN$ requires C, 72.9; H, 8.3; N, 5.3%); τ ($CF_3CO_2H$) 2.3—2.8 (m, 5 aromatic H), $AX_2$ system, $\tau_A$ 4.52, $\tau_X$ 5.90 [$J_{AX}$ 8 Hz, $H_A$ showed additional long range coupling $J_{A\text{-}Me}$ 1 Hz, $C(H_X)_2{-}CH_A{=}CMe_2$], 5.70 (s, $C{\equiv}C{-}CH_2$), 6.78 (s, $NMe_2$), and 8.03 and 8.07 (s, two vinylic Me).

*Base Catalysed Rearrangement of Dimethyl-(3,3-dimethyl)-(3-phenylprop-2-ynyl)ammonium Chloride* (34g). *Formation of 4,4-Dimethyl-3-dimethylamino-1-phenylhex-5-en-1-yne* (35g) *and 3-Dimethylamino-6-methyl-1-phenylhept-5-en-1-yne* (36g).—The ammonium salt (34g) (17.3 g) dissolved in dimethyl sulphoxide (25 ml) was added to a solution prepared from sodium hydride (2.4 g), methanol (3 ml), and dimethyl sulphoxide (50 ml). After 3 h, the mixture was poured into water and extracted with ether (2 × 100 ml). The ethereal extracts were shaken with 2N-hydrochloric acid (2 × 50 ml) and the acidic extracts were neutralised with 5N-sodium hydroxide and extracted with ether (2 × 75 ml). The ethereal extracts were dried and evaporated yielding a pale yellow mixture of amines, which was separated by preparative t l.c. [silica gel–(chloroform–ethyl acetate 3 : 1)] into two components: (i) *4,4-dimethyl-3-di-*

*methylamino*-1-*phenylhex*-5-*en*-1-*yne* (35g) (83%), pale yellow oil; τ 2.4—2.9 (m, 5 aromatic H), ABX system, $\tau_X$ 3.82, $\tau_A$ 4.97, $\tau_B$ 5.00 ($J_{AX}$ 17, $J_{BX}$ 11, $J_{AB}$ 2 Hz, $CH_AH_B{=}CH_X{-}$), 6.69 (s, $C{\equiv}C{-}CH_2$), 7.71 (s, $NMe_2$), and 8.82 and 8.85 (s, two aliphatic Me); *m/e* 227 ($M^+$), 158, and 115. The amine (35g) was characterised as the *picrate*, from benzene, as yellow prisms, m.p. 148° (Found: C, 57.0; H, 5.1; N, 11.7. $C_{22}H_{24}N_4O_7$ requires C, 57.7; H, 5.1; N, 11.7%); and (ii) 3-*dimethylamino*-6-*methyl*-1-*phenylhept*-5-*en*-1-*yne* (36g) (12%), pale yellow oil; τ 2.5—2.9 (m. 5 aromatic H), $AM_2X$ system, $\tau_A$ 4.75, $\tau_X$ 6.46, $\tau_M$ 7.5—7.8 [$J_{AM}$ 7, $J_{MX}$ 8 Hz, $=CH_A{-}C(H_M)_2{-}CH_X{-}NMe_2$], 7.67 (s, $NMe_2$), and 8.29 and 8.35 (s, two vinylic Me); *m/e* 227 ($M^+$), 158, and 115. The amine (36g) was characterised as the *picrate*, yellow prisms from aqueous ethanol, m.p. 121° (Found: C, 58.3; H, 5.2; N, 12.3. $C_{22}H_{24}N_4O_7$ requires C, 57.9; H, 5.3; N, 12.3%).

*Cinnamyldimethyl*(*prop*-2-*ynyl*)*ammonium Bromide* (34h).—A solution of prop-2-ynyl bromide (2.4 g) in ether (10 ml) was added to a solution of *NN*-dimethylcinnamylamine (3.2 g) in ether. The mixture was left at room temperature for 24 h and the resultant oil was crystallised from anhydrous acetone giving *cinnamyldimethyl*(*prop*-2-*ynyl*)*ammonium bromide* (34h), as prisms, m.p. 134—135° (Found: C, 59.8; H, 6.7; N, 5.0; Br, 28.5. $C_{14}H_{18}BrN$ requires C, 60.0; H, 6.4; N, 5.0; Br, 28.6%); $\nu_{max.}$ 3 300 ($C{\equiv}C{-}H$) and 2 120 $cm^{-1}$ ($C{\equiv}C$); τ 2.4—2.7 (m, 5 aromatic H), $ABX_2$ system, $\tau_A$ 2.87, $\tau_B$ 3.65, $\tau_X$ 5.34 [$J_{AB}$ 17, $J_{BX}$ 7.5 Hz, $CH_A{=}CH_B{-}C(H_X)_2$], 5.17br (s, $C{\equiv}C{-}CH_2$), 6.55 (s, $NMe_2$), and 6.78br (s, $H{-}C{\equiv}C$).

*Base Catalysed Rearrangement of Cinnamyldimethyl*(*prop*-2-*ynyl*)*ammonium Bromide* (34h). *Formation of* 3-*Dimethylamino*-4-*phenylhex*-5-*en*-1-*yne* (35h).—The ammonium salt (34h) (2.8 g) in dimethyl sulphoxide (10 ml) was treated with a solution prepared from sodium hydride (0.24 g), methanol (0.5 ml), and dimethyl sulphoxide (25 ml). The mixture was stirred at room temperature for 12 h, poured into water, and extracted with ether. The ethereal solution was extracted with 2N-hydrochloric acid, washed with water, dried, and evaporated giving a neutral fraction (10 mg) which was discarded. The acidic extracts were basified with 5N-sodium hydroxide, extracted with ether, dried, and evaporated giving a pale yellow oil (2.0 g, 99%), identified as pure 3-*dimethylamino*-4-*phenylhex*-5-*en*-1-*yne* (35h) (Found: $M^+$, 199. $C_{14}H_{17}N$ requires *M*, 199); *m/e* 82 ($HC{\equiv}C{-}CH{=}\overset{+}{N}Me_2$); $\nu_{max.}$ 3 300 $cm^{-1}$ ($C{\equiv}C{-}H$); τ 2.78 (s, 5 aromatic H), ABCMNX system, $\tau_C$ 3.88, $\tau_A$ 4.91, $\tau_B$ 4.97, $\tau_N$ 6.35, $\tau_M$ 6.55, $\tau_X$ 7.91 ($J_{AB}$ 1, $J_{BC}$ 17, $J_{AC}$ 11, $J_{CM}$ 8, $J_{MN}$ 11, $J_{NX}$ 2 Hz, $CH_AH_B{=}CH_C{-}CH_M{-}CH_N{C}{\equiv}C{-}H_X$), and 7.72 (s, $NMe_2$). The n.m.r. spectrum showed that the amine (35h) was almost entirely one diasteroisomer (99%). The second diastereoisomer (35h) was just detectable, τ 7.81 (s, $NMe_2$). The amine (35h) was characterised as its *methiodide*, prisms, m.p. 174°, from ethanol–ether (Found: C, 52.55; H, 5.9; N, 4.1; I, 37.4. $C_{15}H_{20}IN$ requires C, 52.7; H, 5.9; N, 4.1; I, 37.4%).

*Dimethyl*-(3,3-*dimethylallyl*)-(1-*phenylprop*-2-*ynyl*)*ammonium Bromide* (34j).—A solution of 1-phenylprop-2-ynyl bromide (4 g) in acetonitrile (5 ml) was added to a solution of *NN*-dimethyl-3,3-dimethylallylamine (3 g) in acetonitrile. After the exothermic reaction was complete, the *salt* was precipitated with ether as a solid (34j), m.p. 151—152° (Found: C, 62.2; H, 7.4; N, 4.4; Br, 25.8. $C_{16}H_{22}BrN$ requires C, 62.3; H, 7.1; N, 4.55: Br, 26.0%); $\nu_{max.}$ 3 300 and 2 130 $cm^{-1}$; τ 2.0—2.3 (m) and 2.5—2.9 (m, 5 aromatic H), AX system, $\tau_A$ 3.10, $\tau_X$ 6.61 ($J_{AX}$ 2 Hz, $H_X{-}C{\equiv}C{-}CH_A$), AXY system, $\tau_A$ 4.60, $\tau_X$ 5.54, $\tau_Y$ 5.72 ($J_{AX}$ 8, $J_{AY}$ 8, $J_{XY}$ 14 Hz, $=CH_A{-}CH_XH_Y{-}$), 6.84 and 6.89 (s, $\overset{+}{N}Me_2$), and 8.12 and 8.14 (s, $CMe_2$).

*Base Catalysed Rearrangement of Dimethyl*-(3,3-*dimethylallyl*)-(1-*phenylprop*-2-*ynyl*)*ammonium Bromide* (34j). *Formation of* 3,3-*Dimethyl*-4-*dimethylamino*-4-*phenylhex*-1-*en*-5-*yne* (35j) *and* 3-*Dimethylamino*-6-*methyl*-3-*phenylhept*-5-*en*-1-*yne* (36j).—The salt (34j) (4 g) in dimethyl sulphoxide (20 ml) was treated with a solution of sodium hydride (0.6 g) and methanol (1 ml) in dimethyl sulphoxide (20 ml) at room temperature. After 12 h, the solution was diluted with water, extracted with ether, and separated into neutral and basic fractions in the usual manner. The neutral fraction (<100 mg) was discarded. The basic fraction (2.8 g, 92%) was separated into two fractions (i) and (ii) by preparative t.l.c. [silica gel–(chloroform–ethyl acetate 3 : 1)]: (i) 3,3-*dimethyl*-4-*dimethylamino*-4-*phenylhex*-1-*en*-5-*yne* (35j) (1.7 g); τ 2.0—2.3 (m) and 2.5—2.8 (m, 5 aromatic H), ABX system, $\tau_X$ 3.32, $\tau_A$ 5.08, $\tau_B$ 5.04 ($J_{AB}$ 2, $J_{BX}$ 16, $J_{AX}$ 10 Hz, $CH_AH_B{=}CH_X{-}$), 7.30 (s, $HC{\equiv}C$), 7.88 (s, $NMe_2$), and 8.92 and 9.19 (s, $CMe_2$). The amine (35j) was characterised as its *picrate*, yellow prisms, m.p. 155° from ethanol (Found: C, 57.7; H, 5.55; N, 12.45. $C_{22}H_{24}N_4O_7$ requires C, 57.9; H, 5.3; N, 12.3%); and (ii) 3-*dimethylamino*-6-*methyl*-3-*phenylhept*-5-*en*-1-*yne* (36j) (0.6 g), *m/e* 201 ($M - C_2H_2$) and 158 ($M - Me_2C{=}CH{-}CH_2$) (Found: $M^+$, 227. $C_{16}H_{21}N$ requires *M*, 227); τ 2.2—2.5 (m) and 2.7—2.9 (m, 5 aromatic H), ABX system, $\tau_X$ 5.09, $\tau_A$,$\tau_B$ *ca.* 7.3, ($J_{AX} = J_{BX} =$ *ca.* 6 Hz, $CH_AH_B{-}CH_X{=}$), 7.44 (s, $H{-}C{\equiv}C$), 7.79 (s, $NMe_2$), and 8.45 and 8.70 (s, two vinylic Me). The amine (36j) was characterised as its *picrate*, yellow prisms, m.p. 139°, from ethanol (Found: C, 57.7; H, 5.0; N, 12.4. $C_{22}H_{24}N_4O_7$ requires C, 57.9; H, 5.3; N, 12.3%).

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