

Base Catalysed Rearrangements Involving Ylide Intermediates. Part 6.^{1,2} The Rearrangements of Diallyl- and Allylpropynyl-ammonium Cations in Protic Media

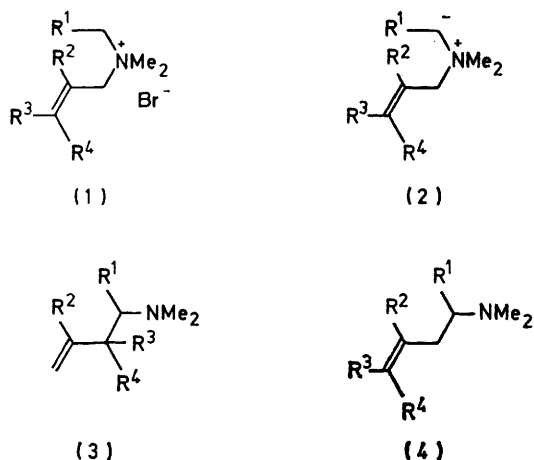
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The base catalysed rearrangements of the cations (1d—j) in aqueous solution yield the isomeric cations (15) or the aldehydes (10) and (11), or mixtures of (15), (10), and (11). This contrasts dramatically with the transformations observed for the cations (1) in aprotic solvents. The cations (15) undergo Hofmann elimination to the naphthalenic amines (12) or (13) and (14). The methiodide of amine (13g) shows a novel consequence of restricted rotation. The n.m.r. spectrum of the methiodide shows that the two protons of the methylene group are diastereotopic.

IN Part I of this series,³ and in other reports,⁴ the base catalysed rearrangements of diallyl- and allylpropynyl-ammonium cations (1a—l) in aprotic media have been described. In most cases, the major pathway in aprotic

and acetylenic ammonium cations under basic conditions in protic solvents. The reactions reported by Babayan⁷ have been associated with some extremely unusual mechanistic proposals. We have therefore reinvestigated some of the reactions described by Babayan. In the main, his experimental results have been confirmed, but additional information has been obtained and different mechanistic proposals are now put forward.

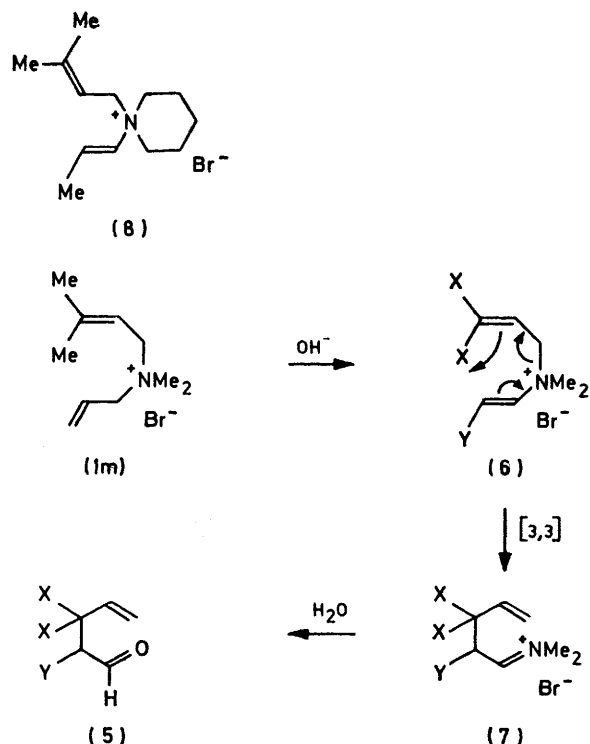
The salt (1c), on treatment with aqueous sodium hydroxide solution, has been reported⁷ to yield the aldehyde (5; X = H, Y = Me). In many similar reactions, the structures of the products were not fully characterised. This pathway (1) → (5) has been described by Stevens⁸ as ' [1,3] migration of allyl with inversion.' We prefer the alternative interpretation given in Scheme 1 and in view of this we have further



| | R ¹ | R ² | R ³ | R ⁴ |
|----|-------------------------|----------------|----------------|----------------|
| a; | Me ₂ C ≡ CH- | H | Me | Me |
| b; | PhCH ≡ CH- | H | Ph | H |
| c; | CH ₂ ≡ CH- | H | H | H |
| d; | PhC ≡ C- | H | Me | Me |
| e; | PhC ≡ C- | H | Ph | H |
| f; | PhC ≡ C- | H | H | H |
| g; | PhC ≡ C- | H | Me | H |
| h; | PhC ≡ C- | Me | H | H |
| j; | PhC ≡ C- | Ph | H | H |
| k; | PhC ≡ C- | H | H | Ph |
| l; | H-C ≡ C- | H | Ph | H |
| m; | CH ₂ ≡ CH- | H | Me | Me |

solvents is a [3,2] sigmatropic rearrangement⁵ of the initially formed ylide (2) leading to the amine (3); the minor pathway is a [1,2] Stevens rearrangement⁶ of the ylide (2) leading to the amine (4). We now report on the base catalysed reactions of diallyl- and allylpropynyl-ammonium cations (1) in protic media.

There have been reports⁷ by Babayan and his group of a new reaction pathway which is available to allylic



SCHEME 1

investigated the rearrangements of diallyl- and allyl-propynyl-ammonium cations in aqueous solution.¹

Our initial studies involved boiling the salt (1m) with 50% aqueous sodium hydroxide. The only neutral product isolated was the aldehyde (5; X = Y = Me) (28%) whose constitution is derived from its spectral properties.

The most reasonable pathway by which the aldehyde (5; X = Y = Me) could be formed from the cation (1m) is shown in Scheme 1. A base catalysed isomerisation of the allyl to a propenyl group⁹ (1 → 6; Y = Me) is followed by a [3,3] sigmatropic rearrangement¹⁰ of the resultant eneammonium salt (6; X = Y = Me) yielding the immonium cation (7; X = Y = Me) which, by hydrolysis, gives the aldehyde (5; X = Y = Me). Evidence for the feasibility of this mechanistic pathway (Scheme 1) has been obtained by rearrangement of an analogous eneammonium salt (8). Alkylation of 1-piperidinoprop-1-ene with 3,3-dimethylallyl bromide apparently gave an intermediate salt (8) which on standing at room temperature in benzene solution gave the aldehyde (5; X = Y = Me) (90%). Similar [3,3] sigmatropic rearrangements of eneammonium salts generated by alkylation of enamines with allylic halides are well known.¹¹

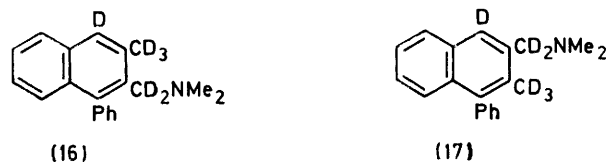
In an analogous manner, generation of the eneammonium salt (6; X = Me, Y = H) by treatment of (2-bromoethyl)dimethyl-(3,3-dimethylallyl)ammonium bromide with aqueous sodium hydroxide at room temperature led to the immediate formation of the aldehyde (5; X = Me, Y = H) (17%), the only other product being *NN*-dimethyl-(3,3-dimethylallyl)amine (60%). The [3,3] rearrangement of allylvinylammonium salts appears to be a very facile process even at room temperature.

In view of the ease of base catalysed isomerisation of acetylenes to allenes,¹² the corresponding reactions of allylprop-2-ynylammonium cations (1d—j) with aqueous sodium hydroxide were examined. These systems, however, gave much more complex mixtures of products. Treatment of the salt (1d) with boiling 50% aqueous sodium hydroxide solution gave as the only neutral product the aldehyde (11d) (12%) which, from its n.m.r. spectrum, was shown to be mainly one isomer. This n.m.r. spectrum showed additional signals attributable to the diastereoisomeric aldehyde (10d) in trace amounts. In addition, three basic products were isolated: the amines (3d) (46%), (4d) (9%), and (12) (17%). Under these strongly basic conditions, the acidic proton α to the quaternary nitrogen in the cation (1d) could be easily removed to form the ylide (2d), which could then rearrange giving the products of [3,2] and [1,2] shifts, that is the amines (3d) and (4d) respectively. The aldehyde (11d) presumably arose *via* a [3,3] sigmatropic rearrangement of the intermediate allenic salt (9d), formed by reprotonation of the ylide (2d) at the alternative site. The formation of amine (12) is best rationalised (Scheme 2) as proceeding *via* $\pi 2 + \pi 4$ intramolecular cycloaddition of the dimethylallyl group to the phenylallene moiety of

the allene (9d), leading eventually, after rearomatisation, to the intermediate salt (15). This salt (15) by a subsequent Hofmann elimination yields the amine (12).

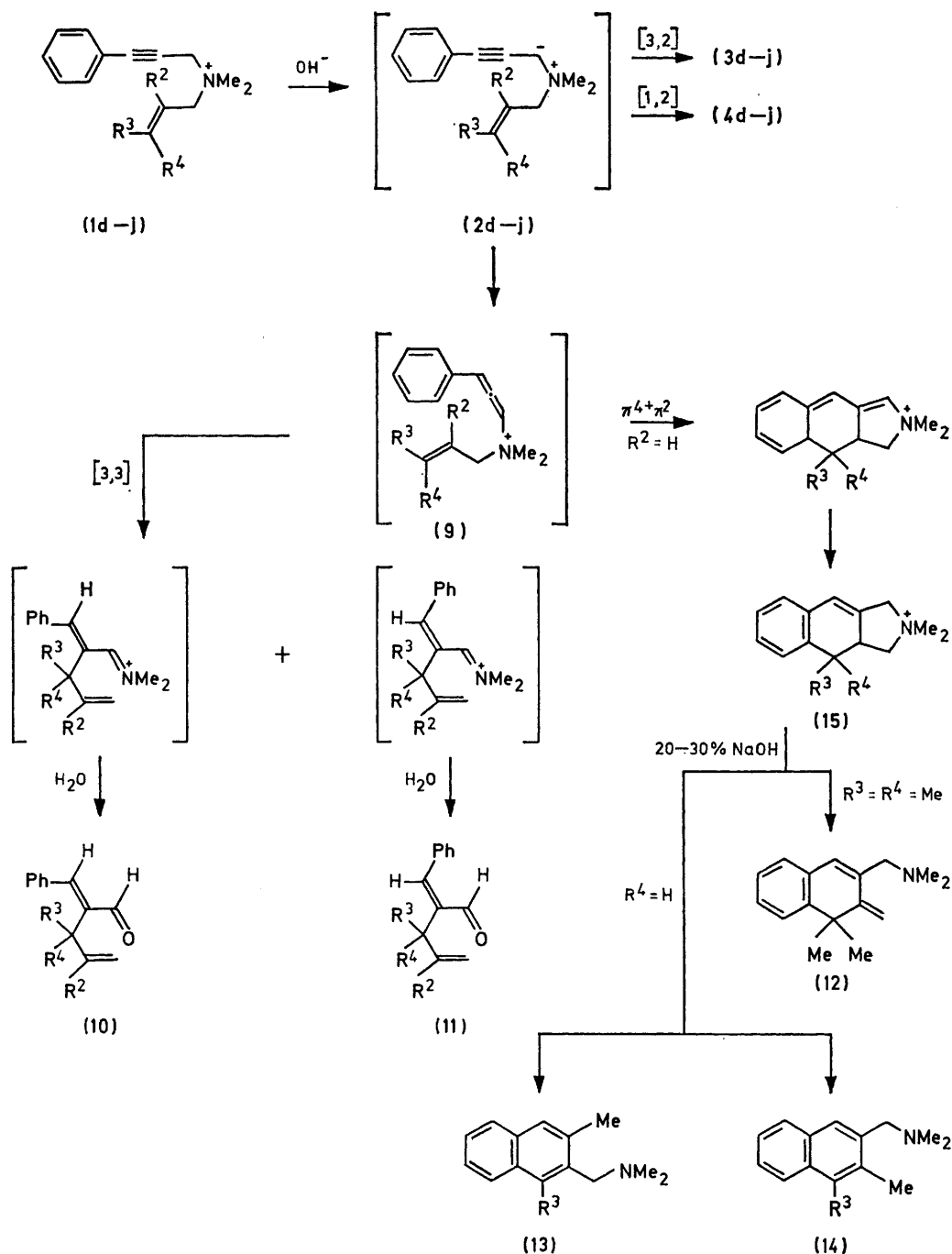
Under similar conditions, the salt (1e) participates in a multiplicity of reaction pathways, leading to the [3,2] sigmatropic rearrangement product (3e) (5%), the [1,2] Stevens rearrangement product (4e) (10%), *p*-terphenyl (7%), which arises by thermal rearrangement of the amine (3e),^{1,3} and the naphthalenic amines (13e) (34%) and (14e) (11%), formed by the $\pi 2 + \pi 4$ intramolecular cycloaddition reaction.* The amines (13e) and (14e) have similar n.m.r. spectra, but their spectral differences were such that constitutional assignments could be made directly. The amine (13e) showed pronounced shielding of the CH₂ and NMe₂ groups, whereas the amine (14e) showed shielding of the aromatic methyl group. This can be attributed to the proximity of these groupings to the adjacent phenyl ring. The phenyl ring in these naphthalenes (13e) and (14e) will be twisted out of the plane of the naphthalene ring, thus causing the observed positive shielding of adjacent groups. The mechanism outlined in Scheme 2 satisfactorily accounts for the transformation (1e) → (3e), (4e), (13e), (14e), and terphenyl.

In agreement with this mechanistic proposal (Scheme 2), treatment of ($\alpha\alpha$ -dideuteriocinnamyl)dimethyl-(3-phenylprop-2-ynyl)ammonium bromide with sodium deuterioxide in D₂O gave the amines (16) and (17) which each contained six deuterium atoms in the positions indicated. All the protons which could undergo base catalysed exchange by the operation of the mechanism shown in Scheme 2 have been exchanged.



In an attempt to reduce the proportion of [3,2] and [1,2] rearrangement products in the mixtures obtained in these base induced transformations, a variety of reaction conditions was tried. The most successful general method involved the treatment of the acetylenic salts (1d—j) with a trace of sodium hydroxide in the minimum volume of water and heating on a steam-bath for up to 12 h. Under these conditions, the salt (1f) was transformed into the aldehyde (10f) (33%) and the isomeric salt (15f) (65%). The structure of the salt (15f) follows from analytical and spectral evidence. Its n.m.r. spectrum shows a single vinylic proton at τ 3.34, a two-proton singlet at τ 5.58 assigned to the vinylic methylene group, a complex five-proton resonance at τ 5.9—7.2 which can be adequately resolved by first-order approximation into an ABMXY system, and two \ddagger -N-Me resonances at τ 6.61 and 6.73. The u.v. spectrum

* This reaction is formulated in Scheme 2 as involving a concerted cycloaddition; an alternative possibility is discussed later in this paper.



SCHEME 2

in ethanol showed λ_{max} at 212 (22 400), 217 (25 000), 223 (19 300), and 265 nm (12 200), typical of 1,2-dihydro-naphthalene derivatives.¹³ The structure (15f) was further proved by cleavage with 25% aqueous sodium hydroxide solution to give *NN*,3-trimethyl-2-naphthalenemethylamine (13f) (80%). The amine (13f) on quaternisation with methyl iodide, followed by Emde reduction¹⁴ with sodium amalgam, gave 2,3-dimethyl-naphthalene (95%).

In a similar manner, the transformations of the salts (1d-j) to the diastereomeric aldehydes (10) and (11)

and/or the salts (15) were carried out and the yields are shown in the Table. The structures of the salts (15) rest mainly on spectral data (see Experimental section) and by cleavage with concentrated sodium hydroxide solution. Under these conditions, the salt (15d) was cleaved to the amine (12) (67%), the salt (15e) to the amines (13e) (39%) and (14e) (13%), and the salt (15g) to the amines (13g) (19%) and (14g) (57%).

The n.m.r. spectra of the methidides of the amines (13g) and (14g) showed features which were of considerable intrinsic interest and which also served to

support constitutional assignments. The methiodide of the amine (13g) showed an AB system for the methylene protons, whereas the corresponding signal for the methiodide of amine (14g) was a sharp singlet. The

Base catalysed transformations of cations (1) to cations (15) and aldehydes (10) and (11)

| | Reactants (1) | | | Product yields (%) † | | |
|---|----------------|----------------|----------------|----------------------|-------|-------|
| | R ² | R ³ | R ⁴ | (15) | (10) | (11) |
| d | H | Me | Me | 45 | Trace | 20 |
| e | H | Ph | H | 100 | | |
| f | H | H | H | 65 | 33 | |
| g | H | Me | H | 80 | 12 | 3 |
| h | Me | H | H | | 76 | Trace |
| j | Ph | H | H | | 70 | 6 |

† Yields are those obtained by treating the salt (1) with a trace of sodium hydroxide in the minimum volume of water at 100 °C.

diastereotopicity of the methylene protons as exhibited by the AB system shown by the methiodide of the amine (13g) is a delightful demonstration of the chirality of the methiodide of amine (13g). The axial chirality is clearly associated with restricted rotation¹⁵ in the naphthylmethyl(trimethyl)ammonium residue which is disposed between two methyl substituents located at positions 1 and 3 of the naphthalene ring.

The n.m.r. spectrum of the methiodide of amine (13e) showed a broad resonance for the methylene protons, whereas the corresponding signal for the methiodide of amine (14e) was very sharp. This phenomenon is identical in origin with that shown by the methiodide of amine (13g), but the free energy of activation for restricted rotation about the naphthyl-CH₂ bond for the methiodide of amine (13e; R³ = Ph) is clearly lower than that for the methiodide of amine (13g; R³ = Me). This reasonable association of the torsional free energy of activation with the size of the group R³ is also in accord with the fact that the consequences of restricted rotation are not observable for the methiodide of the amine (13f; R³ = H). The n.m.r. spectra of the amines (13g) and (14g) showed no restricted rotation even at -70 °C in CS₂ solution, nor as protonated derivatives in trifluoroacetic acid solution.

The structures of the diastereoisomeric aldehydes (10) and (11) were determined mainly by consideration of their u.v. and n.m.r. spectra. Thus, the u.v. spectra of the aldehydes (10) which are assigned the *E*-configuration (*trans*-configuration) all showed absorption maxima in the range 283–287 nm (ϵ 17 000–21 000), whereas the aldehyde (11d) assigned the *Z*-configuration (*cis*-configuration) absorbed at 278 nm (ϵ 10 000). The comparable literature values for *trans*- and *cis*-cinnamaldehyde are λ_{\max} at 287 (ϵ 22 400) and 284 nm (ϵ 12 600) respectively, although the isomeric purity of *cis*-cinnamaldehyde was not unequivocally established.¹⁶

The n.m.r. data also support the assignments (10) and (11) because a distinction can be made between *E*- and *Z*-isomers on the basis of the chemical shifts of the aldehyde protons and the vinyl protons (α to phenyl) when compared with literature values.¹⁷ Thus, the

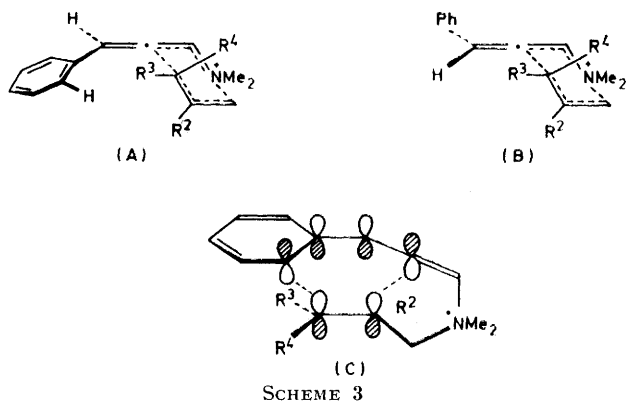
aldehyde protons are in the range τ 0.3–0.5 in the *E*-isomers (10) and τ 0.1–0.2 in the *Z*-isomers (11). In addition, the vinyl protons lie in the region of τ 2.7 in the *E*-isomers (10) and τ ca. 2.3 in the *Z*-isomers (11) in accord with literature values on similar compounds.¹⁷ However, this latter difference is not useful in all cases because the vinyl and phenyl protons may lie in the same region of the n.m.r. spectrum. In one experiment, the *Z*-aldehyde (11d) isolated from the reaction mixture was slowly converted over a period of weeks at room temperature into the *E*-isomer (10d). On addition of the lanthanide shift reagent [Eu(fod)₃]¹⁸ to a deuteriochloroform solution of a 3 : 1 mixture of aldehydes (11d) and (10d), the vinyl proton in the n.m.r. spectrum of the *E*-isomer (10d) was shifted to lower field to a much greater extent than the vinyl proton in the *Z*-isomer (11d). Signals associated with the other protons (=CH₂, CHO, and Me) showed similar shifts for both isomers (10d) and (11d). This is to be expected,¹⁹ since in the *E*-isomer (10d) the vinyl proton is closer to the shift reagent (co-ordinated to the aldehyde oxygen) than in the *Z*-isomer (11d).

The formation of the diastereoisomeric aldehydes (10) and (11) can be rationalised by the mechanism shown in Scheme 2. The stereochemistry of the products (10) and/or (11), however, depends on the stereochemistry of the transition state for the [3,3] sigmatropic rearrangement of the allene (9). Assuming that a chair conformation for the [3,3] rearrangement will be preferred,¹⁰ there are two possible diastereoisomeric transition states (A) and (B) (Scheme 3) for the rearrangement, depending on whether the bond formation step [from the terminal carbon atom of the allyl unit to the central carbon of the allene (9)] takes place in the *cis*-relation to the phenyl substituent [transition state (A)] or in the *trans*-relation to the phenyl substituent [transition state (B)] (see Scheme 3). The transition state (A) leads to an aldehyde of *E*-configuration (10): the transition state (B) leads to an aldehyde of *Z*-configuration (11).

In the rearrangements of the salts (1f, h, and j) in which R³ = R⁴ = H, the major products were the *E*-aldehydes (10f, h, and j) rather than the *Z*-aldehydes (11f, h, and j). This indicates that in the absence of steric interactions, the transition state (A) is preferred. But as the size of the groups R³ and/or R⁴ was increased, the ratio of aldehydes (11) : (10) increased until when R³ = R⁴ = Me in the salt (1d), then only the *Z*-aldehyde (11d) was formed. Although this proposal, based upon relative steric effects, satisfactorily accounts for the product ratios for aldehydes (10) and (11), the problem of why the transition state (A), the relatively more highly hindered transition state, should be preferred in the unsubstituted cases (R³ = R⁴ = H) has not yet been solved. The possibility that transition state (A) is favoured due to secondary orbital interactions²⁰ between the π -orbitals of the phenyl group and the allyl group is attractive. Furthermore, there is a close stereo-electronic similarity between transition state (A), which is apparently preferred for the favoured [3,3] sigmatropic

rearrangement, and transition state (C) (Scheme 3) probably involved in the observed $[\pi 4_s + \pi 2_s]$ cycloaddition (9) \rightarrow (15).

The effect of substituents (Scheme 2; R^2 — R^4) on the competition between [3,3] rearrangement (9) \rightarrow (10) and (11) and intramolecular $[\pi 4_s + \pi 2_s]$ cycloaddition (9) \rightarrow (15) of the allenic intermediate (9) is also unusual. When $R^3 = \text{Ph}$, no [3,3] rearrangement could be detected; this is consistent with the expected activating effect of a phenyl group on $[\pi 4 + \pi 2]$ cycloaddition and the steric inhibition of the [3,3] sigmatropic rearrangement [transition state (A) (Scheme 3)]. The inhibition of the $[\pi 4 + \pi 2]$ cycloaddition when the group $R^2 = \text{Me}$ or Ph indicates that in transition state (C) there is appreciable steric interaction between the group R^2 and the allenic group. In the other examples, mixtures of products (10), (11), and (15) (Table) are always obtained indicating that the difference in free energy between the transition states (A) or (B) or (C) are

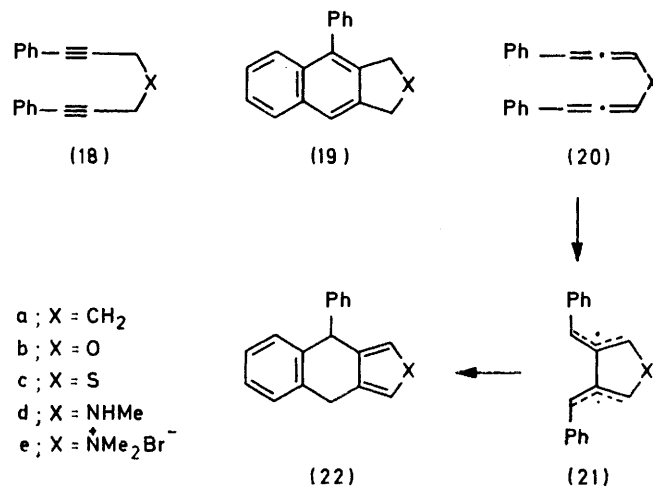


very small and, for this and other reasons, the detailed discussion of substituent effects is unlikely to be profitable.

The difference between the results reported in this paper on the rearrangements of the salts (1) in protic media (aqueous sodium hydroxide) and those reported in Part 1³ for rearrangements of the same salts (1) in aprotic media (sodium methoxide in dimethyl sulphoxide) is quite remarkable. The ylide (2) is presumably the intermediate in both cases, but in protic media reprotonation to the allene (9) can occur, followed by [3,3] rearrangement (9) \rightarrow (10) and (11) and/or $[\pi 4 + \pi 2]$ cycloaddition (9) \rightarrow (15). In aprotic media or strongly basic aqueous solutions, the reprotonation of the ylide (2) is retarded and so other pathways involving the [3,2] sigmatropic and [1,2] Stevens rearrangements compete.

Intramolecular $[\pi 4 + \pi 2]$ cycloadditions involving a styrenoid system and an allene do not appear to have been reported but examples are known involving a styrenoid diene and an acetylenic bond,²¹ an activated olefin,²² and an unactivated olefin.²³ The elegant applications of intramolecular cycloaddition reactions for a variety of syntheses have been reviewed²⁴ and the general principles of such reactions discussed. The base catalysed reactions of bis-(3-phenylprop-2-ynyl) derivatives (18a—d), which give the corresponding naphth-

alenes (19a—d) in good yield²⁵ may not involve an intramolecular $[\pi 4 + \pi 2]$ cycloaddition of the intermediate bisallene (20). Evidence has been provided²⁶ that the reaction (20) \rightarrow (19) probably involves an



intermediate diradical (21), or its equivalent, with subsequent formation of the heterocycle (22) which rearranges to give (19). The comment²⁷ that the salt (18e) fails to undergo a similar cycloaddition is surprising in view of the results now reported. However, in our experience the salt (18e) on treatment with a trace of sodium hydroxide in aqueous solution, initially at room temperature, gave the salt (19e) in high yield in an exothermic reaction. The structure of the salt (19e) was proved by its Emde reduction to the amines (13e) and (14e). By analogy with the results reported²⁶ for other compounds (18) it is probable that the rearrangement (22) \rightarrow (19) proceeds under these mild conditions. The results reported in this paper do not define whether the reactions (9) \rightarrow (15) involve a concerted cycloaddition, as depicted in Scheme 2, or a diradical mechanism for the cycloaddition analogous to the process (20) \rightarrow (22). Other synthetic uses of arylallenes, formed as reaction intermediates, have been reported.²⁸

EXPERIMENTAL

The general directions were given in Part 1.³

Allyldimethyl-(3,3-dimethylallyl)ammonium Bromide (1m).—A solution of *NN*-dimethyl-3,3-dimethylallylamine (12.3 g) in acetonitrile (10 ml) was added to a solution of allyl bromide (12.0 g) in acetonitrile (20 ml). A vigorous exothermic reaction occurred and the mixture was left for 1 h before precipitating the salt with dry ether (200 ml). The solvent was decanted and the colourless, viscous oil was dried under vacuum giving *allyldimethyl-(3,3-dimethylallyl)ammonium bromide (1m)* (22 g); n.m.r.: ABMX₂ system, τ_A 4.30, τ_B 4.17, τ_M 4.00, τ_X 5.66 [J_{AB} 3, J_{AM} 9, J_{BM} 17, J_{MX} 6.5 Hz, $\text{CH}_A\text{H}_B=\text{CH}_M-\text{C}(\text{H}_X)_2^-$], AX₂ system, τ_A 4.60, τ_X 5.75 [J_{AX} 8 Hz, $=\text{CH}_A-\text{C}(\text{H}_X)_2$], 6.77 (s, NMe₂), and 8.11 (s, =CMe₂).

Base Catalysed Rearrangement of Allyldimethyl-(3,3-dimethylallyl)ammonium Bromide (1m). *Formation of 2,3,3-Trimethylpent-4-enal (5; X = Y = Me).*—A solution of the

salt (1m) (4.7 g) in water (30 ml) was refluxed with a solution of sodium hydroxide (10 g) in water (20 ml) for 16 h, cooled, and extracted with ether. The ethereal extracts were separated into neutral and basic fractions using 5*N*-hydrochloric acid and 5*N*-sodium hydroxide. The neutral fraction was 2,3,3-trimethylpent-4-enal (5; X = Y = Me) (0.7 g, 28%); ν_{\max} (liquid film) 2 730, 1 720, 1 380, 1 360, and 940 cm^{-1} ; n.m.r.: AMX₃ system, τ_A 0.30, τ_M 7.78, τ_X 8.98 [J_{AM} 3, J_{AX} 7 Hz, O=CH_A-CH_M-C(H_X)₃], ABX system, τ_A 4.99, τ_B 4.95, τ_X 4.12 (J_{AB} 1, J_{AX} 18, J_{BX} 10 Hz, CH_AH_B=CH_X), and 8.90 (s, >CMe₂). The aldehyde was characterised as its 2,4-dinitrophenylhydrazone, orange needles from ethanol, m.p. 117° (Found: C, 54.75; H, 5.9; N, 18.6. C₁₄H₁₈N₄O₄ requires C, 54.9; H, 5.9; N, 18.3%); τ -0.97br (s, NH), ABX system, τ_A 2.08, τ_B 1.76, τ_X 0.95 [J_{AB} 10, J_{BX} 3 Hz, 2,4-(NO₂)₂C₆H₃], AMX₃ system, τ_A 2.48, τ_M 7.52, τ_X 8.83 [J_{AM} 6.5, J_{MX} 7 Hz, C(H_X)₃-CH_M-CH_A=N], ABX system, τ_A 4.97, τ_B 4.93, τ_X 4.12 (J_{AX} 17, J_{BX} 10, J_{AB} 10 Hz, CH_AH_B=CH_X), and τ 8.93 (s, >CMe₂); m/e 306 (M^+), 238, 237, 221, 210, 183, and 164, m^* 205.2 (238 → 221), 185.1 (306 → 238), 159.4 (210 → 183), and 128 (210 → 164).

Alkylation of 1-Piperidinoprop-1-ene with 3,3-Dimethylallyl Bromide. Formation of 2,3,3-Trimethylpent-4-enal (5; X = Y = Me).—1-Piperidinoprop-1-ene²⁹ (1.5 g) and 3,3-dimethylallyl bromide (2.0 g) were mixed in dry benzene solution (30 ml). After 5 days at room temperature, the resultant crystalline solid was collected giving 3,3-dimethylallylpiperidine hydrobromide. The filtrate was evaporated, giving 2,3,3-trimethylpent-4-enal (5; X = Y = Me) as a liquid (1.35 g, 90%), identical with the sample obtained in the previous experiment.

(2-Bromoethyl)dimethyl-(3,3-dimethylallyl)ammonium Bromide.—A mixture of *NN*-dimethyl-3,3-dimethylallylamine³ (22 g) and 1,2-dibromoethane (36 g) in acetonitrile (100 ml) was stirred for 3 days at room temperature. The solvent was evaporated and, on addition of dry ether, a precipitate was formed which was collected and crystallised from ethyl acetate-methanol giving (2-bromoethyl)dimethyl-(3,3-dimethylallyl)ammonium bromide as prisms, m.p. 110–111° (Found: C, 35.7; H, 6.4; N, 4.7; Br, 53.05. C₉H₁₉NBr₂ requires C, 35.9; H, 6.3; N, 4.6; Br, 53.2%); AX₂ system, τ_A 4.52, τ_X 5.55 [J_{AX} 9 Hz, CH_A-C(H_X)₂], 5.94 (s, NCH₂CH₂Br), 6.54 (s, NMe₂), 8.08 (s), and 8.11 (s, two vinylic Me).

Base Catalysed Rearrangement of (2-Bromoethyl)dimethyl-(3,3-dimethylallyl)ammonium Bromide. Formation of 3,3-Dimethylpent-4-enal (5; X = Me, Y = H).—The ammonium salt (16 g) was stirred with a solution of sodium hydroxide (34 g) in water (150 ml) for 12 h at room temperature. The solution was extracted with ether and separated into neutral and basic fractions using 5*N*-hydrochloric acid and 5*N*-sodium hydroxide. The neutral fraction was 3,3-dimethylpent-4-enal (5; X = Me, Y = H), a liquid (1.0 g, 17%); ν_{\max} 1 720 and 920 cm^{-1} ; AX₂ system, τ_A 0.32, τ_X 7.68 [J_{AX} 3 Hz, C(H_X)₂-CH_AO], ABX system, τ_A , τ_B 5.0, τ_X 4.10 [J_{AX} 17, J_{BX} 10 Hz, CH_AH_B=CH_X], and 8.87 (s, >CMe₂). The aldehyde (5; X = Me, Y = H) was characterised as its 2,4-dinitrophenylhydrazone, plates from methanol, m.p. 119–121° (Found: C, 53.2; H, 5.2; N, 19.1. C₁₃H₁₆N₄O₄ requires C, 53.4; H, 5.5; N, 19.2%); τ -1.02br (s, NH), ABX system, τ_A 2.10, τ_B 1.73, τ_X 0.91 [J_{AB} 9, J_{BX} 2.5 Hz, 2,4-(NO₂)₂C₆H₃], AX₂ system, τ_A 2.56, τ_X 7.58 [J_{AX} 6.5 Hz, C(H_X)₂-CH_A=N], ABX system, τ_A , τ_B 4.97, τ_X 4.14 [J_{AX} 18, J_{BX} 10 Hz, CH_AH_B=CH_X], and 8.88 (s, >CMe₂); m/e 292

(M^+) and 69 [(CH₃)₂C⁺-CH=CH₂]. The basic fraction was *NN*-dimethyl-3,3-dimethylallylamine (3.7 g, 60%).

Rearrangement of Dimethyl-(3,3-dimethylallyl)-(3-phenylprop-2-ynyl)ammonium Chloride (1d) using 50% Sodium Hydroxide Solution. Formation of (Z)-2-(1,1-Dimethylallyl)-cinnamaldehyde (11d), 4,4-Dimethyl-3-dimethylamino-1-phenylhex-5-en-1-yne (3d), 6-Methyl-3-dimethylamino-1-phenylhept-5-en-1-yne (4d), and 1,1-Dimethyl-2-methylene-3-dimethylaminomethyl-1,2-dihydronaphthalene (12).—A mixture of the salt³ (1d) (4.0 g) and a solution of sodium hydroxide (10 g) in water (20 ml) was refluxed for 2 h. After cooling, the solution was extracted with ether and separated into neutral and basic fractions using 5*N*-hydrochloric acid and 5*N*-sodium hydroxide. The neutral fraction was (Z)-2-(1,1-dimethylallyl)cinnamaldehyde (11d), an oil (0.36 g, 12%) (Found: M^+ , 200. C₁₄H₁₆O requires M , 200); τ 0.23 (s, CHO), 2.36 (s, CH=C-CHO), 2.5–2.8 (m, 5 aromatic H), ABX system, τ_A 4.94, τ_B 4.98, τ_X 3.90 (J_{AX} 10, J_{BX} 18, J_{AB} 2 Hz, CH_AH_B=CH_X), and 8.61 (s, >CMe₂); λ_{\max} 274 and 345 nm (ϵ 10 000 and 340). The aldehyde (11d) gave a bright red 2,4-dinitrophenylhydrazone, m.p. 127–128°, from methanol (Found: C, 63.0; H, 5.6; N, 15.0. C₂₀H₂₀N₄O₄ requires C, 63.2; H, 5.3; N, 14.7%); τ -0.9br (s, NH), ABX system, τ_A 2.36, τ_B 1.75, τ_X 1.00 [J_{AB} 10, J_{BX} 2.5 Hz, 2,4-(NO₂)₂C₆H₃], 2.13 (s, CH=N), 2.6–2.8 (m, 5 aromatic H), 2.88 (s, CH=C-CH=N), ABX system, τ_A 4.92, τ_B 4.88, τ_X 3.86 (J_{AX} 10, J_{BX} 18 Hz, CH_AH_B=CH_X), and 8.49 (s, >CMe₂).

In the n.m.r. spectrum of aldehyde (11d), singlets at τ 0.46 and 8.75 could also be detected; they are attributed to the (*E*)-isomer (10d) since the proportion increased in samples of aldehyde (11d) which had been allowed to stand at room temperature for several weeks. The resultant mixture of aldehydes [(11d) and (10d), ratio 3 : 1], showed peaks at τ 0.46 (s), ABX system, τ_A 5.25, τ_B 5.15, τ_X 4.15 (J_{AB} 1, J_{AX} 18, J_{BX} 10 Hz, CH_AH_B=CH_X) and 8.75 (s) from the minor component (10d). On addition of the lanthanide shift reagent [Eu(fod)₃]¹⁸ to the mixture of aldehydes [(11d) and (10d), ratio 3 : 1], the vinyl proton of aldehyde (10d), previously obscured by the aromatic protons, could be seen. This vinyl proton was shifted downfield to a much greater extent than the corresponding vinyl proton of isomer (11d), whereas the other protons (=CH₂, CHO, CMe₂) shifted by similar amounts in each isomer.

The basic fraction (2.74 g, 76%) was a mixture of three amines in the ratio 11 : 2 : 4 (by n.m.r.). The amines were separated by preparative t.l.c. giving (i) 4,4-dimethyl-3-dimethylamino-1-phenylhex-5-en-1-yne (3d) (1.5 g, 46%), identical with an authentic sample (see Part 1),³ (ii) 6-methyl-3-dimethylamino-1-phenylhept-5-en-1-yne (4d) (0.3 g, 9%), identical with an authentic sample,³ and (iii) 1,1-dimethyl-2-methylene-3-dimethylaminomethyl-1,2-dihydronaphthalene (12) (0.57 g, 17%), subsequently characterised by n.m.r. and mass spectrometry.

Rearrangement of Cinnamyl dimethyl-(3-phenylprop-2-ynyl)-ammonium Bromide (1e) with 40% Sodium Hydroxide Solution. Formation of *p*-Terphenyl, 3-Dimethylamino-1,4-diphenylhex-5-en-1-yne (3e), 3-Dimethylamino-1,6-diphenylhex-5-en-1-yne (4e), 1-Phenyl-*NN*,3-trimethyl-2-naphthylmethylamine (13e), and 1-Phenyl-*NN*,2-trimethyl-3-naphthylmethylamine (14e).—A mixture of the salt³ (1e) (3.56 g) and a solution of sodium hydroxide (10 g) in water (25 ml) was refluxed for 4 h, cooled, and extracted with ether. The ethereal extracts were separated into neutral and basic fractions using 5*N*-hydrochloric acid and 5*N*-sodium

hydroxide. The neutral fraction (0.47 g) was a complex mixture which was purified by preparative t.l.c. giving *p*-terphenyl (0.15 g, 7%). The basic fraction (2.32 g) consisted of four amines which were separated by preparative t.l.c. (silica gel, ethyl acetate-chloroform, 1 : 3).

Fraction (i) was 3-dimethylamino-1,4-diphenylhex-5-en-1-yne (3e) (137 mg, 5%), identical with a sample obtained in Part 1.³ Fraction (ii) was 1-phenyl-NN,3-trimethyl-2-naphthylmethylamine (13e) (0.94 g, 34%); *m/e* 230 ($M - \text{HNMe}_2$) and 215 (230 - Me), m^* 192.4 (275 \rightarrow 230), 201 (230 \rightarrow 215) (Found: M^+ , 275. $\text{C}_{26}\text{H}_{21}\text{N}$ requires M , 275); ν_{max} 980, 880, 855, and 840 cm^{-1} ; τ 2.2—2.9 (m, 10 aromatic H), 6.68 (s, $\text{CH}_2\text{-N}$), 7.37 (s, aromatic Me), and 8.01 (s, NMe_2); λ_{max} 229 (ϵ 68 000), 273 (5 000), 283 (5 600), 293 (4 600), and 325 nm (500). The amine (13e) was characterised as its *picrate*, yellow prisms from ethanol, m.p. 205° (Found: C, 61.6; H, 4.6; N, 11.0. $\text{C}_{26}\text{H}_{24}\text{N}_4\text{O}_7$ requires C, 61.9; H, 4.7; N, 11.1%). The amine (13e) also gave a *methiodide*, m.p. 167—168° (Found: C, 60.2; H, 5.8; N, 3.2; I, 30.6. $\text{C}_{21}\text{H}_{24}\text{NI}$ requires C, 60.4; H, 5.8; N, 3.3; I, 30.5%); τ 2.1—2.3 (m, 2 aromatic H), 2.4—2.7 (m, 8 aromatic H), 4.7—5.2 (s, $\text{CH}_2\text{-N}^+$), 6.93 (s, NMe_3), and 7.20 (s, aromatic Me). On addition of trifluoroacetic acid, the broad signal at τ 4.7—5.2 sharpened considerably; λ_{max} 234 (ϵ 77 000), 275sh (5 120), 286 (6 850), 295 (6 100), 320 (1 930), and 334 nm (2 370).

Fraction (iii) was 1-phenyl-NN,2-trimethyl-3-naphthylmethylamine (14e) (0.19 g, 11%); *m/e* 230 and 215; m^* 192.4 and 201 (Found: M^+ , 275. $\text{C}_{20}\text{H}_{21}\text{N}$ requires M , 275); ν_{max} 830, 895, 910, 965, 980, and 1 075 cm^{-1} ; τ 2.2—2.9 (m, 10 aromatic H), 6.45 (s, CH_2N), 7.71 (s, NMe_2), and 7.78 (s, aromatic Me); λ_{max} 229 (ϵ 80 000), 275 (5 700), 284 (7 000), 293 (6 400), and 325 nm (700). The amine (14e) was characterised as its *methiodide*, m.p. 215° (Found: C, 60.6; H, 5.7; N, 3.25; I, 30.7. $\text{C}_{21}\text{H}_{24}\text{IN}$ requires C, 60.4; H, 5.8; N, 3.3; I, 30.5%); τ ($\text{CDCl}_3\text{-CF}_3\text{CO}_2\text{H}$) 1.97 (s, aromatic H), 2.0—2.2 (m, aromatic H), and 2.4—2.9 (m, 8 aromatic H), 5.17 (s, $\text{CH}_2\text{-N}^+$), 6.76 (s, NMe_3), and 7.74 (s, aromatic Me); λ_{max} 233 (ϵ 81 000), 252sh (5 700), 275sh (5 700), 284 (7 100), 294sh (6 270), 316 (1 830), 331 (2 220), and 353 nm (240).

Fraction (iv) was 3-dimethylamino-1,6-diphenylhex-5-en-1-yne (4e) (0.27 g, 10%), identical with a sample obtained in Part 1.³

(α -Dideuteriocinnamyl)dimethyl-(3-phenylprop-2-ynyl)ammonium Bromide.— α -Dideuteriocinnamyl bromide (2.7 g), prepared from the corresponding alcohol³⁰ by treatment with 48% hydrobromic acid, was treated with a solution of NN-dimethyl-3-phenylprop-2-ynylamine (2.0 g) in acetone (10 ml). After 24 h at room temperature, the crystals were collected and crystallised from acetone-ether giving (α -dideuteriocinnamyl)dimethyl-(3-phenylprop-2-ynyl)ammonium bromide (4.5 g), m.p. 143—145°; τ 2.3—2.8 (m, 10 aromatic H), AB system, τ_A 2.82, τ_B 3.68 (J_{AB} 16 Hz, $\text{PhCH}_A=\text{CH}_B\text{-CD}_2$), 4.97 (s, $\text{C}\equiv\text{C-CH}_2\text{-N}^+$), and 6.47 (s, NMe_2).

Rearrangement of (α -Dideuteriocinnamyl)dimethyl-(3-phenylprop-2-ynyl)ammonium Bromide using Sodium Deuterioxide in Deuterium Oxide. Formation of NN-Dimethyl-(1-phenyl-4-deuterio-3-trideuteriomethyl-2-naphthyl)dideuteriomethylamine (16) and NN-Dimethyl-(1-phenyl-4-deuterio-2-trideuteriomethyl-3-naphthyl)dideuteriomethylamine (17).—A solution of sodium (1.2 g) in deuterium oxide (10 ml) was added to the ammonium salt (0.9 g) and the mixture was

refluxed overnight, cooled, and extracted with ether. The extracts were separated into neutral and basic fractions and the resultant basic fraction was separated into two components by preparative t.l.c. Fraction (i) was the *amine* (16), *m/e* 235 ($M - \text{DNMe}_2$) and 218 (235 - CD_2H) (Found: M , 281. $\text{C}_{20}\text{H}_{15}\text{D}_6\text{N}$ requires M^+ , 281); τ 2.2—2.9 (m, 9 aromatic H) and 8.01 (s, NMe_2). Fraction (ii) was the *amine* (17) (Found: M^+ , 281); *m/e* 235 and 218; τ 2.2—2.9 (m, 9 aromatic H) and 7.71 (s, NMe_2).

Base Catalysed Rearrangement of Allyldimethyl-(3-phenylprop-2-ynyl)ammonium Bromide (1f). Formation of (E)-2-Allylcinnamaldehyde (10f) and 3a,4-Dihydro-2,2-dimethylbenz[*f*]isoindolinium Bromide (15f).—A solution of sodium hydroxide (0.3 g) in water (20 ml) was added to the salt (1f)³ (14 g) and the mixture was heated on a steam-bath overnight. The solution was cooled and extracted with ether. The ethereal extracts were dried and evaporated giving (E)-2-allylcinnamaldehyde (10f) as an oil (2.5 g, 33%) (Found: M^+ , 172. $\text{C}_{12}\text{H}_{12}\text{O}$ requires M , 172); *m/e* 171; ν_{max} (liquid film) 2 700, 2 810, 1 680, and 930 cm^{-1} ; τ 0.44 (s, CHO), 2.4—2.8 (m, 5 aromatic H and $\text{CH}=\text{C-CHO}$), ABMX₂ system, τ_A 4.94, τ_B 4.90, τ_M 4.03, τ_X 6.73 [J_{BM} 11, J_{AB} 2, J_{AM} 17, J_{MX} 6, J_{AX} or J_{BX} 1 Hz, $\text{CH}_A\text{H}_B=\text{CH}_M\text{-C}(\text{H}_X)_2$]; λ_{max} 285 nm (ϵ 18 400). The aldehyde (10f) formed a crimson 2,4-dinitrophenylhydrazone, needles from methanol, m.p. 204—206° (Found: C, 61.1; H, 4.8; N, 16.1. $\text{C}_{18}\text{H}_{16}\text{N}_4\text{O}_4$ requires C, 61.4; H, 4.5; N, 15.9%); τ -1.21br (s, NH), ABX system, τ_A 2.07, τ_B 1.68, τ_X 0.87 [J_{AB} 9, J_{BX} 2 Hz, 2,4-(NO_2)₂ C_6H_3], 2.11 (s, $\text{CH}=\text{N}$), 2.5—2.7 (m, 5 aromatic H), and 3.02 (s, $\text{CH}=\text{C-CH}=\text{N}$), ABMX₂ system, τ_A 4.92, τ_B 4.94, τ_M 3.9, τ_X 6.51 [J_{AM} 12, J_{BM} 17, J_{MX} 5.5, J_{BX} 1, J_{AX} 1 Hz, $\text{C}(\text{H}_X)_2\text{-CH}_M=\text{CH}_A\text{H}_B$]; *m/e* 352 (M^+).

The aqueous solution after ether extraction was neutralised with 48% hydrobromic acid and evaporated to dryness. The residual oil was crystallised from ethanol giving 3a,4-dihydro-2,2-dimethylbenz[*f*]isoindolinium bromide (15f) (7 g), m.p. 256—258°. A further, less pure, crop of the salt (15f) (3 g) was obtained from the mother liquors (Found: C, 59.55; H, 6.7; N, 4.9; Br, 28.35. $\text{C}_{14}\text{H}_{18}\text{NBr}$ requires C, 60.0; H, 6.4; N, 5.0; Br, 28.6%); τ 2.7—2.9 (m, 4 aromatic H), 3.34br (s, $\text{CH}=\text{C}$), 5.58 (s, $=\text{C-CH}_2\text{-N}$), ABMX_Y system, τ_A 5.92, τ_B 6.5, τ_M 6.4—6.6, τ_X 6.94, τ_Y 7.18 (J_{AB} 12, J_{AM} 8, J_{MX} 5.5, J_{XY} 15 Hz, $\text{CH}_X\text{H}_Y\text{-CH}_M\text{-CH}_A\text{H}_B\text{-N}^+$), and 6.61 and 6.73 (two s, NMe_2); λ_{max} 212 (ϵ 22 400), 217 (25 000), 223 (19 300), and 265 nm (12 200).

Reaction of 3a,4-Dihydro-2,2-dimethylbenz[*f*]isoindolinium Bromide (15f) with 25% Sodium Hydroxide Solution. Formation of NN-Dimethyl-(3-methyl-2-naphthyl)methylamine (13f).—The ammonium salt (15f) (0.5 g) was refluxed for 3 h with 25% aqueous sodium hydroxide solution (50 ml). After cooling, the solution was extracted with ether and separated into neutral and basic fractions using 5N-hydrochloric acid and 5N-sodium hydroxide. There was very little neutral material. The basic fraction (0.29 g) was the *amine* (13f) (Found: M^+ , 199. $\text{C}_{14}\text{H}_{17}\text{N}$ requires M , 199); *m/e* 154 ($M - \text{Me}_2\text{NH}$); τ 2.2—2.8 (m, 6 aromatic H), 5.53 (s, $\text{CH}_2\text{-N}$), 7.52 (s, aromatic Me), and 7.76 (s, NMe_2). The amine (13f) was characterised as its *hydrochloride*, m.p. 240° (Found: C, 71.1; H, 7.9; N, 5.9; Cl, 14.9. $\text{C}_{14}\text{H}_{18}\text{ClN}$ requires C, 71.3; H, 7.6; N, 6.0; Cl, 15.0%); τ ($\text{CF}_3\text{CO}_2\text{H}$) 2.1—2.7 (m, 6 aromatic H), 5.50 (d, J 3 Hz, $\text{NH-CH}_2\text{Ar}$), 6.95 (d, J 3.5 Hz, NH-Me_2), and 7.42 (s, aromatic Me), λ_{max} 227 (ϵ 115 000), 270sh (4 300), 277 (4 600), 288sh

(3 060), 303sh (610), 310.5 (824), 317.5 (624), and 325 nm (1 080).

Emde Reduction of Amine (13f). Formation of 2,3-Dimethylnaphthalene.—Amine (13f) (1.6 g) was converted to its methiodide using methyl iodide in acetonitrile. The methiodide was recrystallised from ethanol, m.p. 217—219° (Found: C, 52.9; H, 6.1; N, 4.0; I, 37.4. $C_{15}H_{20}IN$ requires C, 52.8; H, 5.9; N, 4.1; I, 37.2%); τ ($CDCl_3$ - CF_3CO_2H) 1.8—2.6 (m, 6 aromatic H), 5.16 (s, CH_2-N^+), 6.70 (s, NMe_3), and 7.40 (s, aromatic Me); λ_{max} . 228 (ϵ 110,000), 270sh (4 250), 278 (4 600), 288sh (3 270), 313 (1 010), 319 (785), and 327.5 nm (1 380).

The methiodide (0.85 g) was refluxed with a suspension of sodium amalgam¹⁴ [prepared from sodium (1 g) and mercury (50 g)] in water (40 ml) with vigorous stirring for 4 h. After cooling, the product was extracted into ether and the ethereal extracts were dried and evaporated giving a solid (0.4 g) which, after purification by vacuum sublimation (70° and 0.5 mmHg), gave 2,3-dimethylnaphthalene (0.3 g), m.p. 102—103°, identical with an authentic sample.

Base Catalysed Rearrangement of Dimethyl-(3,3-dimethylallyl)-(3-phenylprop-2-ynyl)ammonium Bromide (1d). Formation of (Z)-2-(1,1-Dimethylallyl)cinnamaldehyde (11d) and 3a,4-Dihydro-2,2,4,4-tetramethylbenz[f]isoindolinium Chloride (15d).—The ammonium salt (1d)³ (8.0 g) and a solution of potassium hydroxide (0.2 g) in water (10 ml) were heated on a steam-bath for 12 h. After cooling the solution was extracted with ether and the ethereal extracts were separated into neutral and basic fractions using 5N-hydrochloric acid and 5N-sodium hydroxide. The neutral fraction (1.2 g, 20%) was (Z)-2-(1,1-dimethylallyl)cinnamaldehyde (11d) containing a trace of the E-isomer (10d). The basic fraction (0.5 g) was a complex mixture which was not further investigated.

The aqueous layer was acidified with 5N-hydrochloric acid and evaporated giving a solid, which after recrystallisation from ethanol ether gave 3a,4-dihydro-2,2,4,4-tetramethylbenz[f]isoindolinium chloride (15d) (3.0 g, 45%), m.p. 258—260° (Found: C, 72.5; H, 8.6; N, 5.3; Cl, 13.4. $C_{16}H_{22}ClN$ requires C, 72.7; H, 8.3; N, 5.3; Cl, 13.6%); τ 2.5—2.9 (m, 4 aromatic H), 3.31br (s, $CH=C$), AB system, τ_A 5.45, τ_B 5.68 (J_{AB} 16 Hz, $=C-CH_AH_B-N^+$), τ 5.9—6.5 (m, $CH-CH_2-N^+$), 6.56 and 6.76 (two s, NMe_3), and 8.52 and 8.96 (two s, $>CMe_2$); λ_{max} . 212 (ϵ 17 900), 217 (21 700), 224 (17 200), 265 (11 300), and 272 nm (11 000).

Reaction of 3a,4-Dihydro-2,2,4,4-tetramethylbenz[f]isoindolinium Chloride (15d) with 20% Sodium Hydroxide Solution. Formation of 1,1-Dimethyl-2-methylene-3-dimethylaminomethyl-1,2-dihydronaphthalene (12).—The salt (15d) (1.0 g) was heated on a steam-bath for 12 h with a solution of sodium hydroxide (5 g) in water (25 ml). After cooling, the product was extracted into ether and separated into neutral and basic fractions using 5N-hydrochloric acid and 5N-sodium hydroxide. The basic fraction (0.6 g, 67%) was 1,1-dimethyl-2-methylene-3-dimethylaminomethyl-1,2-dihydronaphthalene (12); m/e 212 ($M-Me$), and 169 (212— $CH_2=NMe$), m^* 198 (227— \rightarrow 212) and 135 (212— \rightarrow 169) (Found: M^+ , 227. $C_{16}H_{21}N$ requires M , 227); τ 2.5—3.0 (m, 4 aromatic H), 3.57br (s, $CH=C$), 4.6—4.75 (m, $=CH_2$), 6.82 (s, CH_2N), 7.75 (s, NMe_2), and 8.57 (s, $>CMe_2$). The amine (12) was characterised as its methiodide, from ethanol, m.p. 188—190° (Found: C, 55.3; H, 6.45; N, 3.5; I, 34.4. $C_{17}H_{24}NI$ requires C, 55.3; H, 6.5; N, 3.8; I, 34.4%);

τ 2.6—2.9 (m, 4 aromatic H and $ArCH=C$), 4.13 and 4.51 (two s, $=CH_2$), 5.46 (s, CH_2-N^+), 6.46 (s, NMe_3), and 8.57 (s, $>CMe_2$); λ_{max} . 221 (ϵ 33 800), 228sh (26 400), 236sh (19 000), and 306 nm (14 900).

Base Catalysed Rearrangement of Cinnamyl-dimethyl-(3-phenylprop-2-ynyl)ammonium Bromide (1e). Formation of 3a,4-Dihydro-2,2-dimethyl-4-phenylbenz[f]isoindolinium Bromide (15e).—The ammonium salt (1e)³ (18 g) and a solution of sodium hydroxide (0.4 g) in water (10 ml) were warmed gently on a steam-bath. A vigorous exothermic reaction took place after a few minutes. The solution was left at room temperature for 30 min and extracted with ether. The aqueous solution, on standing at room temperature, gave crystals of 3a,4-dihydro-2,2-dimethyl-4-phenylbenz[f]isoindolinium bromide (15e) (10 g), m.p. 158—160° (Found: C, 67.15; H, 6.1; N, 4.1; Br, 22.1. $C_{20}H_{22}BrN$ requires C, 67.4; H, 6.2; N, 3.9; Br, 22.5%); τ (CD_3OD) 2.62 (s, 5 aromatic H), 2.8—3.1 (m, 5-, 6-, and 7-H), 3.28br (s, $CH=C$), 3.47 (d, J 7 Hz, 8-H), 5.37br (s, $=C-CH_2-N^+$), 5.7—6.4 (m, $PhCH-CH-CH_2-N^+$), and 6.64 and 6.79 (s, NMe_2); λ_{max} . 215sh (ϵ 24 200), 218 (25 700), 253sh (8 710), 268 (9 400), 272sh (9 140), and 328 nm (87). The mother liquors were neutralised with 48% hydrobromic acid, and evaporation followed by crystallisation from water yielded a further crop of the salt (15e) (8 g).

Reaction of 3a,4-Dihydro-2,2-dimethyl-4-phenylbenz[f]isoindolinium Bromide (15e) with 35% Sodium Hydroxide Solution. Formation of NN-Dimethyl-1-phenyl-3-methyl-2-naphthylmethylamine (13e) and NN-Dimethyl-(1-phenyl-2-methyl-3-naphthyl)methylamine (14e).—The salt (15e) (2.0 g) was heated on a steam-bath for 2 h with a solution of sodium hydroxide (11 g) in water (25 ml) and ethanol (5 ml). After cooling, the products were extracted into ether and the ethereal extracts were dried and evaporated giving an oil (0.8 g, 52%) shown by n.m.r. spectroscopy to be a mixture of two amines in the ratio 3 : 1. The amines were separated by preparative t.l.c. giving amine (13e) (0.45 g) and amine (14e) (0.15 g).

Base Catalysed Rearrangement of cis- and trans-Crotyldimethylammonium Bromide (1g). Formation of (E)- and (Z)-2-(1-Methylallyl)cinnamaldehyde (10g) and (11g) and 3a,4-Dihydro-2,2,4-trimethylbenz[f]isoindolinium Bromide (15g).—The mixture of salts (1g)³ (16 g) was heated on a steam-bath for 12 h with a solution of sodium hydroxide (0.2 g) in water (2 ml). After cooling, the mixture was diluted with water and extracted with ether. The ethereal extracts were separated into neutral and basic fractions using 5N-hydrochloric acid and 5N-sodium hydroxide. The neutral fraction (1.5 g, 16%) was shown by n.m.r. spectroscopy to be a mixture of two aldehydes in the ratio 4 : 1, together with two very minor components. The two major components were isolated by preparative t.l.c. Fraction (i) was (E)-2-(1-methylallyl)cinnamaldehyde (10g) (1.0 g), m/e 171 ($M-Me$) and 157 ($M-CHO$) (Found: M^+ , 186. $C_{13}H_{14}O$ requires M , 186); τ 0.47 (d, J 2 Hz, CHO), 2.59 (s, 5 aromatic H), 2.67br (s, $CH=C$) and $ABCMX_3$ system, τ_A 3.70, τ_B 4.98, τ_C 5.03, τ_M 6.28, τ_X 8.67 [J_{AB} 10, J_{AC} 16, J_{AM} 7, J_{BC} 2, J_{MX} 7 Hz, $CH_BH_C(=CH_A-CH_M-C(H_X)_3^-)$]; λ_{max} . 282 (ϵ 17 800) and 226 nm (19 200). The aldehyde (10g) was characterised as its 2,4-dinitrophenylhydrazone from methanol, m.p. 169—171° (Found: C, 59.6; H, 5.0; N, 15.1. $C_{19}H_{18}N_4O_4$ requires C, 59.4; H, 4.9; N, 15.3%); τ -1.08br (s, NH), ABX system, τ_A 2.14, τ_B 1.69, τ_X 0.91 [J_{BX} 2.5, J_{AB} 9 Hz, 2,4-(NO_2)₂C₆H₃], 2.26 (s, $CH=N$), 2.65

(s, 5 aromatic H), 3.04 (s, CH=C), and ABCMX₃ system, τ_A 3.75, τ_B 4.90, τ_C 4.92, τ_M 6.07, τ_X 8.52 [J_{AB} 18, J_{AC} 10, J_{BC} 2, J_{AM} 6, J_{MX} 7 Hz, $CH_BH_C=CH_A-CH_M-C(H_X)_3$]; m/e 366 (M^+).

Fraction (ii) was a mixture (1 : 1 ratio) of (E)- and (Z)-2-(1-methylallyl)cinnamaldehyde (10g) and (11g) (0.4 g) which could not be further purified; τ (peaks attributed to Z-isomer) 0.14 (s, CHO), 2.47 (s, CH=C), and 8.75 (d, J 7 Hz, MeCH), together with peaks which overlap with the E-isomer.

The basic fraction (< 50 mg) was not investigated further. The aqueous solution, after ether extraction, was neutralised with 48% hydrobromic acid and evaporated. Acetone was added and the resultant solid was collected and crystallised from ethanol-ethyl acetate, giving 3a,4-dihydro-2,2,4-trimethylbenz[*f*]isoindolinium bromide (15g) (13 g), m.p. 198—200°; τ 2.6—2.9 (m, 4 aromatic H), 3.38br (s, CH=C), 5.59br (s, =C-CH₂-N⁺), 5.9—6.1 (m) and 6.3—6.5 (m, CH-CH₂-N⁺), 6.63 and 6.74 (two s, NMe₃), 6.9—7.1 (m, MeCH-CH-), and 8.63 (d, J 6 Hz, MeCH); λ_{max} 212 (ϵ 20 400), 217 (23 160), 223 (19 250), 266 (10 900), and 327 nm (59).

*Reaction of 3a,4-Dihydro-2,2,4-trimethylbenz[*f*]isoindolinium Bromide (15g) with 25% Sodium Hydroxide Solution. Formation of NN-Dimethyl-(1,2-dimethyl-3-naphthyl)methylamine (14g) and NN-Dimethyl-(1,3-dimethyl-2-naphthyl)methylamine (13g).*—The salt (15g) (5.0 g) was refluxed with sodium hydroxide solution (25%; 25 ml) for 16 h, cooled, and extracted with ether. The ethereal extracts were dried and evaporated giving an oil (2.7 g, 75%) which was shown by n.m.r. spectroscopy to be a mixture of two amines [(14g) and (13g)] in the ratio 3 : 1. The amines were separated by preparative t.l.c. Fraction (i) was amine (14g), m/e 168 ($M - Me_2NH$) (Found: M^+ , 213. C₁₅H₁₉N requires M , 213); τ 1.9—2.1 (m, aromatic H), 2.2—2.3 (m, aromatic H), 2.6—2.9 (m, 3 aromatic H), 6.51 (s, CH₂-N), 7.42 and 7.52 (two s, 2 aromatic Me), and 7.76 (s, NMe₂). The amine (14g) was characterised as its *methiodide*, from ethanol, m.p. 204—205° (Found: C, 53.8; H, 6.3; N, 3.8; I, 35.7. C₁₆H₂₂IN requires C, 54.1; H, 6.2; N, 4.0; I, 35.8%); τ (CDCl₃-CF₃CO₂H) 1.8—2.5 (m, 5 aromatic H), 5.18 (s, CH₂N⁺), 6.78 (s, NMe₃), and 7.32 and 7.45 (two s, 2 aromatic Me); λ_{max} 232.5 (ϵ 99 500), 275sh (4 100), 280sh (4 600), 284 (4 760), 295sh (3 630), 316 (1 210), and 331 nm (1 640).

Fraction (ii) was amine (13g) (Found: M^+ , 213. C₁₅H₁₉N requires M , 213); m/e 168; τ 2.0—2.1 (m, aromatic H), 2.3—2.4 (m, aromatic H), 2.6—2.9 (m, 3 aromatic H), 6.43 (s, CH₂-N), 7.32 and 7.48 (two s, 2 aromatic Me), and 7.77 (s, NMe₂). The amine (13g) was characterised as its *methiodide*, from ethanol, m.p. 175—177° (Found: C, 54.0; H, 6.4; N, 3.8; I, 35.7. C₁₆H₂₂IN requires C, 54.1; H, 6.2; N, 4.0; I, 35.8%); τ (CDCl₃-CF₃CO₂H) 1.9—2.1 (m, aromatic H), 2.2—2.6 (m, 4 aromatic H), AB system, τ_A 4.84, τ_B 5.10 (J_{AB} 14 Hz, CH_AH_BN⁺), τ 6.73 (s, NMe₃), 7.14 and 7.36 (two s, 2 aromatic Me); λ_{max} 232 (ϵ 92 400), 253sh (3 890), 273sh (4 425), 282 (5 010), 291sh (3 890), 317 (1 118), and 331.5 nm (1 460).

Base Catalysed Rearrangement of Dimethyl-(2-methylallyl)-(3-phenylprop-2-ynyl)ammonium Chloride (1h). Formation of (E)-2-(2-Methylallyl)cinnamaldehyde (10h).—The salt (1h)³ (5.0 g) was refluxed with a solution of potassium hydroxide (0.15 g) in water (8 ml) for 12 h. The products were extracted into ether and the ethereal extracts were separated

into neutral and basic fractions using 5N-hydrochloric acid and 5N-sodium hydroxide. The neutral fraction was (E)-2-(2-methylallyl)cinnamaldehyde (10h) (Found: M^+ , 186. C₁₃H₁₄O requires M , 186); ν_{max} 1 680 and 1 620 cm⁻¹; τ 0.44 (s, CHO), 2.4—2.8 (m, 5 aromatic H and CH=C-CHO), 4.23 (s) and 4.44br (s, =CH₂), 6.85 (s, =CH₂-C=), and 8.19 (s, vinylic Me). A trace of the (Z)-isomer could be detected in the n.m.r. spectrum (singlets at τ 0.14, 6.94, and 8.27); λ_{max} 218 (ϵ 10 100), 225 (9 000), and 283 nm (20 900). The aldehyde (10h) was characterised as its 2,4-dinitrophenylhydrazone, from methanol, m.p. 173—174° (Found: C, 62.05; H, 5.15; N, 15.2. C₁₉H₁₈N₄O₄ requires C, 62.3; H, 4.9; N, 15.3%); τ -1.18br (s, NH), ABX system, τ_A 2.15, τ_B 1.70, τ_X 0.93 [J_{BX} 3, J_{AB} 9 Hz, 2,4-(NO₂)₂C₆H₃], τ 2.10 (s, CH=N), 2.6—2.8 (m, 5 aromatic H), 3.00 (s, CH=C-CH=N), 5.14br and 5.25br (two s, =CH₂), 6.63 (s, =C-CH₂-C=), and 8.08 (s, vinylic Me).

The basic fraction on evaporation yielded < 50 mg of product. The aqueous solution from the ether extraction was neutralised with 5N-hydrochloric acid and evaporated, but no crystalline salt was obtained.

Base Catalysed Rearrangement of Dimethyl-(2-phenylallyl)-(3-phenylprop-2-ynyl)ammonium Bromide (1j). Formation of (E)- and (Z)-2-(2-Phenylallyl)cinnamaldehyde [(10j) and (11j)].—The ammonium salt (1j)³ (16 g) was heated on a steam-bath with a solution of sodium hydroxide (0.2 g) in water (50 ml) for 12 h. The solution was cooled and extracted with ether. The ethereal extracts were dried and evaporated giving an oil (5.5 g), shown to be a mixture of the aldehydes (10j) and (11j) in the ratio 10 : 1. The aldehydes were separated by preparative t.l.c. Fraction (i) was (Z)-2-(2-phenylallyl)cinnamaldehyde (11j) contaminated by ca. 20% of the (E)-isomer; τ 0.13 (s, CHO) and 2.4—2.9 (m, 10 aromatic H and CH=C-CHO), ABX₂ system, τ_A 4.48, τ_B 4.83, τ_X 6.41 [J_{BX} 1 Hz, CH_AH_B=C-C(H_X)₂]. Fraction (ii) was (E)-2-(2-phenylallyl)cinnamaldehyde (10j); τ 0.37 (s, CHO), 2.4—2.75 (m, 10 aromatic H), 2.81 (s, PhCH=C), 4.64 and 5.11 (two s, =CH₂), and 6.35 (s =C-CH₂-); λ_{max} 226 (ϵ 14 000), 245 (13 000), and 283 nm (19 100).

The aldehyde (10j) was characterised as its 2,4-dinitrophenylhydrazone from ethyl acetate, m.p. 194—195° (Found: C, 67.3; H, 4.8; N, 12.8. C₂₄H₂₀N₄O₄ requires C, 67.3; H, 4.7; N, 13.1%); τ -1.19br (s, NH), ABX system, τ_A 2.35; τ_B 1.88; τ_X 0.93 [J_{AB} 9, J_{BX} 2 Hz, 2,4-(NO₂)₂C₆H₃], τ 2.07 (s, CH=N), 2.4—2.8 (m, 10 aromatic H), 2.90 (s, CH=C-), 4.45 and 4.91 (two s, =CH₂), and 6.13 (s, =C-CH₂-C=); m/e 428 (M^+). The aqueous solution from the ether extraction was neutralised with 48% hydrobromic acid and evaporation gave starting material (1j) (6.0 g).

Dimethylbis-(3-phenylprop-2-ynyl)ammonium Bromide (18e).—A solution of NN-dimethyl-(3-phenylprop-2-ynyl)-amine (8.0 g) in ethanol was added to a solution of 3-phenylprop-2-ynyl bromide (9.5 g) in ethanol (20 ml) at 0°. After 3 days, the crystals were collected giving dimethylbis-(3-phenylprop-2-ynyl)ammonium bromide (18e) (16.8 g, 95%), m.p. 176—179° (lit.,²⁷ 179—180°); τ 2.3—2.7 (m, 10 aromatic H), 4.74 (s, two CH₂-N⁺), and 6.30 (s, NMe₂).

Base Catalysed Rearrangement of Dimethylbis-(3-phenylprop-2-ynyl)ammonium Bromide (18e). Formation of 2,2-Dimethyl-4-phenylbenz[*f*]isoindolinium Bromide (19e).—The ammonium salt (18e) (6.0 g) was warmed gently on a steam bath with a solution of sodium hydroxide (0.2 g) in water (15 ml). After a few min, a vigorous exothermic reaction took place, the temperature rising to 100°. After 1 h, the

mixture was cooled and extracted with ether. The ethereal extracts were dried and evaporated but no product was obtained. The aqueous layer was neutralised with 48% hydrobromic acid and evaporated. The resultant solid was recrystallised from ethanol-ether giving 2,2-dimethyl-4-phenylbenz[f]isoindolinium bromide (19e) (5.9 g, 98%), m.p. 260° (Found: C, 67.8; H, 5.9; N, 4.2; Br, 22.9. C₂₀H₂₀BrN requires C, 67.8; H, 5.6; N, 3.9; Br, 22.8%); ν_{\max} , 860, 887, 923, 940, and 990 cm⁻¹; τ (CF₃CO₂H) 2.0—2.8 (m, 10 aromatic H), 4.90 (s, CH₂-N⁺), 5.21 (s, CH₂-N⁺), and 6.58 (s, NMe₂); λ_{\max} , 230 (ϵ 79 650) and 284—292 nm (8 850).

Emde Reduction of 2,2-Dimethyl-4-phenylbenz[f]isoindolinium Bromide (19e). Formation of Amines (13e) and (14e).—The salt (19e) (1.1 g) was refluxed with a suspension of sodium amalgam¹⁴ [prepared from sodium (1 g) and mercury (30 g)] in water (50 ml) for 24 h with vigorous stirring. After cooling, the solution was extracted with ether. The ethereal extracts were dried and evaporated giving an oil, which after separation by preparative t.l.c. gave amine (13e) (50 mg) and amine (14e) (100 mg).

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