

Base Catalysed Rearrangements Involving Ylide Intermediates. Part 7. The Rearrangements of Allyl(pentadienyl)- and Propynyl(pentadienyl)-ammonium Cations. The [5,4] \uparrow Sigmatropic Rearrangement.¹

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The base catalysed rearrangements of the cations (7), (17), (22), and (27) gave the enamines (9), (18), (23), and (28), which on hydrolysis yielded the aldehydes (10), (19), (24), and (29) respectively. The reactions are shown to be concerted [5,4] sigmatropic rearrangements proceeding *via* a nine-membered transition state involving 10 π electrons. The base catalysed rearrangements of the 3-phenylprop-2-ynyl (pentadienyl) ammonium cations (51), (52), (60), and (61), however yield only the products of [1,2], [3,2], and [5,2] sigmatropic rearrangements.

SINCE the publication in 1965 of the Woodward-Hoffmann rules² on the conservation of orbital symmetry in concerted reactions, there has been a renewed effort to search for new kinds of pericyclic reactions and to study the stereochemistry of such processes. For several years we have been interested in the study of anionic sigmatropic rearrangements, particularly those involving ylide intermediates.³ A comprehensive study of the base catalysed sigmatropic rearrangements of bis-allyl-,³ allyl(propynyl)-,³ and allyl(phenacyl)-ammonium salts⁴ has recently been reported. We have now extended these studies to include the base catalysed rearrangements of allyl(pentadienyl)- and propynyl(pentadienyl)-ammonium salts, and during this work the first example of the anionic [5,4] sigmatropic rearrangement¹ has been discovered.[†]

The predictions of the Woodward-Hoffmann rules concerning thermal sigmatropic rearrangements may be summarised as follows:⁶ for a sigmatropic change of order [i,j], the following stereochemical possibilities are considered as 'allowed'.

| i + j | neutral | cationic | anionic |
|--------|---------|----------|---------|
| 4q | as | — | — |
| | sa | as | ss |
| 4q + 1 | — | sa | aa |
| | ss | — | — |
| 4q + 2 | aa | ss | as |
| 4q - 1 | — | aa | sa |

Although from the above Table the number of feasible rearrangements seems infinite only a relatively small number is known. It is only in the past few years that any higher-order rearrangements ($q > 1$, *i.e.* rearrangements of order greater than [3,3]) have been reported. It should be noted that in systems capable of undergoing a higher-order sigmatropic rearrangement, there is *always* the possibility that a simpler sigmatropic rearrangement may compete and take precedence. Thus in the thermal rearrangements of *trans*-pentadienyl phenyl ethers (1) the [5,5] rearrangement⁷ has been

[†] The description [5,4] sigmatropic rearrangement is used, rather than [4,5] sigmatropic rearrangement (ref. 1), to emphasise the relationships between this and other anionic sigmatropic rearrangements including [1,2], [3,2], [5,2], [1,4], and [3,4] rearrangements.

observed to compete favourably with the [3,3] rearrangement, whereas for the corresponding *cis*-pentadienyl phenyl ethers (2), only a [1,5] hydrogen shift was observed. In a similar manner in cationic systems, the [3,4] rearrangement of the cation (3) competes § with [3,3] and [1,2] shifts.⁸ At the time that this work was started there had been no reports, however, of studies of higher-order rearrangements in anionic systems. ¶ We therefore decided to investigate the simplest anionic system capable of undergoing a [5,4] sigmatropic rearrangement, *i.e.* the base catalysed rearrangement of an allyl(pentadienyl)ammonium cation.

The Woodward-Hoffmann predictions⁶ for the possible thermal rearrangement pathways of allyl(pentadienyl)ammonium ylides (4) and (5) are given below (no stereochemistry implied). Although the large number of feasible pathways seemed at first sight to present insuperable problems, the four allowed pathways [3,2; 1,4; 5,4; 3,6] which can proceed *via* suprafacial-suprafacial modes are geometrically most favourable. The [1,4] rearrangement also appears unlikely to predominate in this type of system from recent evidence.¹⁰ For a [5,4] rearrangement to take place preferentially there are three important factors (i) the ylide carbanion must be formed by proton abstraction from the allyl grouping and therefore a carbanion-stabilising group must be attached to the allyl group—we have used a phenyl group; (ii) from an examination of molecular models, it appeared that a *cis*-pentadienyl group would give much better orbital overlap in the transition state; and (iii) a substituent on the pentadienyl group was required to distinguish between the various rearrangement pathways. The reactions initially investigated therefore were the base catalysed rearrangement of

[‡] The formation of 1-methylthio-3-(*p*-tolyl)-*trans*-prop-1-ene as a minor product in the base-induced rearrangement of benzyl allyl sulphide⁵ could formally be considered as a [5,4] rearrangement although other pathways have not been excluded.

§ A more recent example in a β -naphthalenone system may, however, involve only a [3,4] sigmatropic shift (ref. 9).

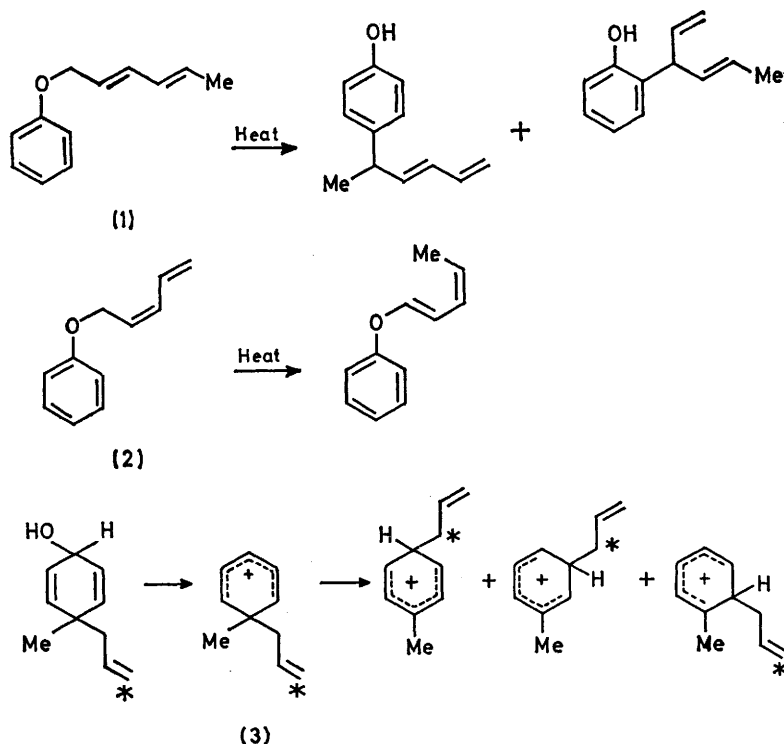
¶ Note added in proof: Since this paper was submitted for publication, three relevant papers have been published. Two describe the application of our method (ref. 1) for the synthesis of conjugated (*Z,E*)-dienes (G. Decodts, G. Dressaire, and Y. Langlois, *Synthesis*, 1979, 510; G. Dressaire and Y. Langlois, *Tetrahedron Letters*, 1980, 21, 67). The third provides an excellent review of the stereochemistry of [3,2] sigmatropic rearrangements (R. W. Hoffmann, *Angew. Chem. Internat. Edn.*, 1979, 18, 563).

substituted cinnamyl dimethyl[(2*Z*)-penta-2,4-dienyl]-ammonium bromides.

The preparation of the (2*Z*)-penta-2,4-dienyldimethylamines (6a—f) was accomplished by the route shown in Scheme 1. The amines (6) were obtained in good yield

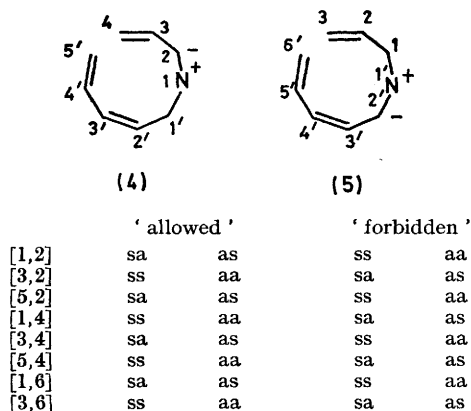
the above amines (6) with the appropriate allyl, or propynyl halide in acetonitrile. The salts were rather unstable, hygroscopic solids or oils which were characterised mainly by their n.m.r. spectra.

Cinnamyl dimethyl-(2*Z*)-2-methylpenta-2,4-dienyl-



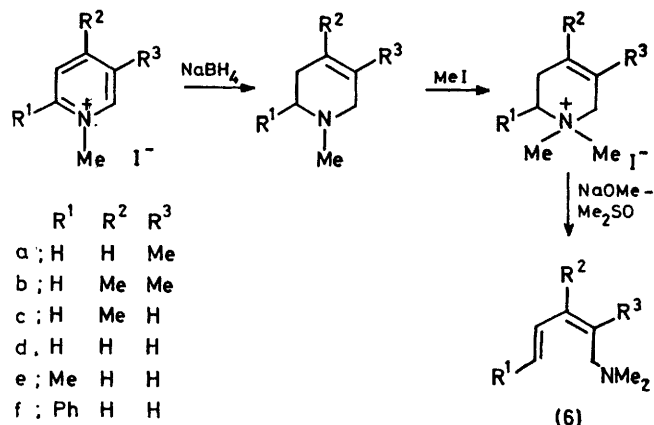
and with a high stereochemical purity. The amines (6d—f) were shown by their n.m.r. coupling constants to have a *cis*-double bond in the 2-position and the amines (6e and f) were shown to have, in addition, a *trans*-double bond in the 4-position. By analogy the

ammonium bromide (7) was treated with sodium methoxide in dimethyl sulphoxide at room temperature for 12 h, and, after pouring into water and extracting with ether, the crude product was examined by n.m.r. spectroscopy. The major product was identified as the enamine (9) arising from a [5,4] sigmatropic rearrangement of the ylide (8, see arrows).



amines (6a—c) are assumed to have the 2*Z*-configuration, which is also required by the method of preparation. An analogous method for the preparation of (*Z,E*)-penta-2,4-dienyldimethylamines has been reported.¹¹

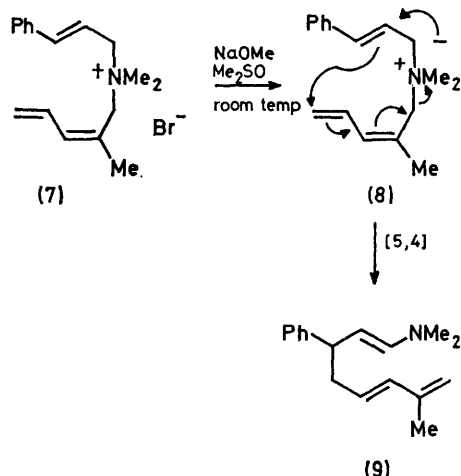
The allyl- and propynyl-[(2-*Z*)-penta-2,4-dienyl]-ammonium salts were all prepared by quaternisation of



SCHEME 1

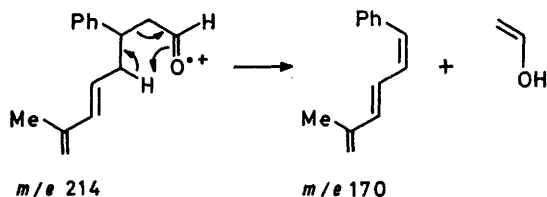
The enamine (9) was purified by distillation and was characterised by its n.m.r. spectrum which showed a singlet at τ 7.52, a doublet at τ 4.14 (J 15 Hz), and a

double doublet at τ 5.67 (J 15, 7 Hz), characteristic of the *trans*-enamine grouping ($-\text{CH}=\text{CH}-\text{NMe}_2$) attached to a CH group. The other features were a *trans*-double bond (J_{XY} 16 Hz) attached to a CH_2 group, a terminal olefinic methylene group at τ 5.20, and a vinylic methyl group at τ 8.27. The mass spectrum showed a molecular ion at m/e 241 followed by fragmentation to the base



peak at m/e 160 by loss of the 4-methylpentadienyl radical.

The enamine was further characterised by hydrolysis to the corresponding aldehyde (10) using dilute aqueous hydrochloric acid. The aldehyde (10) was characterised by its i.r. spectrum [ν_{max} at 1715 ($\text{C}=\text{O}$) and 968 cm^{-1} (*trans* $\text{CH}=\text{CH}$)] and its n.m.r. spectrum (see Experimental section) which provided evidence for a $>\text{CHCH}_2\text{CH}=\text{O}$ grouping with a (2*E*)-4-methylpentadienyl group attached to the CH group. The aldehyde (10) gave a strong molecular ion at m/e 214 in its mass spectrum, followed by loss of CH_3CHO to give m/e 170, consistent with the cyclic fragmentation shown in Scheme 2. The

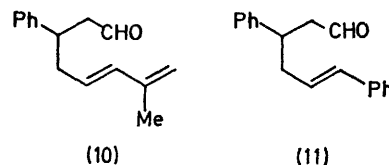


SCHEME 2

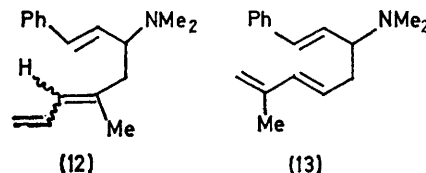
type of fragmentation has previously been observed for the aldehyde (11).³

When the crude reaction product from the base catalysed rearrangement of the salt (7) was immediately treated with dilute acid, and the aldehyde (10) was extracted into ether, neutralisation of the acidic solution followed by ethereal extraction gave a basic fraction. This basic fraction (a complex mixture on t.l.c.) was chromatographed giving an inseparable mixture containing the amines (12) and (13) in low yield (*ca.* 10%, ratio 1:1). The mixture of the amines (12) and (13)

was characterised by its n.m.r. and mass spectra, but an unambiguous assignment of the stereochemistry of the trisubstituted double bond in amine (12) was not possible; a mixture of (*E*)- and (*Z*)-isomers may, in fact, have been present.



To summarise, the base catalysed rearrangement of the salt (7) proceeds at room temperature *via* the ylide (8) giving the *trans,trans*-enamine (9) as the major product arising from a highly specific [5,4] sigmatropic rearrangement. The alternative mechanistic pathway for the transformation (8) \longrightarrow (9) is *via* a [3,2] sigmatropic rearrangement³ leading to the amine (14) followed by a [3,3] Cope rearrangement *at room temperature* leading to the enamine (9) (see Scheme 3). This alternative pathway is unlikely since (i) [3,3] Cope rearrangements at room temperature are normally observed only in exceptional circumstances^{8,12} and (ii) the [3,2] sigmatropic rearrangement product (14) could undergo two possible [3,3] rearrangements [(14) \longrightarrow (9) and (14) \longrightarrow (15)] which would be expected to have similar



rates; however, enamine (15) was not formed and the [3,2] sigmatropic rearrangement product (14) was also not detected. The minor products (12) and (13) are formally derived by [1,2] and [5,2] sigmatropic rearrangements, but their formation in equal amounts is more consistent with an origin involving the radical pair (16).

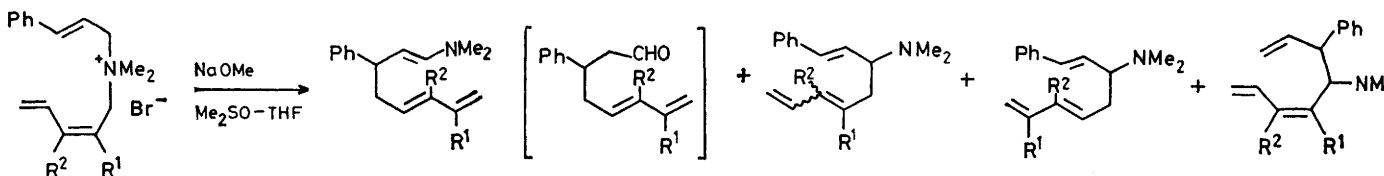
Further examples of the base catalysed rearrangements of cinnamylidimethyl-(2*Z*)-pentadienylammonium salts which undergo [5,4] rearrangement are given in Table 1. Rearrangement of the salt (17) proceeded in an analogous manner to the salt (7). However the salt (22) gave, in addition, the product (26) which arose by [3,2] sigmatropic rearrangement of the alternative ylide (32). In the case of the salt (27), the [3,2] sigmatropic rearrangement is the major reaction pathway [(27) \longrightarrow (31)]. This may reflect the relative acidities of the two methylene groups adjacent to nitrogen in the salt (27). Substitution of the penta-2,4-dienyl unit by methyl groups in (7), (17), and (22) decreases the acidity of the pentadienyl methylene group so that the proton on the cinnamyl group is preferentially removed by base in

these cases. With no methyl substituents on the pentadienyl group of the salt (27), the protons on the pentadienyl group are more acidic and are preferentially abstracted by base to give the ylide (33), which immediately rearranges to the amine (31). The normally

to the aldehyde (29). The n.m.r. spectrum of the unstable aldehyde (29) was complex in the vinylic proton region and the stereochemistry of the disubstituted olefinic bond could not be determined; its i.r. spectrum, however, showed *no* band at 970 cm^{-1} characteristic of

TABLE 1

Base catalysed rearrangements of cinnamyltrimethyl-(2*Z*)-penta-2,4-dienylammonium bromides

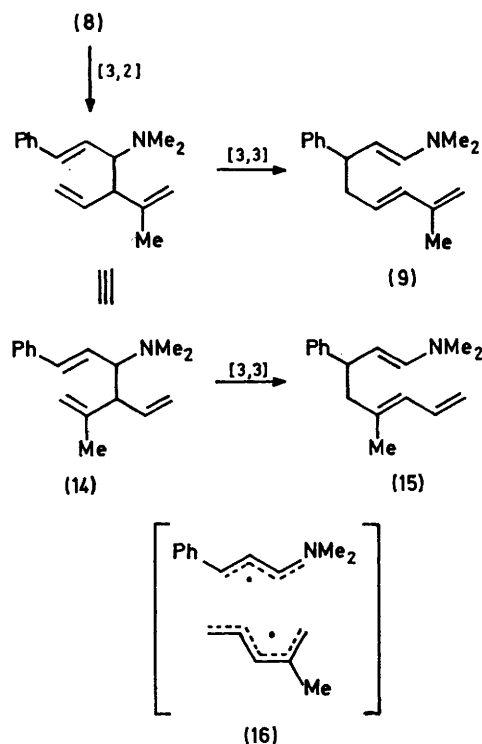


| R ¹ | R ² | (7) | Solvent | Temp. (°C) | (9) <i>a</i> | (10) | (12) | (13) | (26) <i>d</i> | (31) <i>a</i> |
|----------------|----------------|------|------------------------|------------|-------------------|-----------------|------|---------------|---------------|---------------|
| Me | H | (7) | Me ₂ SO | 25 | (9) <i>a</i> | (10) | (12) | (13) | (26) <i>d</i> | (31) <i>a</i> |
| Me | Me | (17) | Me ₂ SO-THF | 0 | (18) <i>a</i> | (19) | (20) | (21) | | |
| H | Me | (22) | Me ₂ SO-THF | 0 | (23) <i>a</i> | (24) | (25) | (26) <i>c</i> | | |
| H | H | (27) | Me ₂ SO-THF | 0 | (28) <i>a,b,c</i> | (29) <i>b,c</i> | (30) | (31) <i>c</i> | | |

a The enamines were characterised as the corresponding aldehydes. *b* In this case the stereochemistry of the disubstituted double bond has not been rigorously proved. *c* In these cases the [1,2] and [5,2] sigmatropic rearrangement products are identical. *d* Predominantly one diastereoisomer. *e* Stereochemistry of the double bonds in doubt.

high stereoselectivity of the [3,2] sigmatropic rearrangement³ is again observed; amines (26) and (31) are formed as predominantly one diastereoisomer in each case.

The [5,4] sigmatropic rearrangement of the salt (27)



SCHEME 3

leads to the minor product (28), but because of the low yield it was impossible to obtain a good n.m.r. spectrum of the enamine (28); it was therefore hydrolysed directly

the *trans*-CH=CH- grouping, as exhibited by the aldehyde (10). The aldehyde (29) may therefore contain a *cis* double bond and the [5,4] sigmatropic rearrangement (27) → (28) may proceed *via* a different stereochemistry from the rearrangement (7) → (9). The stereochemistry of the trisubstituted double bonds in aldehydes (19) and (24) has not been determined; they are assumed to be as shown (Table 1) by analogy with aldehyde (10) and also because the enamine precursors (18) and (23) contain *trans*-enamine double bonds. It would be difficult to visualise an acceptable transition state having good orbital overlap [*cf.* (36)] for the transformations (34) → (35) in which the product contains a *trans*-enamine double bond (between C-2 and C-3) in conjunction with a *cis*-double bond between C-3' and C-4' of the diene unit.*

In order to study further the stereochemistry of the transition state of the [5,4] sigmatropic rearrangement, the salts (37) and (38) containing *trans*-penta-2,4-dienyl units were prepared by the routes shown in Schemes 4 and 5. The *trans*-stereochemistry of the CH=CH moiety of the 4-methylpenta-2,4-dienyl group in salt (38) was easily determined from the n.m.r. coupling constant between the olefinic protons (*J* 15 Hz). In salt (37), a direct comparison with the *cis*-salt (7), of established stereochemistry, showed that they were *not* identical, and therefore the *trans*-stereochemistry could be assigned to the salt (37).

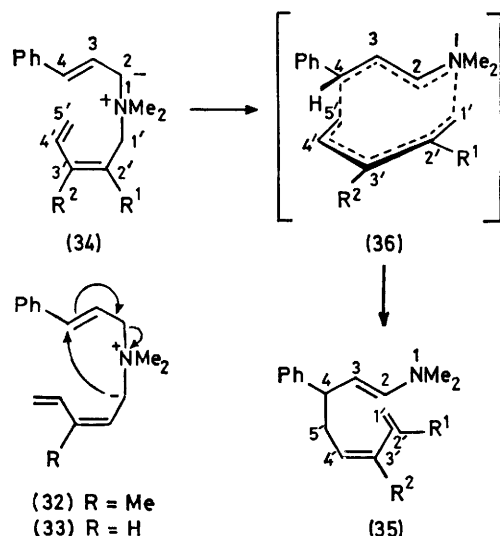
Base catalysed rearrangement of the salts (37) and (38) gave very complex mixtures of products which were treated with acid and separated into neutral and basic fractions. The neutral product from the salt (37) (15% yield) was identified as the aldehyde (10) obtained

* In discussions of stereochemical relationships it is convenient to use the numbering system of formula (4) (*cf.* refs. 2 and 6) as in formulae (34)–(36).

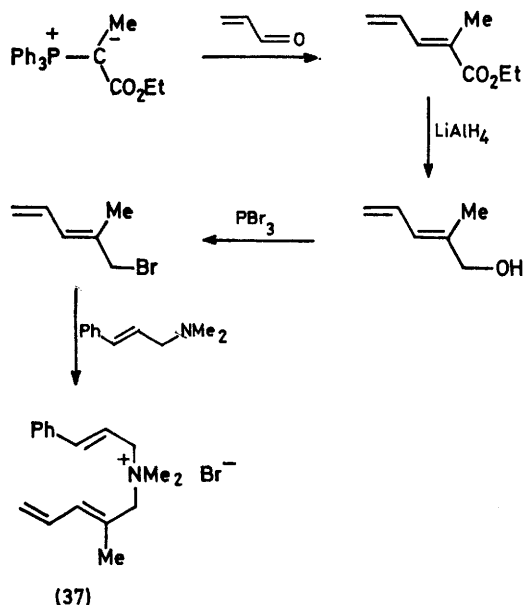
previously. The salt (38) gave the aldehyde (40), of unknown stereochemistry about the trisubstituted double bond. The complex mixtures of basic products from these reactions could not be separated to give

would lead to the same mixture of aldehydes (10) and (40) in each case (see Scheme 3).

The Stereochemistry of the Transition State of the [5,4] Sigmatropic Rearrangement.—The transition state of the [5,4] sigmatropic rearrangement can be regarded as

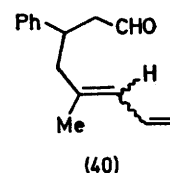


pure products. Although low yields of [5,4] sigmatropic rearrangement products were obtained in these reactions, they provide evidence concerning the stereochemical requirements of the transition state of the [5,4] sigmatropic rearrangement and also rule out the possibility (see Scheme 3) that the [5,4] rearrangement is, in fact, a two-step process involving consecutive



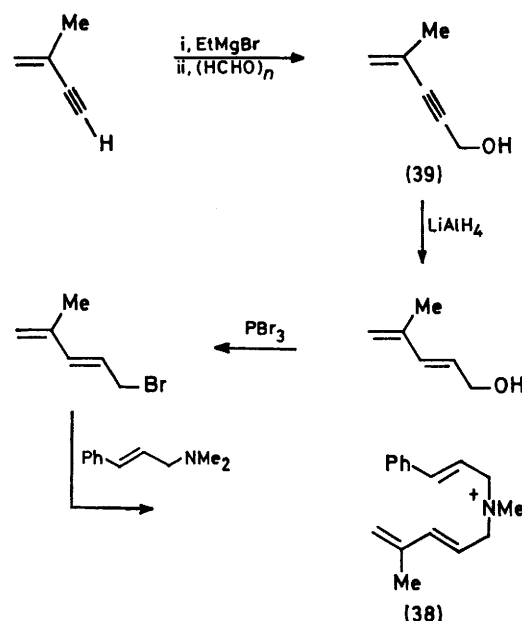
SCHEME 4

[3,2] and [3,3] rearrangements. Thus in a two-step process, the salts (37) and (38) would undergo [3,2] rearrangement to the same amine (14) [although probably different diastereoisomers of amine (14) in each case]³ and subsequent [3,3] rearrangement and hydrolysis



involving the interaction between a pentadienyl radical (5 e) and a vinylideneimmonium radical (5 e) (see Scheme 6).

The geometries of the transition states for the [5,4] rearrangement may be considered⁶ in the terms of a pair of radicals interacting in a suprafacial-suprafacial manner, since the 'allowed' antarafacial-antarafacial mode is stereochemically improbable. Consideration of



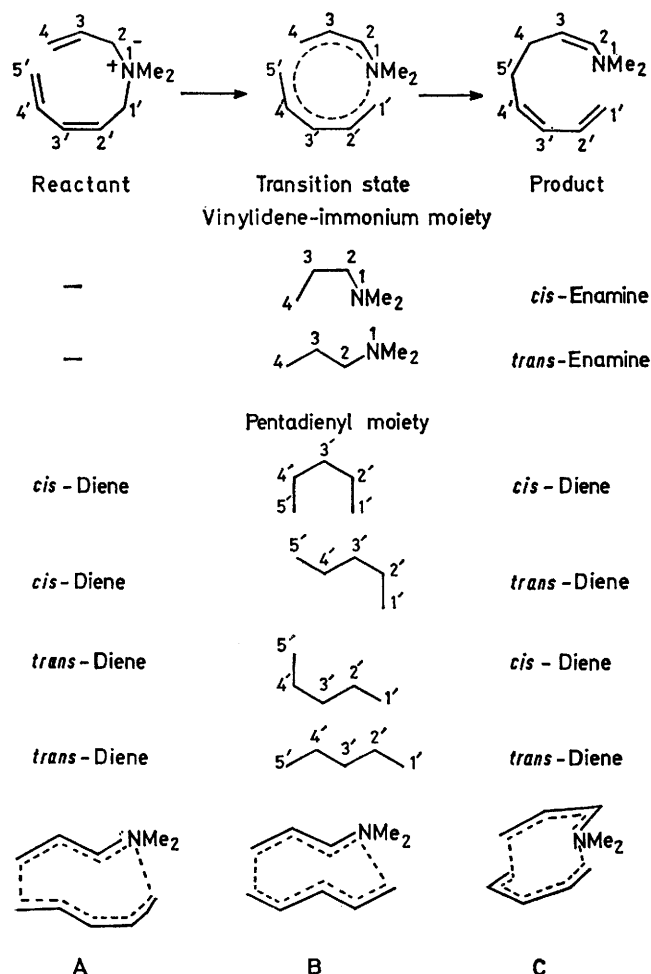
SCHEME 5

the possible stereochemistries of the pentadienyl and vinylideneimmonium moieties of the transition state (Scheme 6) shows that there are three variable factors: (i) the stereochemistry of the C-2,C-3 π -bond, (ii) the stereochemistry of the C-2',C-3' π -bond, and (iii) the stereochemistry of the C-3',C-4' π -bond. Of these three factors, reference to Scheme 6 shows that two [(i) and (iii)] are reflected by the stereochemistry of the product and one (ii) by the stereochemistry of the reactant. This leads to eight * possible diastereoisomeric ss-transition states for the [5,4] sigmatropic rearrangement. Transition-state preference is determined by the stereochemistry of the reactant together with other

* This discussion ignores *exo*- and *endo*-relationships in these transition states, which would otherwise increase the number of possibilities to 16.

factors, such as the avoidance of non-bonded interactions in cisoid systems in the transition state and optimum orbital overlap between the terminal atoms of the two interacting radicals.

Of the four possible *ss*-transition-state geometries available to a *cis*-pentadienyl salt (Scheme 6) the results described in this paper indicate that the reaction proceeds through transition state A for the salts (7), (17), and (22) (*cis*-dienyl salt \rightarrow *trans*-enamine + *trans*-diene). The rearrangement of the *trans*-pentadienyl

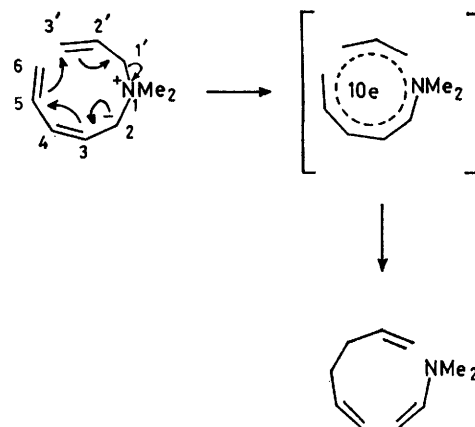


SCHEME 6 Geometrical relationships in *s,s* [5,4] sigmatropic rearrangements

salt (37) probably proceeds through transition state B (*trans*-dienyl salt \rightarrow *trans*-enamine + *trans*-diene) although the geometry of the resulting enamine could not be determined. The rearrangement of the salt (27) may proceed by a transition state having the geometry A or C since the stereochemistry of the product enamine (28) was not rigorously established. The other five transition states remain as possibilities for other [5,4] sigmatropic rearrangements but some are unlikely to be encountered for obvious geometrical reasons.

From the yields of products obtained in the rearrangements of the cinnamyl *cis*- and *trans*-penta-2,4-dienyl-

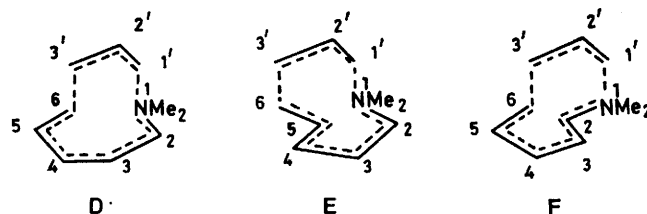
ammonium salts, the most favourable transition state is A (Scheme 6) with a *cis*-pentadienyl unit in a transoid conformation, leading to an all-*trans* product. In transition state B (Scheme 6), it can be seen by examination of molecular models that the orbital overlap is less



SCHEME 7

favourable because the distance between the terminal carbon atoms of the planar pentadienyl unit in the all-*trans* conformation is longer than the distance between these atoms in the cisoid conformation, with a resulting poorer overlap with the terminal atoms of the vinylideneimmonium unit. However, [5,4] rearrangements involving transition states of type B have been observed¹³ for oxanilinium ylides.

Attempts to Induce a [3,6] Sigmatropic Rearrangement.—The [3,6] sigmatropic rearrangement, like the [5,4] sigmatropic rearrangement, is a 10-electron process involving a nine-membered ring transition state (Scheme 7). The transition state may be regarded as being derived by suprafacial-suprafacial interaction of an allyl radical with a butadienyldiene-immonium radical. The three most likely transition states geometries for an *ss* reaction are given in Scheme 8; for good orbital

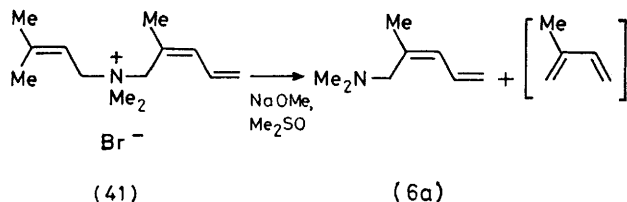


SCHEME 8

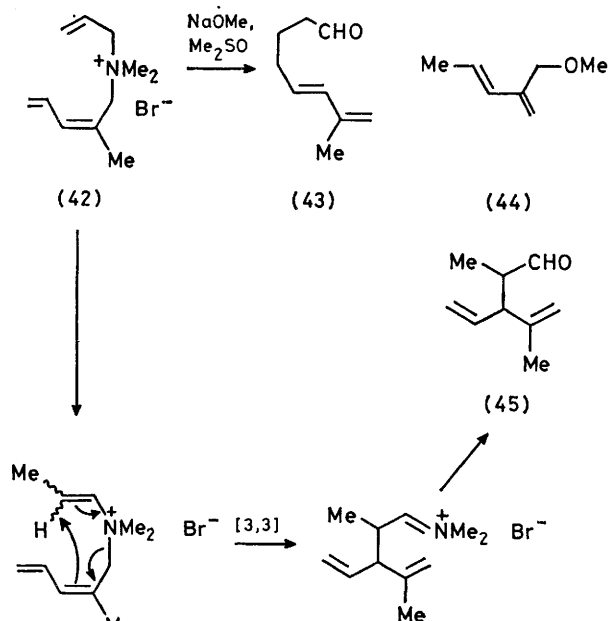
overlap, at least one *cis* double bond is required in the reactant (between C-3 and C-4) and cisoid conformations of the six atom unit, as in E and F, or possibly an all-cisoid conformation, as in D. In all three transition states D—F, however, there will be steric interactions between the groups on the 1 and 6 positions (transition state D), the 1 and 5 positions (transition state E), or the 2 and 6 positions (transition state F).

The base catalysed rearrangements of certain allyl-dimethyl-(*2Z*)-penta-2,4-dienylammonium salts were in-

vestigated in the hope of observing a [3,6] sigmatropic rearrangement. The salt (41) was treated with sodium methoxide in dimethyl sulphoxide solution at room temperature, but only the cleavage product, the amine (6a), was isolated. Presumably isoprene is the other product, although it was not isolated.



Rearrangement of the corresponding allyl salt (42), in which an elimination reaction analogous to (41) \rightarrow (6a) is not possible, gave a complex mixture of products. In an attempt to see whether any [3,6] rearrangement had taken place, the products were treated with dilute acid to hydrolyse any enamines, and the resulting neutral fraction separated into three components by preparative g.l.c. The minor products were the aldehyde (43) which presumably arises by a [5,4] sigmatropic rearrangement, and the cleavage product (44). The major product (45, 20%), isolated as a mixture of diastereoisomers (ratio 1:1), could arise by the route shown in Scheme 9. This pathway has previously been observed in the base catalysed rearrangements of allylic ammonium salts, but *only in aqueous solution*.¹⁴



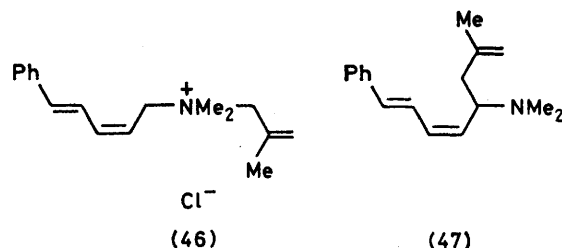
SCHEME 9

The basic products from the rearrangement of salt (42) were a complex mixture which could not be separated.

In a further attempt to induce a [3,6] sigmatropic rearrangement, additional precautions were taken to ensure that the proton was abstracted by the base from the pentadienyl group and not from the allyl group.

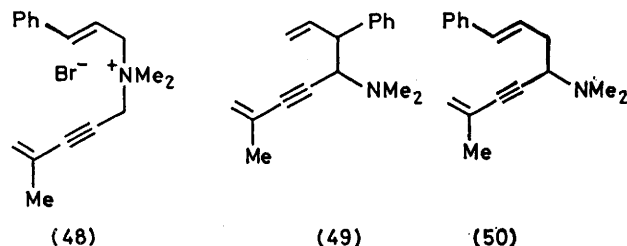
However, rearrangement of the salt (46) gave the amine (47) in high yield, presumably *via* a [3,2] sigmatropic rearrangement.

For the reasons outlined earlier and from the experiments reported above, the [3,6] sigmatropic rearrangement appears to be an unfavourable process. It may, however, be possible to observe a [3,6] rearrangement in a system where an all-*cis* pentadienyl group can be fixed in a *cisoid* conformation in a ring; a [3,6] sigmatropic rearrangement of this type may have been detected¹⁵ for an oxyanilinium ylide system.



Base Catalysed Rearrangement of Allylic(pent-4-en-2-ynyl)ammonium Salts and 3-Phenylprop-2-ynyl(penta-2,4-dienyl)ammonium Salts.—In an attempt to induce a [5,4] sigmatropic rearrangement involving an acetylenic bond, the base catalysed rearrangement of salt (48) was investigated. The salt (48) was prepared from the alcohol (39) by treatment with phosphorus tribromide in ether, followed by reaction of the resulting bromide with cinnamyltrimethylamine. After treatment of the salt (48) with sodium methoxide in dimethyl sulphoxide solution, only the [3,2] sigmatropic rearrangement product (49) (45%, predominantly one diastereoisomer) and the Stevens [1,2] rearrangement product (50) (5%) were isolated.

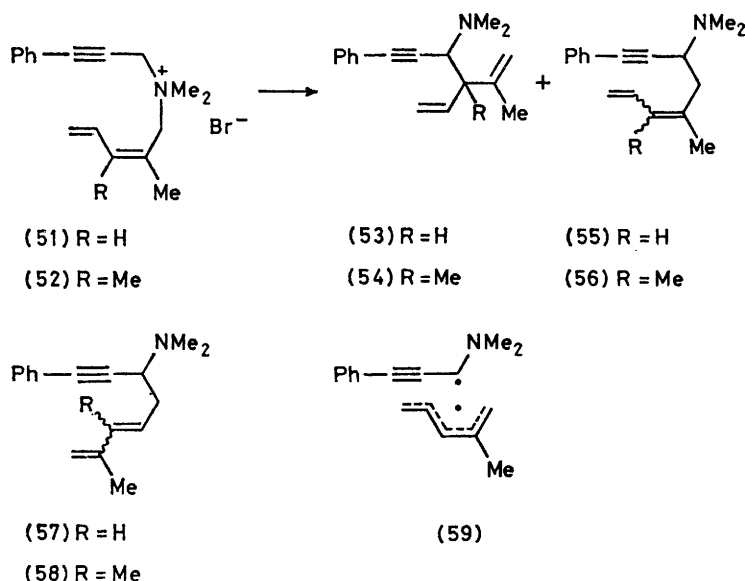
The base-catalysed rearrangements of the 3-phenylprop-2-ynyl salts (51) and (52) similarly gave only products derived from [3,2] rearrangement [(53) and (54)] and [1,2] rearrangement [(55) and (56)] (see Table 2). The stereochemistry of the [1,2] rearrangement products (55) and (56) is not known, but since only one isomer is formed the pentadienyl unit is assumed to have



the same *cis*-stereochemistry as in the starting materials (51) and (52). Surprisingly, no [5,2] rearrangement products [(57) and (58)] were isolated. This high specificity in a Stevens rearrangement¹⁶ would be remarkable if the reaction followed the generally accepted mechanism *via* the radical pair (59), which could recombine to give all three possible isomers (53),

(55), and (57). The above results seem more consistent with a 'concerted forbidden' mechanism¹⁷ for the [1,2] rearrangement but we have recently noted¹⁸ discrimination between [1,2] and [5,2] rearrangements

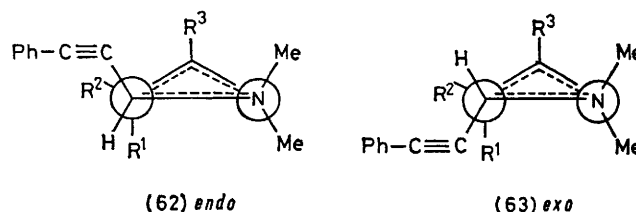
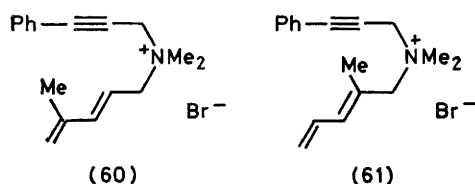
an *endo*-transition state was postulated to explain the observed ratios of diastereoisomeric products. The [3,2] rearrangements of the salts (51), (60), and (61) lead to the same pair of diastereoisomeric amines (53) in



that favours the [5,2] mode. The reasons for discrimination of this sort in reactions that probably involve caged radical pairs will be discussed in later papers of this series and remain a topic for investigation.

To examine these factors more closely in the present

each case. The diastereoisomer ratios (Table 2) indicate that all three reactions must proceed preferentially by either an *endo*-(62) or an *exo*-(63) transition state. By a similar analysis to that described in our earlier paper³ we



context, the rearrangements of the *trans*-pentadienyl salts (60) and (61) were also investigated (see Table 2). However, whilst the [3,2] rearrangement products (53) were the major product in each case, the [1,2] and [5,2] rearrangement products (55) and (57) were also formed in approximately equal amounts in each case, consistent with the operation of a radical pair mechanism.

The stereochemistry of the transition state of the [3,2] sigmatropic rearrangement of allyl(propynyl)ammonium salts has previously been discussed,³ and a preference for

conclude that in the above three cases the *endo*-transition state (62) leads to the major diastereoisomer. The rearrangement (52) \rightarrow (54) also exhibits high stereo-

TABLE 2

Base catalysed rearrangements of 3-phenylprop-2-ynyl(penta-2,4-dienyl)ammonium salts

| Salt | [3,2] Rearrangement | | Diastereoisomer | | [1,2] Rearrangement | | [5,2] Rearrangement | |
|------|---------------------|--------|-----------------|-------|---------------------|----|---------------------|---|
| | product | % | ratio | % | product | % | product | % |
| (51) | (53) | 80 | A : B | 6 : 1 | (55) | 7 | — | — |
| (60) | (53) | ca. 60 | A : B | 3 : 1 | (57) | 5 | (55) | 5 |
| (61) | (53) | ca. 60 | A : B | 1 : 3 | (55) | 5 | (57) | 5 |
| (52) | (54) | 50 | A : B | 6 : 1 | (56) | 12 | — | — |

selectivity and this may again be accounted for in the terms of a preference for an *endo*-transition state.

EXPERIMENTAL

The general directions were given in Part 1.³ Ether refers to diethyl ether throughout.

Synthesis of Substituted (2Z)-Penta-2,4-dienyl-NN-dimethylamines (6): General Procedure.—A solution of methyl iodide (72 g, 0.5 mol) in acetonitrile (50 ml) was added to a solution of the appropriately substituted pyridine (0.5 mol) in acetonitrile (50 ml) at 0 °C with constant stirring. After the vigorous exothermic reaction had subsided, the solvent was evaporated giving an oily methiodide which was washed with ether and dried *in vacuo*.

The crude methiodide was dissolved in 2M-aqueous sodium hydroxide (500 ml) and powdered sodium borohydride (20 g) was added slowly with vigorous stirring. The temperature rose to 50–60 °C and, after the reaction was complete (2 h), sodium chloride (100 g) was added and the solution was extracted with ether (3 × 100 ml). The ethereal extracts were dried and the ether was evaporated giving the crude 1,2,5,6-tetrahydropyridine derivative.

The 1,2,5,6-tetrahydropyridine (*ca.* 0.5 mol), dissolved in acetonitrile (100 ml), was treated with a solution of methyl iodide (1 equiv.) in acetonitrile (50 ml) at 0 °C for 2 h. The solvent was evaporated to give the crude 1,2,5,6-tetrahydropyridine methiodide, which was dissolved in dimethyl sulphoxide (100 ml), and a solution of sodium methoxide (1 mol) in dimethyl sulphoxide (100 ml) was added dropwise with stirring during a period of 1 h. The mixture was stirred overnight at room temperature, poured into water (1 000 ml), and extracted with ether. The ethereal extracts were washed with water, dried, and the ether was distilled off at atmospheric pressure giving the crude (2Z)-penta-2,4-dienyl-N,N-dimethylamine (6), which was purified by distillation.

The following (Z,E)-penta-2,4-dienyl-N,N-dimethylamines were prepared by the above general method.

(2Z)-2-Methylpenta-2,4-dienyl-N,N-dimethylamine (6a) was prepared from 3-picoline in 55% overall yield, b.p. 140–144 °C/760 mmHg (lit.,¹⁹ 144–146 °C); ν_{\max} (liq. film) 1 020, and 900 cm^{-1} ; n.m.r.: ABMX system, τ_A 4.87, τ_B 4.98, τ_M 3.28, τ_X 4.02 (J_{AB} *ca.* 2 Hz, J_{AM} 17 Hz, J_{BM} 11 Hz, J_{MX} 11 Hz, $CH_AH_B=CH_M-CH_X=$), 7.04 (s, CH_2-N), 7.83 (s, NMe_2), and 8.16 (s, vinylic *Me*). The amine (6a) was characterised as its *hydrobromide*, m.p. 197–198 °C from ethanol (Found: C, 46.9; H, 7.4; Br, 38.6; N, 6.95. $C_8H_{16}BrN$ requires C, 46.6; H, 7.7; Br, 38.8; N, 6.8%).

(2Z)-2,3-Dimethylpenta-2,4-dienyl-N,N-dimethylamine (6b) was prepared in 16% overall yield from 3,4-dimethylpyridine, b.p. 160–164/760 mmHg; ν_{\max} (liq. film) 1 024, 895, and 842 cm^{-1} ; n.m.r.: ABX system, τ_A 4.92, τ_B 4.76, τ_X 2.92 (J_{AB} 2 Hz, J_{AX} 10 Hz, J_{BX} 17 Hz, $CH_AH_B=CH_X-C=$), 6.97 (s, CH_2-N), 7.80 (s, NMe_2), and 8.15 (s, two vinylic *Me*). The amine (6b) was characterised as its *picrate*, m.p. 109–111 °C from ethanol (Found: C, 48.6; H, 5.7; N, 15.1. $C_{15}H_{20}N_4O_7$ requires C, 48.9; H, 5.4; N, 15.2%).

(2Z)-3-Methylpenta-2,4-dienyl-N,N-dimethylamine (6c) was prepared from 4-picoline; n.m.r.: ABX system, τ_A 4.68, τ_B 4.76, τ_X 3.20 (J_{AB} 2 Hz, J_{AX} 10 Hz, J_{BX} 18 Hz, $CH_AH_B=CH_X-$) AX₂ system, τ_A 4.52, and τ_X 6.95 [J_{AX} 8 Hz, $=CH_A-C(H_X)_2-N$], 7.79 (s, NMe_2), and 8.14 (m, *J ca.* 2 Hz, vinylic *Me*). The amine (6c) was characterised as the *picrate*, m.p. 130–131 °C

from ethanol (Found: C, 47.3; H, 5.3; N, 15.8. $C_{14}H_{18}N_4O_7$ requires C, 47.5; H, 5.1; N, 15.8%).

(2Z)-Penta-2,4-dienyl-N,N-dimethylamine (6d) was prepared from pyridine; n.m.r. ABLMNX₂ system, τ_A 4.75, τ_B 4.82, τ_L 3.30, τ_M 3.84, τ_N 4.45, τ_X 6.90 [J_{AB} *ca.* 0 Hz, J_{BL} 11 Hz, J_{AL} 19 Hz, J_{LM} 10 Hz, J_{MN} 10 Hz, J_{NX} 7 Hz, $CH_AH_B=CH_L-CH_M=CH_N-C(H_X)_2-N$], and 7.76 (s, NMe_2). The amine (6d) was characterised as its *picrate*, m.p. 83–84 °C from ethanol (Found: C, 45.6; H, 4.65; N, 16.7. $C_{13}H_{16}N_4O_7$ requires C, 45.9; H, 4.7; N, 16.5%).

(2Z,4E)-Hexa-2,4-dienyl-N,N-dimethylamine (6e) was prepared in 57% overall yield from 2-picoline, b.p. 140 °C/760 mmHg; n.m.r.: A₃KLMNX₂ system, τ_A 8.23, τ_K 4.30, τ_L 3.80, τ_M 3.98, τ_N 4.67, τ_X 6.98 [J_{AK} 7 Hz, J_{KL} 14 Hz, J_{LM} 10.5 Hz, J_{MN} 11 Hz, J_{NX} 7 Hz, $C(H_A)_3-CH_K=CH_L-CH_M=CH_X)_2-NMe_2$], and 7.78 (s, NMe_2). The amine (6e) was characterised as the *picrate*, m.p. 133–135 °C from ethanol (Found: C, 47.7; H, 5.1; N, 15.7. $C_{14}H_{18}N_4O_7$ requires C, 47.5; H, 5.1; N, 15.8%).

1-Methyl-2-phenyl-1,2,3,6-tetrahydropyridine (with D. Cummings).—A solution of 2-phenylpyridine²⁰ methiodide (60 g) in ethanol (500 ml) was treated with powdered sodium borohydride (8 g) with vigorous stirring for 3 days at room temperature. The solution was poured into water and extracted with ether; the ethereal extracts were washed with water, dried, and evaporated giving a colourless oil (19 g) which rapidly darkened on standing at room temperature and was converted into its methiodide without further purification. The oil was identified as 1-methyl-2-phenyl-1,2,3,6-tetrahydropyridine¹¹ [Found: M^+ , 173, m/e 118 ($CH_2=\dot{N}=CHPh$) and m/e 91 ($PhCH_2^+$). $C_{12}H_{15}N$ requires M , 173]; n.m.r.: τ 2.7–2.8 (m, 5 aromatic *H*), 4.27 (br s, $-CH=CH-$), 6.5–7.3 (m, $CH-N-CH_2$), 7.5–7.8 (m, $=C-CH_2$) and 7.98 (s, NMe). On addition of CF_3CO_2H , the broad singlet at τ 4.27 was transformed into a broad AB quartet (J_{AB} *ca.* 10 Hz). The amine was characterised as its *methiodide*, m.p. 174–175 °C from ethanol (Found: C, 49.6; H, 5.75; I, 40.25, N, 4.3; $C_{13}H_{18}IN$ requires C, 49.5; H, 5.7; I, 40.3; N, 4.4%); n.m.r.: τ 2.1–2.4 (m) and 2.5–2.8 (m, 5 aromatic *H*), ABFNMN system, τ_A 5.04, τ_B 5.72, τ_F 3.83, τ_N 4.14, τ_M , τ_N , 6.8–7.4, τ_X 4.51 (J_{AB} 17 Hz, J_{AB} , J_{BE} *ca.* 2 Hz, J_{EF} 10 Hz, J_{FM} , J_{FN} *ca.* 2 Hz, J_{MX} 8.5 Hz, J_{NX} 6 Hz, $CH_AH_BCH_E=CH_F-CH_MCH_N-CH_X-Ph$), and 6.65 and 6.81 (2 × s, NMe_2).

(2Z,4E)-5-Phenylpenta-2,4-dienyl-N,N-dimethylamine (6f) ¹¹ (with D. Cummings).—A solution of 1-methyl-2-phenyl-1,2,3,6-tetrahydropyridine methiodide (18 g) in dimethyl sulphoxide (50 ml) was treated dropwise with stirring with a solution prepared from sodium hydride (6.4 g), dimethyl sulphoxide (100 ml), and methanol (20 ml). After stirring overnight at room temperature the solution was poured into water and extracted with ether. The ethereal extracts were washed with water and separated into neutral and basic fractions using 5M-aqueous hydrochloric acid and 5M-aqueous sodium hydroxide. The basic fraction was a pale-brown oil (9.2 g, 86%) identified as (2Z,4E)-5-phenylpenta-2,4-dienyl-N,N-dimethylamine (6f) (Found: M^+ , 187, m/e 143 ($M - NMe_2$), m/e 142 and m/e 128. $C_{13}H_{17}N$ requires M , 187); n.m.r.: τ 2.5–2.9 (m, 5 aromatic *H*), ABMNX₂ system, τ_A 3.46, τ_B 2.9, τ_M 3.71, τ_N 4.41, τ_X 6.84 [J_{AB} 15 Hz, J_{BM} 11 Hz, J_{MN} 11 Hz, J_{NX} 7 Hz, $PhCH_A=CH_B-CH_M=CH_N-C(H_X)_2-NMe_2$], and 7.74 (s, NMe_2). The amine (6f) was characterised as its *methiodide*, m.p. 144–145 °C from ethanol (Found: C, 50.8; H, 6.3; I, 38.6; N, 3.9. $C_{14}H_{20}IN$ requires C, 51.1; H,

6.1; I, 38.6; N, 4.2%); n.m.r. ($\text{CDCl}_3\text{-CF}_3\text{CO}_2\text{H}$): τ 2.35—2.9 (m, 5 aromatic H), ABCMX_2 system, τ_A , τ_B , τ_C 2.8—3.6, τ_M 4.51, τ_X 5.76 [J_{CM} ca. 10 Hz, J_{MX} 8 Hz, $\text{PhCH}_A=\text{CH}_B\text{-CH}_C=\text{CH}_M\text{-C}(\text{H}_X)_2\text{-N}$], and 6.86 (s, NMe_3).

Cinnamylidimethyl-[(2Z)-2-methylpenta-2,4-dienyl]ammonium Bromide (7).—A solution of (2Z)-2-methylpenta-2,4-dienyl-*N,N*-dimethylamine (6a) (5 g) in acetonitrile (25 ml) was added to a solution of cinnamyl bromide (8 g) in acetonitrile (25 ml). After 12 h at room temperature, the solution was diluted with dry ether (500 ml) and the white precipitate of cinnamylidimethyl-[(2Z)-2-methylpenta-2,4-dienyl]ammonium bromide (7) (12.0 g) was collected, m.p. 158—160 °C (Found: C, 63.1; H, 7.6; Br, 24.9; N, 4.15. $\text{C}_{17}\text{H}_{24}\text{BrN}$ requires C, 63.3; H, 7.4; Br, 25.0; N, 4.3%); ν_{max} 978 and 922 cm^{-1} ; n.m.r. (CD_3OD): τ 2.3—2.7 (m, 5 aromatic H), ABX_2 system, τ_A 2.93, τ_B 3.51, τ_X 5.76 [J_{AB} 16 Hz, J_{BX} 7.5 Hz, $\text{CH}_A=\text{CH}_B\text{-C}(\text{H}_X)_2\text{-N}$], ABXY system, τ_A 4.64, τ_B 4.58, τ_X 3.55, τ_Y 3.60 (J_{AB} 2 Hz, J_{AX} 9.5 Hz, J_{BX} 15.5 Hz, J_{XY} 11 Hz, $\text{CH}_A\text{H}_B=\text{CH}_X\text{-CH}_Y\text{-}$), 5.78 (s, $\text{CH}_2\text{-N}$), 6.90 (s, NMe_2), and 7.91 (s, vinylic Me).

Base-catalysed Rearrangement of Cinnamylidimethyl-[(2Z)-2-methylpenta-2,4-dienyl]ammonium Bromide (7). *Formation of (1E,5E)-1-Dimethylamino-7-methyl-3-phenylocta-1,5,7-triene (9), (1E)-3-Dimethylamino-5-methyl-1-phenylocta-1,5,7-triene (12), and (1E,5E)-3-Dimethylamino-7-methyl-1-phenylocta-1,5,7-triene (13).*—A solution of the ammonium salt (7) (6.4 g) in dimethyl sulphoxide (50 ml) was treated with a solution prepared from sodium hydride (0.48 g), methanol (1 ml), and dimethyl sulphoxide (50 ml) at room temperature for 12 h. The solution was poured into water and extracted with ether; the ethereal extracts were washed with water, dried, and evaporated to give an oil (4.5 g). The n.m.r. spectrum of the oil showed that it was a mixture of at least 3 amines having signals for the NMe_2 groups at τ 7.50, 7.72, and 7.77 in the approximate ratio (4 : 2 : 1). The major component could be obtained in a purer form, although not entirely free from contaminants, by distillation giving (1E,5E)-1-dimethylamino-7-methyl-3-phenylocta-1,5,7-triene (9) as a pale yellow oil, b.p. 120 °C/1 mmHg [Found: M , 241.1827; m/e 160, m/e 115, m/e 91, m^+ 51.8 (160 \rightarrow 91). $\text{C}_{17}\text{H}_{23}\text{N}$ requires M , 241.1830; ν_{max} 1640 and 965 cm^{-1} ; n.m.r. τ 2.5—2.9 (m, 5 aromatic H), ABMN_2XY system, τ_A 4.15, τ_B 5.67, τ_M 6.75, τ_N 7.3—7.6, τ_X 4.47, and τ_Y 3.90 [J_{AB} 15 Hz, J_{BM} 7 Hz, J_{MN} ca. 7 Hz, J_{NX} 7 Hz, J_{XY} 16 Hz, $\text{Me}_2\text{N-CH}_A=\text{CH}_B\text{-CH}_M\text{-C}(\text{H}_N)_2\text{-CH}_X=\text{CH}_Y\text{-}$], 5.20 (br s, $=\text{CH}_2$), 7.52 (s, NMe_2), and 8.27 (s, vinylic Me).

The enamine (9) was characterised as the corresponding aldehyde (8). A solution of the enamine (9) in ether was shaken with 5*M*-aqueous hydrochloric acid; the ethereal layer was separated, washed with water, dried, and evaporated giving (5E)-7-methyl-3-phenylocta-5,7-dienal (10) as a colourless unstable oil (Found: M , 214.1358, m/e 170 and 105. $\text{C}_{15}\text{H}_{18}\text{O}$ requires M , 214.1358); ν_{max} 1715, 968, and 888 cm^{-1} ; n.m.r.: τ 2.6—3.0 (m, 5 aromatic H), $\text{ABL}_2\text{MN}_2\text{X}$ system, τ_A 3.90, τ_B 4.54, τ_L 7.59, τ_M 6.71, τ_N 7.30, τ_X 0.41 [J_{AB} 16 Hz, J_{BL} 7 Hz, J_{LM} 7 Hz, J_{MN} 7 Hz, J_{NX} 1.5 Hz, $-\text{CH}_A=\text{CH}_B\text{-C}(\text{H}_L)_2\text{-CH}_M\text{-C}(\text{H}_N)_2\text{-CH}_X\text{O}$], τ 5.16 (s, $=\text{CH}_2$), and 8.27 (s, vinylic Me).

The minor basic products were isolated by treatment of the crude product with 2*M*-aqueous hydrochloric acid, followed by extraction of the neutral products into ether. The acidic layer was neutralised with 5*M*-sodium hydroxide and extracted with ether. The ethereal extracts were washed with water, dried, and evaporated to give a pale

yellow oil. Its n.m.r. spectrum showed that it was mainly one component (NMe_2 at τ 7.72) with several minor components. The major component (0.5 g) was isolated by preparative t.l.c. and shown to be a mixture (ratio 1 : 1) of two amines: (i) (1E)-3-dimethylamino-5-methyl-1-phenylocta-1,5,7-triene (12), a pale yellow oil, n.m.r.: τ 2.7—3.0 (m, 5 aromatic H), ABXY system, τ_A 4.16, τ_B 3.43, τ_X 3.97, τ_Y 4.05 (J_{AB} 10 Hz, J_{BX} 17 Hz, J_{BY} 10 Hz, J_{XY} ca. 1 Hz, $\text{C}=\text{CH}_A\text{-CH}_B=\text{CH}_X\text{H}_Y$), ABXYZ system, τ_A 3.68, τ_B 4.00, τ_X 6.93, τ_Y , τ_Z 7.3—7.8 (J_{AB} 16 Hz, J_{BX} 9 Hz, J_{XY} 9 Hz, J_{XZ} 6 Hz, $\text{PhCH}_A=\text{CH}_B\text{-CH}_X\text{-CH}_Y\text{H}_Z$), τ 7.72 (s, NMe_2) and 8.23 (s, vinylic Me), and (ii) (1E,5E)-3-dimethylamino-7-methyl-1-phenylocta-1,5,7-triene (13), a pale yellow oil (Found: M , 241. $\text{C}_{17}\text{H}_{23}\text{N}$ requires M , 241); n.m.r.: τ 2.7—3.0 (m, 5 aromatic H), ABLMNXY system, τ_A 3.64, τ_B 3.8—4.1, τ_L 7.05, τ_M , τ_N 7.3—7.8, τ_X 4.42, τ_Y 3.87 (J_{AB} 14 Hz, J_{BL} 9 Hz, J_{LM} 9 Hz, J_{LN} 6 Hz, J_{NX} 7 Hz, J_{XY} 15 Hz, $\text{PhCH}_A=\text{CH}_B\text{-CH}_L\text{-CH}_M\text{H}_N\text{-CH}_X=\text{CH}_Y\text{-}$), τ 5.18 (s, $=\text{CH}_2$), 7.72 (s, NMe_2), and 8.23 (s, vinylic Me).

Cinnamylidimethyl-[(2Z)-2,3-dimethylpenta-2,4-dienyl]ammonium Bromide (17).—A solution of (2Z)-2,3-dimethylpenta-2,4-dienyl-*N,N*-dimethylamine (6b) (2.1 g) in acetonitrile (10 ml) was added to a solution of cinnamyl bromide (3.0 g) in acetonitrile (15 ml). After 5 min the solution was diluted with dry ether (200 ml), and the white precipitate was collected giving cinnamylidimethyl-[(2Z)-2,3-dimethylpenta-2,4-dienyl]ammonium bromide (17) (5.0 g), m.p. 143—144 °C (Found: C, 64.1; H, 7.9; Br, 23.8; N, 3.9. $\text{C}_{18}\text{H}_{26}\text{BrN}$ requires C, 64.0; H, 7.7; Br, 23.8; N, 4.2%); n.m.r.: τ 2.4—2.7 (m, 5 aromatic H), ABX system, τ_A 4.60, τ_B 4.71, τ_X 3.65 (J_{AX} 17 Hz, J_{BX} 10.5 Hz, $\text{CH}_A\text{H}_B=\text{CH}_X$), ABX_2 system, τ_A 2.8, τ_B 2.90, τ_X 5.30 [J_{BX} 7.5 Hz, $\text{CH}_A=\text{CH}_B=\text{C}(\text{H}_X)_2$], τ 5.40 (s, $\text{CH}_2\text{-N}$), 6.80 (s, NMe_2), and 7.93 (s) and 8.14 (s, two vinylic Me).

Base-catalysed Rearrangement of Cinnamylidimethyl-[(2Z)-2,3-dimethylpenta-2,4-dienyl]ammonium Bromide (17). *Formation of (1E)-6,7-Dimethyl-1-dimethylamino-3-phenylocta-1,5,7-triene (18), (1E)-5,6-Dimethyl-3-dimethylamino-1-phenylocta-1,5,7-triene (20), and (1E)-6,7-Dimethyl-3-dimethylamino-1-phenylocta-1,5,7-triene (21).*—A solution of the ammonium salt (17) (4.0 g) in dimethyl sulphoxide-tetrahydrofuran (100 ml, 1 : 1 mixture) at -5 °C was treated with a solution prepared from sodium hydride (0.5 g), methanol (5 ml), and dimethyl sulphoxide (20 ml). After stirring for 1 h at -5 °C to $+5$ °C, the mixture was poured into water and extracted with ether. The ethereal extracts were washed with water, dried, and evaporated giving an oil (2.3 g) which was shown by its n.m.r. spectrum, to be a mixture of an enamine (NMe_2 at τ 7.48) and an allylic amine (NMe_2 at τ 7.68) (ratio ca. 3 : 2). The enamine (18) could not be fully characterised, but additional peaks at τ 5.64 (dd, J 8, 13 Hz) and 4.12 (d, J 13 Hz) are indicative of the structure proposed. The enamine (18) was characterised as the aldehyde (19). The crude rearrangement product was shaken with dilute hydrochloric acid and extracted with ether. The ethereal extracts were washed with water, dried, and evaporated giving a neutral fraction (0.7 g) which after preparative t.l.c. (silica gel, benzene) gave 6,7-dimethyl-3-phenylocta-5,7-dienal (19) as an unstable colourless oil (0.5 g) [Found: M 228, m/e 184 ($M - \text{CH}_2 = \text{CH-OH}$), m/e 169 (184— CH_3), 161, 133, 105, and m/e 91. $\text{C}_{16}\text{H}_{20}\text{O}$ requires M 228]; ν_{max} 2720 and 1723 cm^{-1} ; n.m.r.: τ 2.6—2.9 (m, 5 aromatic H), $\text{AL}_2\text{MN}_2\text{X}$ system, τ_A 0.39, τ_L 7.26, τ_X 6.71, τ_N 7.54, τ_4 4.55 [J_{AL} 2 Hz, J_{LM} 7 Hz, J_{MN} 7 Hz, J_{NX} 7 Hz, $\text{OCH}_A\text{-C}(\text{H}_L)_2\text{-CH}_M\text{-C}(\text{H}_N)_2\text{-CH}_X\text{-}$],

τ 5.06 and 5.14 (2 br s, $=\text{CH}_2$), and 8.19 and 8.27 (2 s, two vinylic Me).

The minor component in the neutral fraction was cinnamaldehyde (100 mg).

The basic products were isolated by neutralising the above hydrochloric acid extracts followed by ether extraction. The ethereal extracts were dried and evaporated giving an oil (0.8 g) which was shown by its n.m.r. spectrum to be a complex mixture. The mixture was purified by preparative t.l.c. (silica gel, chloroform-ethyl acetate 3:2) giving an inseparable mixture of (1E)-5,6-dimethyl-3-dimethylamino-1-phenylocta-1,5,7-triene (20) and (1E)-6,7-dimethyl-3-dimethylamino-1-phenylocta-1,5,7-triene (21) in the ratio (2:1); ν_{max} 968 cm^{-1} . The n.m.r. spectrum of the mixture could be assigned as follows: (i) (1E)-5,6-dimethyl-3-dimethylamino-1-phenylocta-1,5,7-triene (20), n.m.r.: τ 2.6–2.9 (m, 5 aromatic H), ABMX₂ system, τ_A 3.68, τ_B 3.95, τ_M 6.7–7.0, τ_X 7.3–7.6 [J_{AB} 16 Hz, J_{BM} 8 Hz, $\text{PhCH}_A=\text{CH}_B-\text{C}(\text{H}_X)_2$], AXY system, τ_A 3.15, τ_X 4.90, τ_Y 5.04 [J_{AX} 17 Hz, J_{AY} 11 Hz, $\text{CH}_X\text{H}_Y=\text{CH}_A^-$], τ 7.68 (s, NMe_2), and 8.24 and 8.29 (2 s, two vinylic Me).

(ii) (1E)-6,7-Dimethyl-3-dimethylamino-1-phenylocta-1,5,7-triene (21), n.m.r.: τ 2.6–2.9 (m, 5 aromatic H), ABMN₂X system, τ_A 3.56, τ_B ca. 3.8, τ_M 6.7–7.0, τ_N 7.3–7.6, τ_X ca. 4.40 [J_{AB} 16 Hz, J_{NX} ca. 7 Hz, $\text{PhCH}_A=\text{CH}_B-\text{CH}_M-\text{C}(\text{H}_N)_2-\text{CH}_X^-$], τ 5.04 and 5.14 (2 br s, $=\text{CH}_2$), 7.68 (s, NMe_2), and 8.15 and 8.19 (2 s, two vinylic Me).

Cinnamylidimethyl-[(2Z)-3-methylpenta-2,4-dienyl]dimethylammonium Bromide (22).—A solution of (2Z)-3-methylpenta-2,4-dienyl-N,N-dimethylamine (6c) (5.0 g) in acetonitrile (10 ml) was added to a solution of cinnamyl bromide (8 g) in acetonitrile (20 ml). After 30 min at room temperature, the solution was diluted with dry ether (400 ml) and the precipitate was collected giving cinnamylidimethyl-[(2Z)-3-methylpenta-2,4-dienyl]ammonium bromide (22) (12 g) as a white hygroscopic solid, which tended to polymerise readily on standing: n.m.r.: τ 2.5–2.8 (m, aromatic H), ABX system, τ_A 4.60, τ_B 4.70, τ_X ca. 3.75 [J_{AB} ca. 1 Hz, J_{AX} 18 Hz, J_{BX} 10 Hz, $\text{CH}_A\text{H}_B=\text{CH}_X^-$], ABX₂ system, τ_A 2.90, τ_B 2.80, τ_X 5.45 [J_{BX} 8 Hz, $\text{PhCH}_A=\text{CH}_B-\text{C}(\text{H}_X)_2$], AX₂ system, τ_A ca. 4.5, τ_X 5.54 [J_{AX} 9 Hz, $=\text{CH}_A-\text{C}(\text{H}_X)_2-\text{N}^+$], τ 6.70 (s, NMe_2) and 8.02 (s, vinylic Me).

Base Catalysed Rearrangement of Cinnamylidimethyl-[(2Z)-3-methylpenta-2,4-dienyl]ammonium Bromide (22). Formation of (1E)-1-Dimethylamino-6-methyl-3-phenylocta-1,5,7-triene (23), (1E)-3-Dimethylamino-6-methyl-1-phenylocta-1,5,7-triene (25), and (5Z)-4-Dimethylamino-6-methyl-3-phenylocta-1,5,7-triene (26).—The ammonium salt (22) (8.0 g) was dissolved in dimethyl sulphoxide-tetrahydrofuran (1:1 mixture; 200 ml), cooled to -5°C , and treated dropwise with a solution prepared from sodium hydride (1.0 g), methanol (5 ml), and dimethyl sulphoxide (50 ml). After stirring for 1 h at -5 to $+5^\circ\text{C}$, the mixture was poured into water and extracted with ether. The ethereal extracts were washed with water, dried, and evaporated giving an oil (5.0 g, 83%). The spectral properties of the crude product indicated that the major component was the enamine, (1E)-1-dimethylamino-6-methyl-3-phenylocta-1,5,7-triene (23); ν_{max} 1645 cm^{-1} ; n.m.r.: τ 2.6–2.9 (m, 5 aromatic H), ABX system, τ_A 5.00, τ_B 5.15, τ_X ca. 3.7 [J_{AX} 18 Hz, J_{BX} 11 Hz, $\text{CH}_A\text{H}_B=\text{CH}_X^-$], ABMN₂X system, τ_A 4.14, τ_B 5.67, τ_M 6.76, τ_N 7.5–7.6, τ_X 4.56 [J_{AB} 14 Hz, J_{BM} 8 Hz, J_{MN} ca. 8 Hz, J_{NX} 7 Hz, $\text{CH}_A=\text{CH}_B-\text{CH}_M-\text{C}(\text{H}_N)_2-\text{C}(\text{H}_X)=$], τ 7.48 (s, NMe_2), and 8.33 (s, vinylic Me). The n.m.r. spectrum of the crude product also showed, in

addition to the NMe_2 group of enamine (23) at τ 7.48, the presence of amines having NMe_2 resonances at τ 7.72 and 7.76 in the approximate ratio 6:2:1.

The crude product was shaken with dilute hydrochloric acid, and the neutral product was extracted into ether, washed with water, dried, and evaporated giving 6-methyl-3-phenylocta-5,7-dienal (24) (1.9 g) as an unstable colourless oil [Found: M , 214.1358; m/e 170 ($M - \text{CH}_2=\text{CHOH}$), m/e 155 ($170 - \text{CH}_3$), m^* 141.3 ($170 \rightarrow 155$). $\text{C}_{15}\text{H}_{18}\text{O}$ requires M , 214.1358; ν_{max} 2718, 1720, 1603, 986, and 895 cm^{-1} ; n.m.r.: $\text{AL}_2\text{MN}_2\text{X}$ system, τ_A 0.41, τ_L 7.30, τ_M 6.73, τ_N 7.54, τ_X 4.65 [J_{AL} 2 Hz, J_{LM} 7 Hz, J_{MN} 8 Hz, J_{NX} 8 Hz, $\text{OCH}_A-\text{C}(\text{H}_L)_2-\text{CH}_M-\text{C}(\text{H}_N)_2-\text{CH}_X=$], τ 2.7–2.9 (m, 5 aromatic H), ABX system τ_A 5.10, τ_B 4.95, τ_X 3.73 (J_{AX} 11 Hz, J_{BX} 18 Hz, $\text{CH}_A\text{H}_B=\text{CH}_X^-$), and τ 8.34 (s, vinylic Me).

The extract of acid-soluble product from above was neutralised with 5M-sodium hydroxide and extracted with ether. The ethereal extracts were washed with water, dried, and evaporated giving an oil (2.0 g) which had spectral properties indicating that some aldehyde (24) was still present in the mixture. The mixture was separated by preparative t.l.c. (silica gel, chloroform-ethyl acetate, 2:1) giving the following. (i) A further sample of aldehyde (24) (0.8 g). (ii) (5Z)-4-Dimethylamino-6-methyl-3-phenylocta-1,5,7-triene (26) as a colourless oil (0.15 g); n.m.r.: τ 2.6–3.0 (m, 5 aromatic H), ABX system, τ_A , τ_B 4.8–5.1, τ_X 3.48 (J_{AX} 10 Hz, J_{BX} 17 Hz, $\text{CH}_A\text{H}_B=\text{CH}_X^-$), ABFMNX system, τ_A , τ_B 4.8–5.1, τ_F 3.80, τ_M 6.26, τ_N 6.62, τ_X 4.8–5.1 (J_{AF} 16 Hz, J_{BF} 8 Hz, J_{FM} 10 Hz, J_{MN} 10 Hz, J_{NX} 9 Hz, $\text{CH}_A\text{H}_B=\text{CH}_F-\text{CH}_M-\text{CH}_N-\text{CH}_X=$), τ 7.76 (s, NMe_2), and 8.32 (s, vinylic Me). (iii) (1E)-3-Dimethylamino-6-methyl-1-phenylocta-1,5,7-triene (25) as a colourless oil (0.4 g). The amine (25) was shown to be a mixture of isomers in the approximate ratio 3:1 [Found: M , 241; m/e 226 ($M - \text{CH}_3$), m/e 196 ($M - \text{HNMe}_2$), m/e 181 ($196 - \text{CH}_3$), m/e 160 ($\text{PhCH}=\text{CH}-\text{CH}=\text{NMe}_2$). $\text{C}_{17}\text{H}_{23}\text{N}$ requires M , 241; n.m.r.: τ 2.6–2.9 (m, 5 aromatic H), ABX system, τ_A 4.98, τ_B 4.94, τ_X 3.26 [J_{AX} 17 Hz, J_{BX} 11 Hz, $\text{CH}_A\text{H}_B=\text{CH}_X^-$], ABMN₂X system, τ_A 3.60, τ_B 3.84, τ_M 7.07, τ_N 7.4–7.6, τ_X 4.60 [J_{AB} 16 Hz, J_{BM} 8 Hz, J_{MN} 5 Hz, J_{NX} ca. 9 Hz, $\text{PhCH}_A=\text{CH}_B-\text{CH}_M-\text{C}(\text{H}_N)_2-\text{CH}_X=$], τ 7.72 (s, NMe_2), 8.20 (s, vinylic Me, major isomer), and 8.26 (s, vinylic Me, minor isomer).

Cinnamylidimethyl-[(2Z)-penta-2,4-dienyl]ammonium Bromide (27).—A solution of (2Z)-penta-2,4-dienyl-N,N-dimethylamine (6d) (5.0 g) in acetonitrile (20 ml) was added to a solution of cinnamyl bromide (8.0 g) in acetonitrile (20 ml). After the exothermic reaction had subsided, the solution was filtered and diluted with dry ether (500 ml). The resulting precipitate was collected giving cinnamylidimethyl-[(2Z)-penta-2,4-dienyl]ammonium bromide (27) as a white hygroscopic solid (11.0 g), m.p. 142–143 $^\circ\text{C}$ (Found, C, 62.2; H, 7.3; Br, 26.3; N, 4.4. $\text{C}_{10}\text{H}_{22}\text{BrN}$ requires C, 62.3; H, 7.1; Br, 26.0; N, 4.5%); n.m.r.: 2.5–2.7 (m, 5 aromatic H), ABX₂ system, τ_A 2.80, τ_B 2.98, τ_X 5.38 [J_{BX} 7 Hz, $\text{CH}_A=\text{CH}_B-\text{C}(\text{H}_X)_2-\text{N}^+$], ABEFMX₂ system, τ_A 4.50, τ_B 4.64, τ_E ca. 3.7, τ_F 3.40, τ_M 4.35, τ_X 5.46 [J_{AB} 0 Hz, J_{BE} 11 Hz, J_{EF} ca. 11 Hz, J_{FM} 11 Hz, J_{MX} 8 Hz, $\text{CH}_A\text{H}_B=\text{CH}_E-\text{CH}_F=\text{CH}_M-\text{C}(\text{H}_X)_2-\text{N}^+$].

Base Catalysed Rearrangement of Cinnamylidimethyl-[(2Z)-penta-2,4-dienyl]ammonium Bromide (27). Formation of 1-Dimethylamino-3-phenylocta-1,5,7-triene (28), (1E,5Z)-3-Dimethylamino-1-phenylocta-1,5,7-triene (30), and

(5Z)-4-Dimethylamino-3-phenylocta-1,5,7-triene (31).—The ammonium salt (27) (8.0 g) was dissolved in dimethyl sulphoxide-tetrahydrofuran (1:1 mixture; 200 ml), cooled to -5°C , and treated with a solution prepared from sodium hydride (1.0 g), methanol (5 ml), and dimethyl sulphoxide (25 ml) during a period of 30 min. After stirring overnight, the solution was poured into water and extracted with ether. The extracts were washed with water, dried, and evaporated giving an oil (5.8 g). The n.m.r. spectrum of the oil indicated that the enamine (NMe_2 at τ 7.49) was the minor component, the major component having an NMe_2 group at τ 7.75; the ratio of the two peaks was approximately 1:4. The crude product was shaken with dilute hydrochloric acid and extracted with ether. The ethereal extracts were dried and evaporated giving 3-phenylocta-5,7-dienal (29) as a colourless oil (1.1 g) [Found: M , 200; m/e 182, m/e 156 ($M - \text{CH}_2 = \text{CHOH}$), m/e 117, 115, 105, and 91. $\text{C}_{14}\text{H}_{16}\text{O}$ requires M , 200]; ν_{max} (liquid film) 2720, 1725, 1005, 910, 760, and 700 cm^{-1} ; n.m.r.: τ 2.6–3.0 (m, 5 aromatic H), and ABCDELMN $_2$ X system, τ_A 4.84, τ_B 4.95, τ_C 3.78, τ_D ca. 4.0, τ_E ca. 4.45, τ_L 7.61, τ_M 6.73, τ_N 7.32, τ_X 0.40 [J_{AB} ca. 1 Hz, J_{AC} 16 Hz, J_{BC} 10 Hz, J_{CD} 10 Hz, J_{DE} masked, J_{EL} 7 Hz, J_{LM} 7 Hz, J_{MN} 7 Hz, J_{NX} 2 Hz, $\text{CH}_A\text{H}_B = \text{CH}_C - \text{CH}_D = \text{CH}_E - \text{C}(\text{H}_L)_2 - \text{CH}_M - \text{C}(\text{H}_N)_2 - \text{CH}_X\text{O}$].

The extract of acid-soluble product from above was neutralised with 5M-sodium hydroxide and extracted with ether. The ethereal extracts were dried and evaporated giving an oil which was separated by preparative t.l.c. into three fractions. (i) A further sample of the aldehyde (29) (0.45 g). (ii) (5Z)-4-Dimethylamino-3-phenylocta-1,5,7-triene (31) as a colourless oil (1.2 g) [Found: M , 277; m/e 160, 117, 115, and 110 ($\text{CH}_2 = \text{CH} - \text{CH} = \text{CH} - \text{CH} = \text{NMe}_2$). $\text{C}_{16}\text{H}_{21}\text{N}$ requires M , 227]; ν_{max} 1005, 910 cm^{-1} ; the n.m.r. spectrum indicated that the amine (31) was mainly one diastereoisomer, n.m.r.: τ 2.7–3.0 (m, 5 aromatic H), ABCDEMNXYZ system τ_A , τ_B , τ_Y , τ_Z , 4.8–5.1, τ_C 3.55, τ_D 3.95, τ_E ca. 4.8, τ_M 6.26, τ_N 6.60, τ_X 3.80 (J_{AC} 16.5 Hz, J_{BC} 11.5 Hz, J_{CD} 10.5 Hz, J_{DE} ca. 10 Hz, J_{EM} ca. 10 Hz, J_{MN} 10 Hz, J_{NX} 8 Hz, J_{XY} 10.5 Hz, J_{XZ} 17 Hz, $\text{CH}_A\text{H}_B = \text{CH}_C - \text{CH}_D = \text{CH}_E - \text{CH}_M - \text{CH}_N - \text{CH}_X = \text{CH}_Y\text{H}_Z$), and τ 7.75 (s, NMe_2 , major diastereoisomer) and 7.85 (s, NMe_2 minor diastereoisomer). The amine (31) was characterised as the *picrate*, m.p. 122–123 $^{\circ}\text{C}$ from ethanol (Found: C, 57.1; H, 5.35; N, 12.1. $\text{C}_{22}\text{H}_{24}\text{N}_4\text{O}_7$ requires C, 57.8; H, 5.3; N, 12.3%). (iii) (1E,5Z)-3-Dimethylamino-1-phenylocta-1,5,7-triene (30) as a colourless oil (0.1 g) [Found: M , 227; m/e 160, m/e 110, m^* 113 (227 \rightarrow 160). $\text{C}_{16}\text{H}_{21}\text{N}$ requires M , 227]; ν_{max} 1037, 998, 964, 910, and 895 cm^{-1} . Some of the coupling constants in the n.m.r. spectrum were determined after addition of a small quantity of $\text{Eu}(\text{fod})_3$ shift reagent; further addition of shift reagent causes line broadening and probably some decomposition; n.m.r.: τ 2.5–2.9 (m, 5 aromatic H), ABCDEMN $_2$ XY system, τ_A 4.78, τ_B 4.89, τ_C 3.38, τ_D ca. 3.8, τ_E ca. 4.6, τ_M ca. 7.5, τ_N 6.62, τ_X ca. 3.8, τ_Y 3.60 [J_{AB} 2 Hz, J_{BO} 10.5 Hz, J_{AO} 16.5 Hz, J_{CD} ca. 11 Hz, J_{DE} ca. 11 Hz, J_{EM} ca. 11 Hz, J_{MN} ca. 9 Hz, J_{NX} 6 Hz, J_{XY} 15.5 Hz, $\text{CH}_A\text{H}_B = \text{CH}_C - \text{CH}_D = \text{CH}_E - \text{C}(\text{H}_M)_2 - \text{CH}_N - \text{CH}_X = \text{CH}_Y - \text{Ph}$], and τ 7.73 (s, NMe_2).

(2E)-Ethyl 2-Methylpenta-2,4-dienoate.—The ester was prepared by a Wittig reaction from triphenylphosphonium 1-ethoxycarbonyl ethylide and acrolein according to the method of House:²¹ ν_{max} 1720 cm^{-1} ; n.m.r.: ABMX system τ_A 4.40, τ_B 4.47, τ_M 3.29, τ_X 2.82 [J_{AB} ca. 1 Hz, J_{BM} 17 Hz, J_{AM} 10 Hz, J_{BX} 2 Hz, J_{MX} 10 Hz, $\text{CH}_A\text{H}_B = \text{CH}_M -$

$\text{CH}_X =$], A_2X_2 system, τ_A 8.70, τ_X 5.77 [J_{AX} 8 Hz, $\text{C}(\text{H}_A)_3 - \text{C}(\text{H}_X)_2 - \text{O}$], and τ 8.05 (s, vinylic Me).

(2E)-2-Methylpenta-2,4-dienol.—A solution of (2E)-ethyl 2-methylpenta-2,4-dienoate (5.6 g) in dry ether (20 ml) was added dropwise to a stirred suspension of lithium aluminium hydride (1.5 g) in dry ether (50 ml). After stirring for 3 h, the solution was cooled to 0°C and water was added carefully followed by dilute sulphuric acid (20 ml). The solution was extracted with ether, dried, and evaporated giving (2E)-2-methylpenta-2,4-dienol (4.0 g) as a colourless liquid, b.p. 67–68 $^{\circ}\text{C}/10\text{ mmHg}$ (lit.,²¹ b.p. 67–68 $^{\circ}\text{C}/10\text{ mmHg}$); n.m.r.: ABMX system, τ_A 4.77, τ_B 4.77, τ_M 3.35, τ_X 3.88 [J_{AM} 18 Hz, J_{BM} 10 Hz, J_{MX} 11 Hz, $\text{CH}_A\text{H}_B = \text{CH}_M - \text{CH}_X =$], τ 5.92 (s, CH_2OH), 7.92 (br s, removed by D_2O shake, OH), and 8.20 (s, vinylic Me).

(2E)-2-Methylpenta-2,4-dienyl Bromide.—A solution of phosphorus tribromide (4.0 g) in dry ether (10 ml) was added dropwise to a stirred solution of (2E)-2-methylpenta-2,4-dienol (2.0 g) in dry ether (20 ml) at 0°C . After 3 h, the ethereal solution was decanted onto solid sodium hydrogen carbonate (10 g), stirred for 30 min, filtered, and evaporated giving (2E)-2-methylpenta-2,4-dienyl bromide (3 g) which was used immediately. Distillation causes decomposition and partial isomerisation to (2E)-4-methylpenta-2,4-dienyl bromide.

Cinnamyl dimethyl-[(2E)-2-methylpenta-2,4-dienyl]-ammonium Bromide (37).—A solution of cinnamyl dimethylamine (3.0 g) in acetonitrile (25 ml) was added to a solution of freshly prepared (2E)-2-methylpenta-2,4-dienyl bromide (3.0 g) in acetonitrile (10 ml). After 1 h at room temperature, the solvent was evaporated and dry ether (100 ml) was added to the residual oil. The resultant white solid which formed was collected giving cinnamyl dimethyl-[(2E)-2-methylpenta-2,4-dienyl] ammonium bromide (37) (5.0 g); n.m.r.: (CD_3OD) τ 2.3–2.75 (m, 5 aromatic H), ABX_2 system, τ_A 2.92, τ_B 3.50, τ_X 5.76 [J_{AB} 16 Hz, J_{BX} 7.5 Hz, $\text{PhCH}_A - \text{CH}_B - \text{C}(\text{H}_X)_2$], ABMX system, τ_A 4.60, τ_B 4.50, τ_M 3.52, τ_X 3.28 [J_{AB} 1 Hz, J_{BM} 15.5 Hz, J_{AM} 9.5 Hz, J_{MX} 10.5 Hz, $\text{CH}_A\text{H}_B = \text{CH}_M - \text{CH}_X$], τ 5.86 (s, $\text{CH}_2 - \text{N}^+$), 6.88 (s, NMe_2), and 7.92 (s, vinylic Me).

Base Catalysed Rearrangement of Cinnamyl dimethyl-[(2E)-2-methylpenta-2,4-dienyl] ammonium Bromide (37). Formation of (5E)-7-Methyl-3-phenylocta-5,7-dienal (10).—The ammonium salt (37) (2.0 g) was dissolved in dimethyl sulphoxide (25 ml) and treated with a solution prepared from sodium hydride (0.12 g), methanol (2 ml), and dimethyl sulphoxide (20 ml). The solution was stirred at room temperature for 1 h and poured into water, dried, and evaporated giving an oil (1.26 g). The n.m.r. spectrum showed that approximately 25% of enamine (9) was present. The mixture was shaken with dilute hydrochloric acid and extracted with ether. The ethereal extracts were dried and evaporated giving (5E)-7-methyl-3-phenylocta-5,7-dienal (10) (0.25 g), identical with the sample obtained previously. The hydrochloric acid solution was basified with 5M-sodium hydroxide and extracted with ether. The ethereal extracts were dried and evaporated giving an oil (1.0 g), which could not be purified by preparative t.l.c.

4-Methylpent-4-en-2-ynol (39).—A solution of isopropenylacetylene (66 g) in dry ether (100 ml) was added dropwise during 1 h with vigorous stirring to a suspension of ethyl magnesium bromide [prepared from bromoethane (120 g) and magnesium (24 g) in dry ether (100 ml)]. The mixture

was stirred at room temperature for 1.5 h and solid para-formaldehyde (100 g) was added during 1 h with vigorous stirring. The suspension was stirred overnight, poured onto ice-2M-sulphuric acid and extracted with ether. The ethereal extracts were dried and evaporated giving a yellow liquid which after distillation gave 4-methylpent-4-en-2-ynol (39) (80 g, 83%), b.p. 67–70/30 mmHg; ν_{\max} 3350, 2220, and 1605 cm^{-1} ; n.m.r.: ABX₂ system, τ_A 4.72, τ_B 4.78, τ_X 8.13 [J_{BX} 1 Hz, $\text{CH}_A\text{H}_B=\text{C}(\text{H}_X)_2$], τ 5.66 (s, CH_2OH), and 7.05 (br s, removed by D₂O shake, OH).

(2E)-4-Methylpenta-2,4-dienol.—4-Methylpent-4-en-2-ynol (39) (6.0 g) was added dropwise to a stirred suspension of lithium aluminium hydride (1.2 g) in dry ether (50 ml). The mixture was heated under reflux for 4 h, cooled, and an excess of lithium aluminium hydride was carefully decomposed with water and dilute sulphuric acid (20 ml). The ethereal layer was dried, evaporated, and distilled giving (2E)-4-methylpenta-2,4-dienol as a colourless liquid (4.0 g, 65%), b.p. 90 °C/50 mmHg; ν_{\max} 3350 and 970 cm^{-1} ; n.m.r.: ABX₂ system, τ_A 3.80, τ_B 4.30, τ_X 5.80 [J_{AB} 15 Hz, J_{BX} 5.5 Hz, $\text{CH}_A=\text{CH}_B-\text{C}(\text{H}_X)_2-\text{OH}$], ABX₃ system, τ_A , τ_B , 5.00 τ_X 8.16 [J_{AX} , J_{BX} 1 Hz, $\text{CH}_A\text{H}_B=\text{C}(\text{H}_X)_2$], and τ 7.19 (br s, removed by D₂O shake, OH).

(2E)-4-Methylpenta-2,4-dienyl Bromide.—A solution of phosphorus tribromide (11 g) in dry ether (50 ml) was added dropwise to a solution of (2E)-4-methylpenta-2,4-dienol (5.0 g) in dry ether (50 ml) at 0 °C. After 16 h the solution was decanted onto solid sodium hydrogencarbonate, stirred for 30 min, filtered, and evaporated giving (2E)-4-methylpenta-2,4-dienyl bromide (4.2 g) as a colourless oil which rapidly darkened. The bromide was used immediately since it equilibrated with the 2-methyl isomer on standing or on distillation.

Cinnamylidimethyl-[(2E)-4-methylpenta-2,4-dienyl]ammonium Bromide (38).—(2E)-4-Methylpenta-2,4-dienyl bromide (4.1 g) dissolved in acetonitrile (20 ml) was treated with a solution of cinnamylidimethylamine (4.8 g) in acetonitrile (25 ml). After 2 h at room temperature, the solution was evaporated and the resultant sticky solid was triturated with dry ether giving cinnamylidimethyl-[(2E)-4-methylpenta-2,4-dienyl]ammonium bromide (38) as an unstable white hygroscopic solid (8.5 g); n.m.r.: τ 2.3–2.8 (m, 5 aromatic H), ABX₂ system, τ_A 2.90, τ_B 3.55, τ_X 5.48 [J_{AB} 16 Hz, J_{BX} 8 Hz, $\text{PhCH}_A=\text{CH}_B-\text{C}(\text{H}_X)_2-\dot{\text{N}}^+$], ABX₂ system, τ_A 3.24, τ_B 4.30, τ_X 5.64 [J_{AB} 15 Hz, J_{BX} 8 Hz, $\text{CH}_A=\text{CH}_B-\text{C}(\text{H}_X)_2-\dot{\text{N}}^+$], τ 4.5–4.8 (br s = CH_2), 6.71 (s, $\dot{\text{N}}\text{Me}_2$), and 8.15 (s, vinylic Me). The n.m.r. spectrum indicated that cinnamylidimethylamine hydrobromide was also present as an impurity but the salt (38) could not be purified since it polymerised readily on standing; the crude salt was therefore rearranged by base as soon as possible after its preparation.

Base Catalysed Rearrangement of Cinnamylidimethyl-[(2E)-4-methylpenta-2,4-dienyl]ammonium Bromide (38). Formation of 5-Methyl-3-phenylocta-5,7-dienal (40).—The ammonium salt (38) (7.5 g) was dissolved in dimethyl sulphoxide (25 ml) and treated with a solution prepared from sodium hydride (1.0 g), methanol (5 ml), and dimethyl sulphoxide (25 ml). After stirring at room temperature overnight, the mixture was poured into water and extracted with ether. The ethereal extracts were washed with water, dried, and evaporated to give an oil (5.1 g) which contained an aldehyde (ν_{\max} 1720 cm^{-1}) but very little enamine (n.m.r. τ 7.5, $\dot{\text{N}}\text{Me}_2$). The crude product was shaken with dilute hydro-

chloric acid and extracted with ether. The ethereal extracts were dried and evaporated and the residual oil (1.0 g) purified by preparative t.l.c. giving 5-methyl-3-phenylocta-5,7-dienal (40) [Found: M , 214; m/e 170, 155, 117, and 105, m^* 141.3 (170 \rightarrow 155)]. C₁₅H₁₈O requires M , 214; ν_{\max} 2825, 2722, 1725, 988, 965, and 900 cm^{-1} ; n.m.r.: τ 2.6–3.0 (m, 5 aromatic H), AM₂NX₂ system τ_A 0.40, τ_M 7.33, τ_N 6.59, τ_X 7.66 [J_{AM} 2 Hz, J_{MN} 8 Hz, J_{NX} ca. 8 Hz, $\text{OCH}_A-\text{C}(\text{H}_M)_2-\text{CH}_N-\text{C}(\text{H}_X)_2$], ABMX system τ_A , τ_B 4.9–5.2, τ_M 3.53, τ_X 4.23 (J_{AM} 11 Hz, J_{BM} 16 Hz, J_{MX} 11 Hz, $\text{CH}_A\text{H}_B=\text{CH}_M-\text{CH}_X$), and τ 8.29 (s, vinylic Me). The aldehyde (40) was contaminated by ca. 5% of aldehyde (10) which may arise from the salt (37) being an impurity in the starting salt (38).

The acid-soluble extracts were basified with 5M-sodium hydroxide and extracted with ether. The ethereal extracts were dried and evaporated giving an oil (3.0 g). Attempted separation of this complex mixture by preparative t.l.c. gave the aldehyde (40) (0.28 g), cinnamylidimethylamine (0.1 g), and several other fractions which were not obtained pure enough for their structures to be determined.

Dimethyl-(3,3-dimethylallyl)-[(2Z)-2-methylpenta-2,4-dienyl]ammonium Bromide (41).—A solution of (2Z)-2-methylpenta-2,4-dienyl-N,N-dimethylamine (6a) (5.0 g) in acetonitrile (20 ml) was added to a solution of 3,3-dimethylallyl bromide (6 g) in acetonitrile (30 ml). After 2 h at room temperature, the solution was diluted with ether (200 ml) and the precipitate was collected giving dimethyl-(3,3-dimethylallyl)-[(2Z)-2-methylpenta-2,4-dienyl]ammonium bromide (41) as a gum (7.0 g) [Found: C, 56.8; H, 8.7; Br, 29.2; N, 5.2. C₁₃H₂₄BrN requires C, 56.9; H, 8.8; Br, 29.2; N, 5.1%]; n.m.r.: ABMX system, τ_A , τ_B 4.6–4.8, τ_M 2.96, τ_X 3.56 (J_{AM} 16 Hz, J_{BM} 10 Hz, J_{MX} 11 Hz, $\text{CH}_A\text{H}_B=\text{CH}_M-\text{CH}_X$), AX₂ system, τ_A ca. 4.6, τ_X 5.59 [J_{AX} 8 Hz, $=\text{CH}_A-\text{C}(\text{H}_X)_2-\dot{\text{N}}^+$], τ 5.47 (s, $\text{CH}_2-\dot{\text{N}}^+$), 6.78 (s, $\dot{\text{N}}\text{Me}_2$), 7.89 (s, vinylic Me), and 8.07 and 8.12 (2 s, $=\text{CMe}_2$).

Base Catalysed Rearrangement of Dimethyl-(3,3-dimethylallyl)-[(2Z)-2-methylpenta-2,4-dienyl]ammonium Bromide (41) Formation of (2Z)-2-Methylpenta-2,4-dienyl-N,N-dimethylamine (6a).—A solution of the ammonium salt (41) (5.4 g) in dimethyl sulphoxide (25 ml) was treated with a solution prepared from sodium hydride (0.5 g), methanol (1 ml), and dimethyl sulphoxide (25 ml) at room temperature overnight. The mixture was poured into water and extracted with ether, and the extracts were separated into neutral and basic fractions using 5M-hydrochloric acid and 5M-sodium hydroxide. The neutral fraction contained very little product. The basic fraction (2.5 g) was entirely (2Z)-2-methylpenta-2,4-dienyl-N,N-dimethylamine (6a).

Allyldimethyl-[(2Z)-2-methylpenta-2,4-dienyl]ammonium Bromide (42).—A solution of (2Z)-2-methylpenta-2,4-dienyl-N,N-dimethylamine (6a) (5.0 g) in acetonitrile (15 ml) was added to a solution of allyl bromide (5.0 g) in acetonitrile (15 ml). The solution was diluted with dry ether (200 ml) and the precipitate was collected giving allyldimethyl-[(2Z)-2-methylpenta-2,4-dienyl]ammonium bromide (42) (8.0 g); n.m.r.: ABMX system, τ_A 4.66, τ_B 4.67, τ_M 2.95, τ_X 3.54 (J_{AB} 2 Hz, J_{BM} 11 Hz, J_{AM} 16 Hz, J_{MX} 11 Hz, $\text{CH}_A\text{H}_B=\text{CH}_M-\text{CH}_X$), ABCX₂ system, τ_A , τ_B , τ_C , 3.8–4.4, τ_X 5.47 [J_{CX} ca. 5 Hz, $\text{CH}_A\text{H}_B=\text{CH}_C-\text{C}(\text{H}_X)_2-\dot{\text{N}}^+$], τ 5.47 (s, $\text{CH}_2-\dot{\text{N}}^+$), 6.73 (s, $\dot{\text{N}}\text{Me}_2$), and 7.89 (s, vinylic Me).

Base Catalysed Rearrangement of Allyldimethyl-[(2Z)-2-methylpenta-2,4-dienyl]ammonium Bromide (42). Form-

ation of (5E)-7-Methylocta-5,7-dienal (43), (3E)-2-(Methoxymethylene)penta-1,3-diene (44), and 2,4-Dimethyl-3-vinylpent-4-enal (45).—The salt (42) (5.0 g) was dissolved in dimethyl sulphoxide (20 ml) and treated with a solution prepared from sodium hydride (1.0 g), methanol (2 ml), and dimethyl sulphoxide (30 ml) at room temperature for 12 h. The mixture was poured into water, extracted with ether, and separated into neutral and basic fractions using 5M-hydrochloric acid and 5M-sodium hydroxide. The neutral fraction (1.4 g) was shown to be a mixture of three components (in the approximate ratio 3:1:1) by g.l.c. Preparative g.l.c. gave very small quantities (<20 mg) of each compound so that the products could be identified by their n.m.r. spectra.

(i) 2,4-Dimethyl-3-vinylpent-4-enal (45), a colourless oil, was a mixture of diastereoisomers (approximate ratio 1:1); diastereoisomer A, n.m.r.: ABCLMN₃X system, τ_A , τ_B 4.8—5.3, τ_C 4.30, τ_L 7.10, τ_M 7.45, τ_N 9.02, τ_X 0.46, [J_{CL} 9 Hz, J_{LM} 7 Hz, J_{MX} 3 Hz, J_{MN} 7 Hz, $CH_AH_B=CH_C-CH_L-CH_M(CH_XO)-C(H_N)_3$], τ ca. 4.86 and ca. 5.18 (2 s, =CH₂) and 8.34 (s, vinylic Me); diastereoisomer B, n.m.r.: ABCLMN₃X system, τ_A , τ_B 4.8—5.3, τ_C 4.30, τ_L 7.10, τ_M 7.45, τ_N 8.99, τ_X 0.51 [J_{CL} 9 Hz, J_{LM} 7 Hz, J_{MX} 3 Hz, J_{MN} 7 Hz, $CH_AH_B=CH_C-CH_L-CH_M(CH_XO)-C(H_N)_3$], τ ca. 4.86 and ca. 5.18 (2 s, =CH₂), and 8.28 (s, vinylic Me).

(ii) (3E)-2-(Methoxymethylene)penta-1,3-diene (44), a colourless oil; n.m.r.: ABX₃ system, τ_A 3.90, τ_B 4.12, τ_X 8.23 [J_{AB} 17 Hz, J_{BX} 5.5 Hz, $CH_A=CH_B-C(H_X)_3$], τ 4.94 (s, =CH₂), 5.94 (s, CH₂O), and 6.66 (s, MeO).

(iii) (5E)-7-Methylocta-5,7-dienal (43), a colourless oil; n.m.r.: AB₂L₂M₂N₂X system, τ_A 3.88, τ_B 4.46, τ_L 7.90, τ_M ca. 8.25, τ_N ca. 7.6, τ_X 0.26 [J_{AB} 16 Hz, J_{BL} 6 Hz, J_{LM} ca. 7 Hz, J_{MN} ca. 7 Hz, J_{NX} 1.5 Hz, $CH_A=CH_B=C(H_L)_2-C(H_M)_2-C(H_N)_2-CH_XO$], τ 5.13 (s, =CH₂), and 8.20 (s, vinylic Me).

Dimethyl-(2-methylallyl)-[(2Z,4E)-5-phenylpenta-2,4-dienyl]ammonium Chloride (46) (with D. Cummings).—2-Methylallyl chloride (0.8 g) was added to a solution of (2Z,4E)-5-phenylpenta-2,4-dienyl-N,N-dimethylamine (6f) (1.9 g) in acetonitrile (10 ml). After 3 days at room temperature the solution was diluted with dry ether (200 ml) and the precipitate was collected giving dimethyl-(2-methylallyl)-[(2Z,4E)-5-phenylpenta-2,4-dienyl]ammonium chloride (46) (2.65 g) as a white solid, m.p. 156—158 °C; n.m.r.: τ 2.1—2.5 (m, 2 aromatic H), 2.8—3.0 (m, 3 aromatic H and 4-H), 3.2—3.5 (m, 3-H and 5-H), ca. 4.4 (m, 2-H), 4.55 and 4.60 (2 br s, =CH₂), 5.33 (d, J 8 Hz, CH₂-N⁺), 5.72 (s, CH₂-N⁺), 6.82 (s, NMe₂), and 8.08 (s, vinylic Me).

Base Catalysed Rearrangement of Dimethyl-(2-methylallyl)-[(2Z,4E)-5-phenylpenta-2,4-dienyl]ammonium Chloride (46). Formation of (1E,3Z)-5-Dimethylamino-7-methyl-1-phenylocta-1,3,7-triene (47) (with D. Cummings).—A solution of the salt (46) (2.65 g) in dimethyl sulphoxide (25 ml) was treated with a solution prepared from sodium hydride (0.6 g), methanol (5 ml), and dimethyl sulphoxide (25 ml) at room temperature for 1 h. The mixture was poured into water and extracted with ether. The ethereal extracts were washed with water, dried, and evaporated giving (1E,3Z)-5-dimethylamino-7-methyl-1-phenylocta-1,3,7-triene (47) as a pale yellow oil (1.6 g, 80%) [Found: M , 241.183 2; m/e 196 ($M - HNMe_2$) 186 ($M - C_4H_7$), and 117, m^* 73.5 (186 → 117). C₁₇H₂₃N requires M , 241.183 0]; n.m.r.: τ 2.5—2.9 (m, 5 aromatic H), ABMNXY₂ system, τ_A 3.46, τ_B 2.97, τ_M 3.65, τ_N 4.64, τ_X 6.3—6.5, τ_Y 7.4—8.0 [J_{AB} 15 Hz, J_{BM} 10.5 Hz, J_{MN} 10.5 Hz, J_{MX} 10.5 Hz, $PhCH_A=$

$=CH_B-CH_M=CH_N-CH_X-C(H_Y)_2$], τ 5.27 (br s, =CH₂), 7.74 (s, NMe₂), and 8.26 (s, vinylic Me).

4-Methylpent-4-en-2-ynyl Bromide.—4-Methylpent-4-en-2-ynol (39) (9.6 g) in dry ether (100 ml) at 0 °C was treated with pyridine (0.2 g) followed by a solution of phosphorus tribromide (14 g) in dry ether (150 ml). The solution was allowed to warm to room temperature, stirred for 4 h, poured into saturated sodium hydrogen carbonate solution, and extracted with ether. The extracts were dried and evaporated giving 4-methylpent-4-en-2-ynyl bromide as a yellow oil (11 g, 70%); ν_{max} 2220 cm⁻¹; n.m.r.: ABX₃ system, τ_A 4.59, τ_B 4.62, τ_X 8.11 [J_{BX} 2 Hz, $CH_AH_B=C-C(H_X)_3$], and τ 5.90 (s, CH₂Br).

Cinnamyl dimethyl-(4-methylpent-4-en-2-ynyl)ammonium Bromide (48).—A mixture of 4-methylpent-4-en-2-ynyl bromide (5.5 g) and cinnamyl dimethylamine (5.5 g) in acetonitrile (20 ml) reacted exothermically and dilution of the solution with dry ether (200 ml) gave a very hygroscopic precipitate of cinnamyl dimethyl-(4-methylpent-4-en-2-ynyl)ammonium bromide (48) (10 g); ν_{max} 2240, 980 cm⁻¹; n.m.r.: τ 2.4—2.8 (m, 5 aromatic H), ABX₂ system, τ_A 2.88, τ_B 3.66, τ_X 5.34 [J_{AB} 15.5 Hz, J_{BX} 7.5 Hz, $PhCH_A=CH_B-C(H_X)_2-N^+$] ABX₃ system, τ_A 4.61, τ_B 4.66, τ_X 8.15 [J_{BX} 1 Hz, $CH_AH_B=C-C(H_X)_3$], τ 5.16 (s, CH₂-N⁺), and 6.53 (s, NMe₂).

Base Catalysed Rearrangement of Cinnamyl dimethyl-(4-methylpent-4-en-2-ynyl)ammonium Bromide (48). Formation of 5-Dimethylamino-2-methyl-6-phenylocta-1,7-dien-3-yne (49) and (7E)-5-Dimethylamino-2-methyl-8-phenylocta-1,7-dien-3-yne (50).—A solution of the ammonium salt (48) (3.2 g) in dimethyl sulphoxide (25 ml) was treated with a solution prepared from sodium hydride (0.24 g), methanol (2 ml), and dimethyl sulphoxide (25 ml). After stirring for 4 h at room temperature, the solution was poured into water and extracted with ether. The ethereal extracts were washed with water, dried, and evaporated giving an oil (1.8 g) which was separated into two components by preparative t.l.c. Fraction (i) was 5-dimethylamino-2-methyl-6-phenylocta-1,7-dien-3-yne (49) (1.1 g), a pale yellow oil [Found: M , 239; m/e 122 ($M - PhCH-CH=CH_2$). C₁₇H₂₁N requires M , 239]; n.m.r.: τ 2.77 (br s, 5 aromatic H), ABMXY system, τ_A 4.96, τ_B 4.92, τ_M 3.84, τ_X 6.58, τ_Y 6.30 [J_{AM} 18 Hz, J_{BM} 10 Hz, J_{MX} 8 Hz, J_{XY} 11 Hz, $CH_AH_B=CH_M-CH_X-CH_Y-$], τ 4.97 (br s, CH₂), 7.73 (s, NMe₂), and 8.31 (br s, vinylic Me). The amine (49) was mainly one diastereoisomer and only a trace of the other diastereoisomer (NMe₂ at τ 7.81) could be detected in the n.m.r. spectrum. The amine (49) formed a picrate, m.p. 133—135 °C from ethanol (Found: C, 58.7; H, 5.4; N, 11.6. C₂₃H₂₄N₄O₇ requires C, 59.0; H, 5.1; N, 12.0%). Fraction (ii) was (7E)-5-dimethylamino-2-methyl-8-phenylocta-1,7-dien-3-yne (50) (0.13 g), a pale yellow oil [Found: M , 239.166 6; m/e 173 ($M - C_5H_9$), m/e 122 ($M - PhCH=CH-CH_2$). C₁₇H₂₁N requires M , 239.167 4]; n.m.r.: τ 2.6—2.9 (m, 5 aromatic H), ABX₂Y system, τ_A 3.58, τ_B 3.74, τ_X 7.48, τ_Y 6.47 [J_{AB} 16 Hz, J_{BX} 7 Hz, J_{XY} 7 Hz, $PhCH_A=CH_B-C(H_X)_2-CH_Y-NMe_2$], ABX₃ system, τ_A 4.76, τ_B 4.84, τ_X 8.13 [J_{BX} 1 Hz, $CH_AH_B=C-C(H_X)_3$]; and τ 7.73 (s, NMe₂).

Dimethyl-[(2Z)-2-methylpenta-2,4-dienyl](3-phenylprop-2-ynyl)ammonium Bromide (51).—A solution of (2Z)-2-methylpenta-2,4-dienyl-N,N-dimethylamine (6a) (2.8 g) in acetonitrile (10 ml) was added to a solution of 3-phenylprop-2-ynyl bromide (4.0 g) in acetonitrile (20 ml). After 1 h

at room temperature the solution was diluted with dry ether (200 ml) and the hygroscopic precipitate was collected giving *dimethyl-[(2Z)-2-methylpenta-2,4-dienyl]-(3-phenylprop-2-ynyl)ammonium bromide* (51) as a sticky solid (6.5 g) (Found: C, 60.0; H, 6.8; Br, 23.75; N, 4.1 $C_{17}H_{22}BrN$ H_2O requires C, 60.4; H, 6.5; Br, 23.6; N, 4.1%); ν_{max} 2 220 cm^{-1} ; n.m.r.: τ 2.4–2.8 (m, 5 aromatic H), ABMX system, τ_A 4.65, τ_B 4.68, τ_M 2.85, τ_X 3.57 (J_{BM} 10 Hz, J_{AM} 15 Hz, J_{MX} 11 Hz, $CH_AH_B=CH_M-CH_X$), τ 4.88 (s, $C\equiv C-CH_2-N$), 5.32 (s, $CH=C-CH_2-N$), 6.50 (s, NMe_2), and 7.89 (s, vinylic Me).

Base Catalysed Rearrangement of Dimethyl-[(2Z)-2-methylpenta-2,4-dienyl]-(3-phenylprop-2-ynyl)ammonium Bromide (51). Formation of 3-Dimethylamino-5-methyl-1-phenyl-4-vinylhex-5-en-1-yne (53) and (5Z)-3-Dimethylamino-5-methyl-1-phenylocta-5,7-dien-1-yne (55).—A solution of the ammonium salt (51) (2.2 g) in dimethyl sulphoxide (25 ml) was treated with a solution prepared from sodium hydride (0.24 g), methanol (0.5 ml), and dimethyl sulphoxide (25 ml) at room temperature for 12 h. The mixture was poured into water and extracted with ether. The ethereal extracts were washed with water and separated into neutral and basic fractions using 5M-hydrochloric acid and 5M-sodium hydroxide. The neutral fraction contained very little material. The basic fraction (1.5 g) consisted of two components by t.l.c. Separation by preparative t.l.c. (silica gel, chloroform–ethyl acetate 3:1) gave fraction (i) 3-dimethylamino-5-methyl-1-phenyl-4-vinylhex-5-en-1-yne (53) (1.2 g) as a mixture of diastereoisomers A and B in the ratio 6:1 [Found: M , 239.166 6; m/e 194 ($M - NMe_2$), m/e 158 ($Ph\equiv C-CH=NMe_2$), m/e 115 ($Ph\equiv C-CH_2^+$). $C_{17}H_{21}N$ requires M , 239.167 4]; ν_{max} 1 640, 917, and 895 cm^{-1} ; n.m.r.: τ 2.4–2.8 (m, 5 aromatic H), ABMXY system, τ_A , τ_B 4.7–5.2, τ_M 4.08, τ_X 7.01, τ_Y 6.34 (J_{AB} ca. 2 Hz, J_{AM} 18 Hz, J_{BM} 9 Hz, J_{MX} 8 Hz, J_{XY} 11 Hz, $CH_AH_B=CH_M-CH_X-CH_Y-NMe_2$), τ 5.10 (s, $=CH_2$), 7.10 (s, NMe_2), 8.10 (s, vinylic Me, diastereoisomer A), and 8.15 (s, vinyl Me, diastereoisomer B). Fraction (ii) was (5Z)-3-dimethylamino-5-methyl-1-phenylocta-5,7-dien-1-yne (55) (0.1 g) [Found: M , 239.166 6; m/e 158 ($Ph\equiv C-CH=NMe_2$). $C_{17}H_{21}N$ requires M , 239.167 4]; n.m.r.: τ 2.4–2.8 (m, 5 aromatic H), ABMX system, τ_A 4.86, τ_B 4.98, τ_M 3.30, τ_X 3.98 (J_{AM} 16.5 Hz, J_{BM} 11 Hz, J_{MX} 11 Hz, $CH_AH_B=CH_M-CH_X$), AXY system, τ_A 6.26, τ_X 7.39, τ_Y 7.41, (J_{AX} 8.5 Hz, J_{AY} 7.5 Hz, $CH_A-CH_XH_Y$), τ 7.67 (s, NMe_2), and 8.10 (s, vinylic Me).

Dimethyl-[(2Z)-2,3-dimethylpenta-2,4-dienyl]-(3-phenylprop-2-ynyl)ammonium Bromide (52). A solution of (2Z)-2,3-dimethylpenta-2,4-dienyl-*N,N*-dimethylamine (6b) (2.6 g) in acetonitrile (10 ml) was added to a solution of 3-phenylprop-2-ynyl bromide (4.0 g) in acetonitrile (10 ml). After 12 h at room temperature, the solution was diluted with dry ether (200 ml) and the precipitate was collected giving *dimethyl-[(2Z)-2,3-dimethylpenta-2,4-dienyl]-(3-phenylprop-2-ynyl)ammonium bromide* (52) as a white hygroscopic solid; ν_{max} 2 220 and 923 cm^{-1} ; n.m.r.: τ 2.5–2.9 (m, 5 aromatic H), ABX system, τ_A 4.70, τ_B 4.57, τ_X 2.97 (J_{BX} 16 Hz, J_{AX} 11 Hz, $CH_AH_B=CH_X$), τ 5.27 (s, CH_2-N), 5.48 (s, CH_2N), 6.70 (s, NMe_2), 7.94 (s, vinylic Me), and 8.11 (s, vinylic Me).

Base Catalysed Rearrangement of Dimethyl-[(2Z)-2,3-dimethylpenta-2,4-dienyl]-(3-phenylprop-2-ynyl)ammonium Bromide (52). Formation of 3-Dimethylamino-4,5-dimethyl-1-

phenyl-4-vinylhex-5-en-1-yne (54) and (5Z)-3-Dimethylamino-5,6-dimethyl-1-phenylocta-5,7-dien-1-yne (56).—A solution of the ammonium salt (52) (4.0 g) in dimethyl sulphoxide (25 ml) was treated with a solution prepared from sodium hydride (0.48 g), methanol (1 ml), and dimethyl sulphoxide (25 ml). After 1 h at room temperature, the solution was poured into water and extracted with ether. The ethereal extracts were washed with water, and separated into neutral and basic fractions using 5M-hydrochloric acid and 5M-sodium hydroxide. The neutral fraction contained very little product. The basic fraction (2.2 g) consisted of three components by t.l.c.; preparative t.l.c. gave fraction (i), 3-dimethylamino-4,5-dimethyl-1-phenyl-4-vinylhex-5-en-1-yne (54) as a mixture of diastereoisomers A and B (ratio 2:1) (0.33 g). Fraction (ii) was mainly (54), diastereoisomer B with only a trace of diastereoisomer A (0.95 g). Diastereoisomer A, n.m.r.: τ 2.4–2.9 (m, 5 aromatic H), ABX system, τ_A 4.87, τ_B 4.90, τ_X 3.80 (J_{AB} 1 Hz, J_{AX} 11 Hz, J_{BX} 17 Hz, $CH_AH_B=CH_X$), τ 5.08 (br s, $=CH_2$), 6.32 (s, $CH-NMe_2$), 7.65 (s, NMe_2), 8.15 (br s, vinylic Me), and 8.69 (s, C-Me). Diastereoisomer B, n.m.r.: τ 2.4–2.9 (m, 5 aromatic H), ABX system, τ_A 4.89, τ_B 4.93, τ_X 3.76 (J_{AB} 1 Hz, J_{AX} 11 Hz, J_{BX} 18 Hz, $CH_AH_B=CH_X$), τ 5.10 (br s, $=CH_2$), 6.30 (s, $CH-NMe_2$), 7.70 (s, NMe_2), 8.18 (s, vinylic Me), and 8.66 (s, C-Me). The mass spectra of the diastereoisomers were identical [Found: M , 253.183 2; m/e 237 ($M - CH_3$) m/e 158 ($Ph\equiv C-CH=NMe_2$). $C_{18}H_{23}N$ requires M , 253.183 0]. Diastereoisomer B was characterised as the *picrate*, from ethanol, m.p. 144–145 °C (Found: C, 59.5; H, 5.5; N, 11.3. $C_{24}H_{26}N_4O_7$ requires C, 59.8; H, 5.4; N, 11.6%). Fraction (iii) was (5Z)-3-dimethylamino-5,6-dimethyl-1-phenylocta-5,7-dien-1-yne (56) (0.28 g) [Found: M , 253.183 2; m/e 208 ($M - NHMe_2$), m/e 158 ($Ph\equiv C-CH=NMe_2$), m/e 151 ($M - Ph\equiv CH$), m/e 155 ($Ph\equiv C-CH_2^+$), and m/e 102 ($Ph\equiv \dot{C}H$). $C_{18}H_{23}N$ requires M , 253.183 0].

Dimethyl-[(2E)-4-methylpenta-2,4-dienyl]-(3-phenylprop-2-ynyl)ammonium Bromide (60).—A solution of 3-phenylprop-2-ynyl-*N,N*-dimethylamine (3.0 g) in acetonitrile (20 ml) was added to a solution of (2E)-4-methylpenta-2,4-dienyl bromide (2.2 g) in acetonitrile (10 ml). After 12 h at room temperature, the solvent was evaporated and the oily residue was washed several times with dry ether, giving *dimethyl-[(2E)-4-methylpenta-2,4-dienyl]-(3-phenylprop-2-ynyl)ammonium bromide* (60) as a colourless oil (4.5 g) which could not be crystallised; ν_{max} 2 220 and 980 cm^{-1} ; n.m.r.: τ 2.4–2.8 (m, 5 aromatic H), ABX₂ system, τ_A 3.19, τ_B 4.24, τ_X 5.40 [J_{AB} 16 Hz, J_{BX} 8 Hz, $-CH_A=CH_B-C(H_X)_2-N$], τ 4.83 (s, $=CH_2$), 5.04 (s, $-CH_2N$), 6.51 (s, NMe_2), and 8.13 (s, vinylic Me).

Base Catalysed Rearrangement of Dimethyl-[(2E)-4-methylpenta-2,4-dienyl]-(3-phenylprop-2-ynyl)ammonium Bromide (60). Formation of 3-Dimethylamino-5-methyl-1-phenyl-4-vinylhex-5-en-1-yne (53), 3-Dimethylamino-5-methyl-1-phenylocta-5,7-dien-1-yne (55), and (5E)-3-Dimethylamino-7-methyl-1-phenylocta-5,7-dien-1-yne (57).—A solution of the salt (60) (3.3 g) in dimethyl sulphoxide (25 ml) was treated with a solution prepared from sodium hydride (0.5 g), methanol (1 ml), and dimethyl sulphoxide (25 ml). After 12 h at room temperature, the solution was poured into water and extracted with ether. The ethereal extracts were washed with water and separated into neutral and basic fractions using 5M-hydrochloric acid and 5M-sodium

hydroxide. The resulting ethereal solutions were dried and evaporated giving a neutral fraction (<100 mg) and a basic fraction (1.65 g) which was separated into two components by preparative t.l.c. (silica gel, chloroform-ethyl acetate, 4 : 1).

Fraction (i) was 3-dimethylamino-5-methyl-1-phenyl-4-vinylhex-5-en-1-yne (53), obtained as a mixture of diastereoisomers A and B in the ratio 3 : 1 (1.3 g) having n.m.r. spectra identical to those of samples obtained previously. Fraction (ii) was a mixture of the two amines, (55) and (57) in an approximate ratio of 1 : 1 (0.2 g) [Found: M , 239; m/e 194 ($M - \text{NHMe}_2$), 179 ($194 - \text{CH}_3$), 158 ($\text{PhC}\equiv\text{C}-\text{CH}^+\text{NMe}_2$), and 115 ($\text{PhC}\equiv\text{C}-\text{CH}_2^+$). $\text{C}_{17}\text{H}_{21}\text{N}$ requires M , 239]. 3-Dimethylamino-5-methyl-1-phenylocta-5,7-dien-1-yne (55), n.m.r.: τ 2.4–2.8 (m, 5 aromatic H), ABMX system, τ_A 4.88, τ_B 5.00, τ_M 3.40, τ_X 4.03 (J_{AB} 1 Hz, J_{BM} 9 Hz, J_{AM} 16 Hz, J_{MX} 11 Hz, $\text{CH}_A\text{H}_B=\text{CH}_M-\text{CH}_X=$), AXY system, τ_A 6.27, τ_X , τ_Y 7.4–7.6 (J_{AX} ca. 8 Hz, $\text{CH}_A-\text{CH}_X\text{H}_Y$) τ 7.68 (s, NMe_2), and 8.15 (s, vinylic Me). (5E)-3-Dimethylamino-7-methyl-1-phenylocta-5,7-dien-1-yne (57), n.m.r.: τ 2.4–2.8 (m, 5 aromatic H), ABX_2Y system, τ_A 3.74, τ_B 4.30, τ_X 6.42, τ_Y 7.4–7.6 [J_{AB} 16 Hz, J_{BX} 7 Hz, J_{XY} 8 Hz, $\text{CH}_A=\text{CH}_B-\text{C}(\text{H}_X)_2-\text{CH}_Y-\text{NMe}_2$], τ 5.11 (br s, $=\text{CH}_2$), 7.68 (s, NMe_2), and 8.15 (s, vinylic Me).

Dimethyl-[(2E)-2-methylpenta-2,4-dienyl]-(3-phenylprop-2-ynyl)ammonium Bromide (61).—A solution of 3-phenylprop-2-ynyl- N,N -dimethylamine (2.2 g) in acetonitrile (10 ml) was added to a solution of (2E)-2-methylpenta-2,4-dienyl bromide (2.0 g) in acetonitrile (10 ml). After 12 h at room temperature the solution was evaporated giving an oil (4 g), which after washing with dry ether gave dimethyl-[(2E)-2-methylpenta-2,4-dienyl]-(3-phenylprop-2-ynyl)-ammonium bromide (61) as an extremely hygroscopic solid; ν_{max} , 2220 cm^{-1} ; n.m.r.: τ 2.3–2.8 (m, 5 aromatic H), 3.3–3.7 (m, 3- H and 4- H), 4.4–4.8 (m, $=\text{CH}_2$), 5.00 (s, $=\text{CH}_2-\text{N}^+$), 5.40 (s, $=\text{CH}_2-\text{N}^+$), 6.48 (s, NMe_2), and 7.90 (s, vinylic Me).

Base Catalysed Rearrangement of Dimethyl-[(2E)-2-methylpenta-2,4-dienyl]-(3-phenylprop-2-ynyl)ammonium Bromide (61). Formation of 3-Dimethylamino-5-methyl-1-phenyl-4-vinylhex-5-en-1-yne (53), 3-Dimethylamino-5-methyl-1-phenylocta-5,7-dien-1-yne (55), and (5E)-3-Dimethylamino-7-methyl-1-phenylocta-5,7-dien-1-yne (57).—A solution of the ammonium salt (61) (3.0 g) in dimethyl sulphoxide was treated with a solution prepared from sodium hydride (0.5 g), methanol (1 ml), and dimethyl sulphoxide (25 ml). After 14 h at room temperature, the solution was poured into water and extracted with ether. The extracts were washed with water and separated into neutral and basic fractions using 5M-hydrochloric acid and 5M-sodium hydroxide. The neutral fraction contained very little material. The basic fraction (2.2 g) was a mixture of three components, which were separated by preparative-t.l.c. Fraction (i) was 3-dimethylamino-5-methyl-1-phenyl-4-vinylhex-5-en-1-yne (53) (1.3 g), obtained as a mixture of

diastereoisomers A and B in the ratio 1 : 3; n.m.r. (diastereoisomer B): τ 2.5–2.8 (m, 5 aromatic H), ABMX system, τ_A 4.84, τ_B 4.88, τ_M 4.04, τ_X 6.91, τ_Y 6.40 (J_{AB} 1 Hz, J_{AM} 17 Hz, J_{BM} 10 Hz, J_{MX} 7 Hz, J_{XY} 11 Hz, $\text{CH}_A\text{H}_B=\text{CH}_M-\text{CH}_X-\text{CH}_Y\text{NMe}_2$), τ 5.13–5.18 (m, $=\text{CH}_2$), 7.70 (s, NMe_2), and 8.15 (s, vinylic Me). Fraction (ii) was an inseparable mixture (0.2 g) of 3-dimethylamino-5-methyl-1-phenylocta-5,7-dien-1-yne (55) and (5E)-3-dimethylamino-7-methyl-1-phenylocta-5,7-dien-1-yne (57) in an approximate ratio of 1 : 1, identical with the mixture obtained previously.

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