Base Catalysed Rearrangements Involving Ylide Intermediates. Part 11.[1] Rearrangements of 3-Phenylprop-2-ynylammonium Ylides

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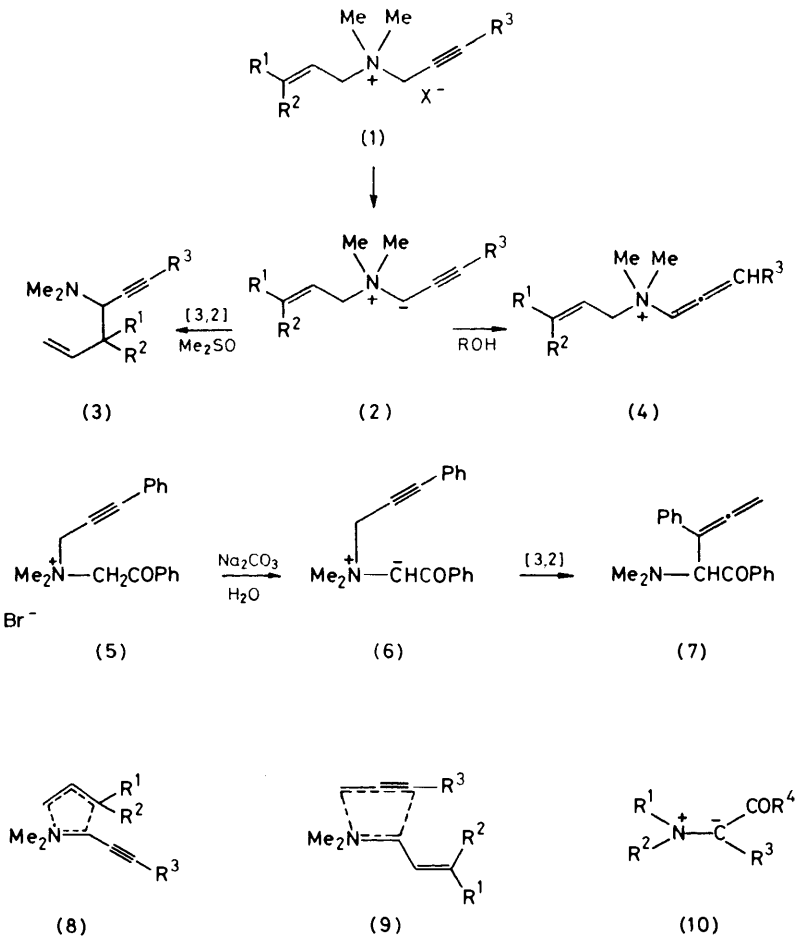
The propynylammonium salt (5) reacts with aqueous sodium hydroxide to give the allene (7) and a new ylide (11). The simultaneous formation of (7) and (11) suggests that the apparent [3,2] sigmatropic rearrangement of the propynyl ylide (6) to the allene (7) may involve a two-stage mechanism. The reactions of the ylide (11) are described, as are those of the allene (7) and a number of similar allenes derived from the propynylammonium salts (23) and (27). Three types of reaction are recognised for the allenes including a novel [1,3] rearrangement involving the migration of a dimethylamino-group. The base catalysed rearrangements of the bicyclic propynylammonium salts (52) and (56) do not show the inhibition expected for concerted [3,2] sigmatropic rearrangements in such bicyclic systems. This observation provides further evidence for a two-stage mechanism for the apparent [3,2] sigmatropic rearrangement of propynylammonium ylides.

It was shown in Part 1 of this series [2] that the base catalysed rearrangement of allylpropynylammonium salts (1) proceeds in aprotic solvents by a [3,2] rearrangement of the ylide (2) to give the product (3). In protic solvents the reaction of the ylide (2) takes a different course; [3] the ylide is re-protonated to give the allene (4) which subsequently yields a variety of products. A number of other examples of reactions involving similar isomerisation followed by cyclisation reactions have been recognised.[4] The failure of the propynyl group to participate in [3,2] rearrangements as the migrating three-centre unit in these examples is due either to the availability of an alternative mode of [3,2] rearrangement [(2) ⟶ (3)] or to the possibility of isomerisation to give an allene. Nevertheless a number of examples have been recognised in which a propynyl group does



Scheme 1

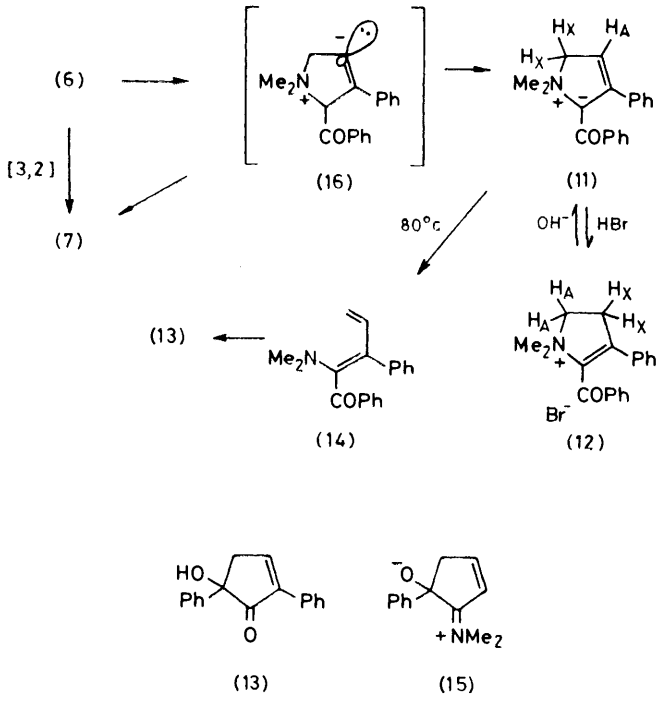
apparently participate in a [3,2] rearrangement. Thus the salt (5) was shown [5] to rearrange under mildly basic conditions, presumably *via* the ylide (6), to give the [3,2] rearrangement product (7) in high yield. Other apparent [3,2] rearrangements in which a propynyl group participates have been recognised for ammonium salts,[6] sulphonium salts,[7] ethers,[8] and related compounds.[9]

These reactions of propynylammonium salts are summarised in Scheme 1. The alternative modes of concerted [3,2] rearrangement of the two possible ylides, derivable from the salt (1), would involve the transition states (8) and (9); of these two possibilities (8) appears to be more favourable from simple stereochemical considerations, and rearrangements apparently involving transition states analogous to the stereochemically unfavourable system (9) are restricted to cases where the alternative mode of [3,2] rearrangement is not available. The involvement of the propynyl group in [3,3] sigmatropic rearrangements has, however, been widely exploited [10] and there does not appear to be any serious inhibition of reactions of this type as a result of the steric requirements of a participating propynyl grouping.

RESULTS AND DISCUSSION

The recognition that allenes analogous to (7) could be obtained by the base catalysed rearrangement of propynylammonium salts prompted us to investigate the generality of the reaction and the reactions of the allenes. Furthermore the isolation of a variety of acyl-stabilised ammonium ylides (10) in work that has been described in earlier papers of this series,[1,11,12] suggested the possibility of isolating propynylammonium ylides such as (6). The reaction of the salt (5) with cold aqueous sodium hydroxide, reaction conditions that had previously yielded ammonium ylides, gave, in addition to the allene (7), a product having some of the properties expected for the ylide (6). However, on heating, this new reaction product failed to undergo a [3,2] rearrangement to give (7). Reaction with cold aqueous hydrobromic acid gave a quaternary salt which differed from the salt (5). The reaction product had the molecular formula $C_{19}H_{19}NO$ (high-resolution mass spectrum) identical with that of the ylide (6) and an i.r. spectrum ($\nu_{max.}$ 1 575 and 1 520 cm^{-1}) consistent with an acyl ylide structure. The n.m.r. spectrum showed an AX_2 system (τ_A 5.27, τ_X 5.79, J_{AX} 2 Hz), inconsistent with the structure (6), suggesting the presence of a $C{=}CH_A{-}C(H_X)_2$ grouping. This spectroscopic information suggested that this new product was the cyclic ylide (11), derivable from the ylide (6) by an intramolecular nucleophilic addition to the triple bond followed by a prototropic shift (Scheme 2). The salt formed by the reaction with hydrobromic acid therefore has the structure (12), in accord with its i.r. spectrum ($\nu_{max.}$ 1 645 cm^{-1}) and its n.m.r. spectrum, which included an A_2X_2 system (τ_A 5.61, τ_X 6.34, J_{AX} 7 Hz) assignable to a $C(H_A)_2{-}C(H_X)_2$ grouping. The ylide (11) was regenerated when the salt (12) was treated with aqueous sodium hydroxide.

The new ylide (11) was thermally rather stable and reacted only slowly on heating under reflux in benzene to give a mixture of products from which the hydroxycyclopentenone (13) could be isolated after chromatography. The structure (13) was assigned on the basis of the molecular formula, i.r. spectrum ($\nu_{max.}$ 3 500 and 1 715 cm^{-1}), and n.m.r. spectrum (AX_2 system, τ_A 2.18, τ_X 6.97, J_{AX} 3 Hz) of this product. The hydroxycyclopentenone (13) is derivable from the ylide (11) by a



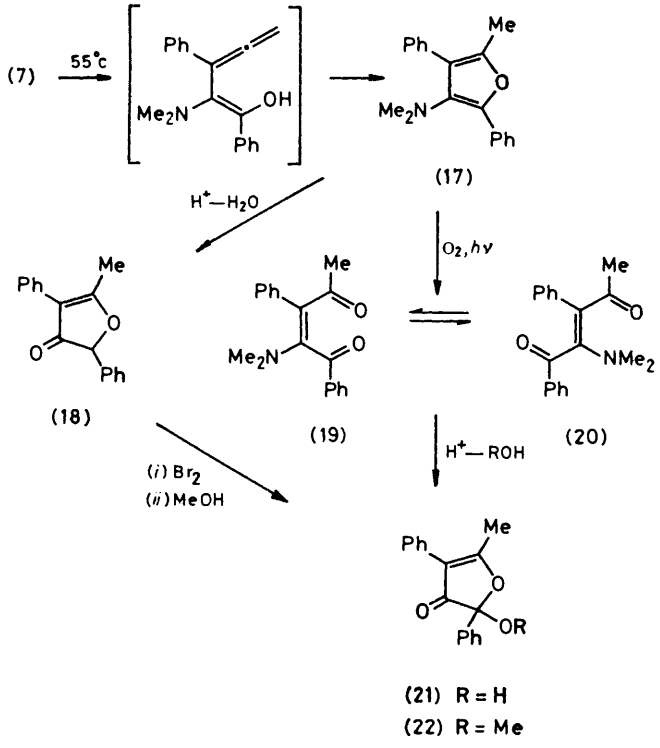
SCHEME 2

reaction sequence involving ring-fission to give the dienamine (14) followed by cyclisation to give the betaine (15) and hydrolysis of (15) during the isolation procedure.

The simultaneous formation of the ylide (11) and the allene (7) suggests that both compounds could be derived from the vinyl anion (16), in which the electron pair associated with the vinyl anion occupies an sp^2 orbital [see (16)] ideally located for the required elimination reaction, (16) ⟶ (7). The process (6) ⟶ (16) ⟶ (7) represents a mechanistic extreme for a [3,2] rearrangement in which bond-making is completed before bond-breaking commences; the opposite mechanistic extreme is of course a radical-pair mechanism in which bond-breaking is completed before bond-making commences. The mechanism of the transformation (6) ⟶ (7) will be discussed further at a later point in this paper. An excellent discussion of concertedness in [3,3] rearrangements has recently been published [13] and it has been shown, by a study of appropriate secondary deuterium isotope effects, that the relative timing of the bond-breaking and bond-making processes depends upon the structure of the reactant. We note that in the reaction (6) ⟶ (7) the intermediate (16) is formed by nucleo-

philic addition to an acetylene to give a vinyl anion, a reaction having ample analogy,[14,15] and that the stereochemical requirements of such a reaction can be met in an *endo*-5 process.[16] It is worth noting that an analogous two-stage mechanism for the [3,2] rearrangement of an allylic ylide would be unfavourable on both electronic and steric [16,17] grounds.

The chemistry of the allene (7) was investigated since this type of allene derivative has been relatively little



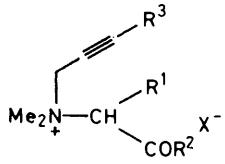
SCHEME 3 Reactions of the allene (7)

studied.[18] Heating the allene (7) (55 °C, 9 h) gave an isomeric compound lacking an i.r. absorption assignable to a carbonyl group; the n.m.r. spectrum indicated the presence of two phenyl groups, an NMe_2 group (τ 7.23), and a CMe group (τ 7.89). On this basis the compound was assigned the furan structure (17), derivable from the allene (7) by the reaction sequence shown in Scheme 3. This sequence involves intramolecular nucleophilic addition of an enolic hydroxyl group to one of the allene double bonds, a reaction with ample precedent.[15,19] The dimethylaminofuran (17) was rather unstable and decomposed on exposure to light and air. Two stable reaction products were obtained after the decomposition products had been treated with hydrochloric acid.

The first product, $C_{17}H_{14}O_2$, was identified as the furan-3(2*H*)-one (18) on the basis of its i.r. spectrum ($\nu_{max.}$ 1 755 cm^{-1}) and its n.m.r. spectrum (τ 4.33, $-CH<$, and τ 8.10, CMe). This product is readily accounted for by hydrolysis of the 3-dimethylaminofuran (17), and analogous hydrolysis of 3-aminofurans has been used [20] for the synthesis of furan-3(2*H*)-ones.

The second product, $C_{19}H_{19}NO_2$, was obtained as a mixture of two stereoisomers, separable by crystallisation. The molecular formula and i.r. spectra (isomer A, $\nu_{max.}$ 1 660 and 1 625 cm^{-1}; isomer B, $\nu_{max.}$ 1 655 and 1 620 cm^{-1}) strongly suggested that these isomers were the *E*- (19) and *Z*- (20) isomers of the vinylogous amide formed by singlet oxygen oxidation of the furan system of (17). The major isomer A showed two NMe signals in its n.m.r. spectrum which coalesced to a singlet at +16 °C; such behaviour is consistent with the NMe_2 group of a vinylogous amide structure and supports the structural assignment (19) or (20) (*cf.* ref. 21). The second isomer evidently has a slightly higher barrier to rotation about the C–NMe_2 bond and two NMe signals are observable in the n.m.r. spectrum of a solution at 35 °C. The interconversion of the *E*- and *Z*-isomers (19) and (20) is not unexpected and rapid equilibration of *E*- and *Z*-isomers has been reported for many olefins having analogous structures.[21a] On the basis of the spectroscopic data it is not possible to assign the structures (19) and (20) to the individual isomers A and B. The sensitised photooxidation of furans to enediones by singlet oxygen is a well known reaction [22] and many examples have been studied; it has been noted on a previous occasion [23] that the reaction can proceed spontaneously without the addition of a sensitiser when an arylfuran is involved.

Acidic hydrolysis of the vinylogous amides, (19) and (20), gave the 2-hydroxyfuran-3(2*H*)-one (21) if aqueous acid was used and a mixture of (21) and its methyl ether (22) if aqueous acidic methanol was used. The structure of the methyl ether (22) was confirmed by an independent synthesis from the furan-3(2*H*)-one (18) by a sequence of bromination at C-2 followed by methanolysis (*cf.* ref. 24).



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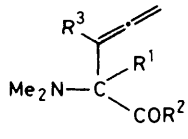
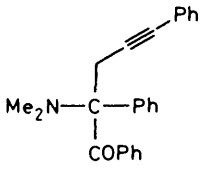


(24)

a; R^1=H, R^2=CMe_3, R^3=Ph
b; R^1=H, R^2=OMe, R^3=Ph
c; R^1=H, R^2=Me, R^3=Ph
d; R^1=R^2=Ph, R^3=H
e; R^1=R^2=R^3=Ph

The base-catalysed rearrangements of the propynylammonium salts (23a—d) also gave allenes (24a—d), using either aqueous sodium hydroxide (23a and c) or methanolic sodium methoxide (23b and d). The aqueous sodium hydroxide-catalysed rearrangement of the salt (23e) gave a mixture of the products of apparent [3,2] (24e) and [1,2] (25) rearrangements, together with a small quantity of the pentynone (26) of unknown origin. The greater tendency of the α-phenylphenacyl salt (23e) to give the product of the non-allowed Stevens [1,2]

rearrangement is in accord with the recognised tendency [25] for the analogous α-methylphenacyl prop-2-enyl and penta-2,4-dienyl ylides to rearrange by this non-allowed pathway. The rearrangement of the fluorenyl salt (27) took place in methanolic sodium methoxide at reflux temperature to give the allene (28). The rearrangement of the structurally analogous benzhydrylammonium salt (29), however, proceeded *via* the alternative ylide, produced by proton abstraction from the benzhydryl methine group, to give the product (30) of a [1,2] rearrangement.



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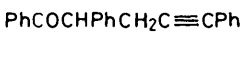

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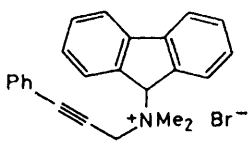

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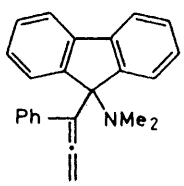

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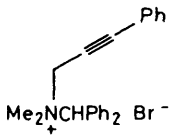

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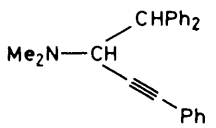
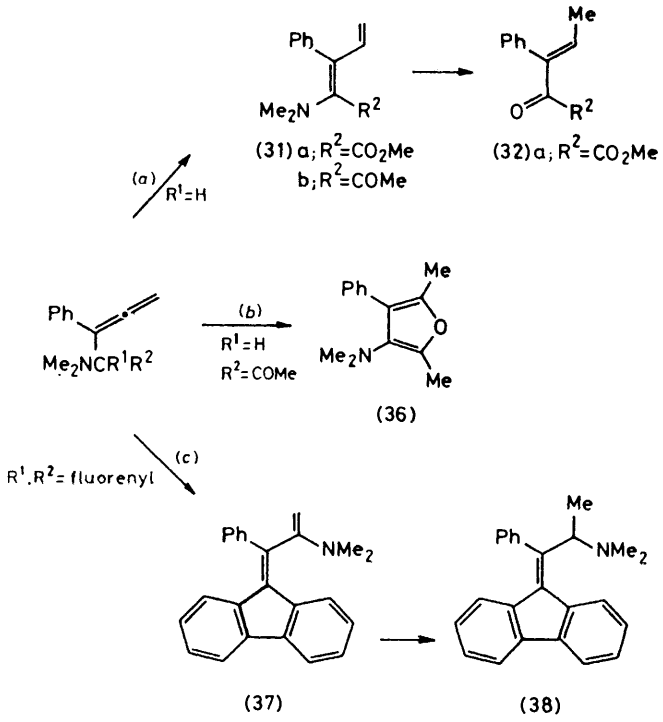


(30)

The new amino-allenes (24b and c) and (28) were found to undergo a number of different types of reaction which are summarised in Scheme 4. Thus the allenes (24b and c) reacted with sodium methoxide in dimethyl sulphoxide to give initially the unstable conjugated dienes (31a and b) respectively [Scheme 4, route (*a*)]. The diene (31a) reacted further with hydrochloric acid to give the βγ-unsaturated α-keto-ester (32a), characterised by analysis and its spectroscopic properties ($\nu_{max.}$ 1 735 and 1 680 cm^{-1}; n.m.r. AX_3 system, τ_A 2.86, τ_X 8.09, J_{AX} 7 Hz) and by further acidic hydrolysis to give the lactone (33). The diene (31b) was unstable under the conditions used for the isomerisation (24c) ⟶ (31b) and the cyclopentenone (34) was obtained as the reaction product. The formation of (34) appears to involve cyclisation of the diene (31b) to give the betaine (35) which is hydrolysed to (34) during product isolation, a reaction sequence which is closely analogous to the formation of the cyclopentenone (13) from the diene (14).

Although the allene (7) reacted readily by route (*b*) to



(31) a; R^2=CO_2Me b; R^2=COMe

(32) a; R^2=CO_2Me

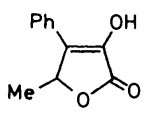
(36)

(37)

(38)

SCHEME 4 Reactions of allenes (24b and c) and (28)

give the dimethylaminofuran (17), the only further example of this reaction was observed for the allene (24c) [Scheme 4, route (*b*)]. In this case, however, furan formation required a high reaction temperature (138 °C) and the product (36) was insufficiently stable for complete characterisation. The lack of carbonyl absorption in its i.r. spectrum and signals assignable to two C-Me groups (τ 7.34 and 7.76) and an NMe_2 group (τ 7.70) in its n.m.r. spectrum provide reasonable support for the structural assignment (36). The allene (28) is unable to react by either route (*a*) or route (*b*) (Scheme 4) and instead undergoes thermal rearrangement at 80 °C to give a quantitative yield of the conjugated



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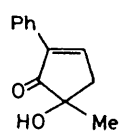

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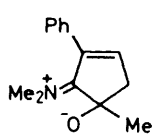
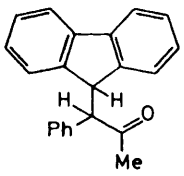


(35)

diene (37). The structure (37) is assigned to this reaction product on the basis of its spectroscopic properties, particularly the n.m.r. spectrum which shows signals assignable to two weakly coupled olefinic protons (τ 5.94, 6.04) and an NMe_2 group (τ 7.26). Confirmation of the structure was obtained by catalytic hydrogenation

which gave the dihydro-derivative (38) in which the position of the NMe_2 group was shown very clearly by its n.m.r. spectrum which indicated the presence of the CHMe grouping (AX_3 system, τ_A 5.62, τ_X 8.70, J_{AX} 7 Hz).



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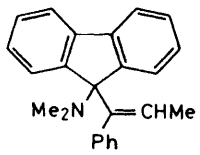


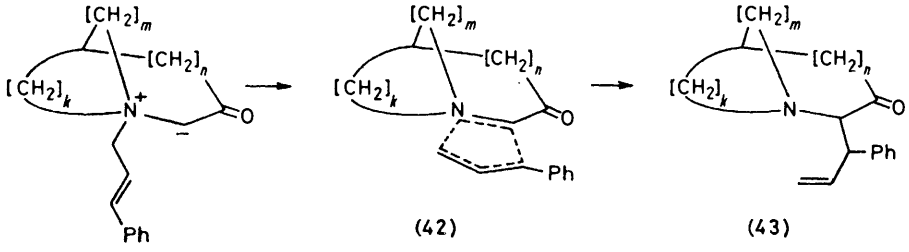
(40)

Further confirmation was obtained by reductive hydrolysis (zinc dust, 2N sulphuric acid) which gave the ketone (39) having a CH–CH unit (AB system, τ_A 5.20, τ_B 6.38, J_{AB} 10 Hz) and a COMe grouping ($\nu_{max.}$ 1 710 cm^{-1}; τ 7.94) in its structure. The [1,3] rearrangement (28) ⟶ (37) is apparently a unique example of migration of a dimethylamino-group in a [1,3] sigmatropic process. The structure (28) of the allene was therefore rigorously confirmed by hydrogenation to give the dihydro-derivative (40) which was shown to have a C=CHMe grouping in its structure (AX_3 system, τ_A 4.13, τ_X 7.55, J_{AX} 7 Hz). Comparison of the structures (39) and (40) provides excellent evidence for the migration of the dimethylamino-group in the [1,3] rearrangement (28) ⟶ (37). This reaction proceeds quantitatively at a fairly low reaction temperature, and it is tempting to speculate that it may represent an allowed ($_\pi 2_s + {}_\sigma 2_a$) or ($_\pi 2_a + {}_\sigma 2_s$) [1,3] sigmatropic process.[26]

The Rearrangement Reaction of Bicyclic Propynylammonium Salts.[27]—We have shown in a previous paper in this series[1] that the normally rapid [3,2] rearrangement of cinnamylammonium ylides may be inhibited, or even prevented, by the incorporation of the ylide system into a bicyclic framework (41) that requires that the π-bonding generated between the N^+ and C^- centres of the ylide in the transition state for a concerted rearrangement (42) is adjacent to the bridgehead. Thus the rearrangement (41) ⟶ (43) has only been achieved for the azabicyclo[3.3.1]nonane derivative (41a) and fails for the azabicyclo[2.2.2]octane derivative (41b) and the azabicyclo[3.2.1]octane derivative (41c).

The possibility that the rearrangement of propynylammonium ylides (44) can involve either a concerted [3,2] sigmatropic process [(44) ⟶ (45) ⟶ (46)] or a two-stage process [(44) ⟶ (47) ⟶ (46)] prompted an examination of this rearrangement in the same bicyclic systems that had previously been used[1] to examine the stereochemical requirements of the [3,2] rearrangement of allylic ammonium ylides. Thus the transition state (45) for a concerted rearrangement requires the development of π-bonding between the N^+ and C^- centres of the ylide (44) [*cf.* (42)] whereas the two-stage reaction pathway (44) ⟶ (47) ⟶ (46) does not require the development of such π-bonding at any stage (see Scheme 5).

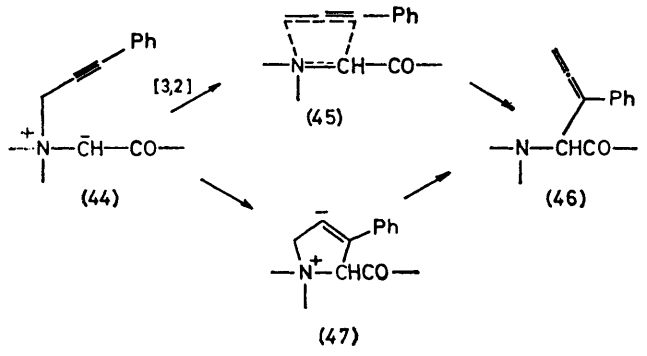
The base catalysed rearrangement of the *N*-propynylisoquinolinium derivative (48) was first examined as a model for the rearrangement of a *transoid* propynyl-



(41) (42) (43)

a; $k = 3$, $m = n = 1$
b; $k = m = 2$, $n = 0$
c; $k = 3$, $m = 1$, $n = 0$

ammonium ylide. This reaction was carried out conveniently at room temperature, using sodium hydride in dimethyl sulphoxide, to give the allene (49) in 86% yield. Unfortunately these partly heterogeneous reaction conditions allow for only a qualitative comparison of reaction rates but they do give rise to particularly

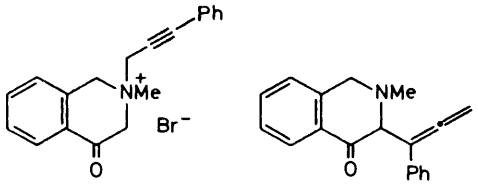


(44) (45) (46) (47)

SCHEME 5

clean reactions, presumably because reactions analogous to (6) ⟶ (11) are prevented when an aprotic solvent is used.

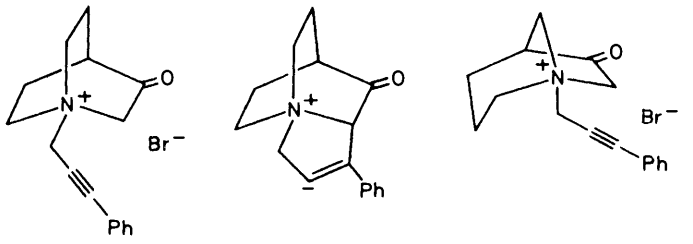
The bicyclic salt (50) remained unchanged under similar reaction conditions but on heating the reaction mixture to 80—90 °C slow decomposition occurred to give a complex mixture of products which was not further examined. This result is consistent with the



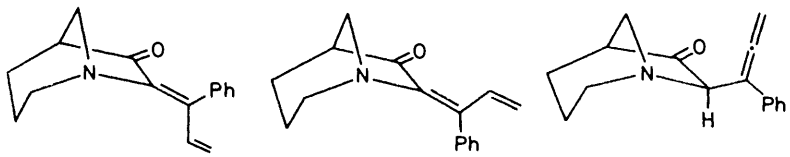
(48) (49)

failure of other ylides based upon the azabicyclo[2.2.2]-octane system to rearrange [1] and could reflect either the failure to permit the π-bonding required in a transition state analogous to (45) or the difficulty in producing the sterically strained tricyclic intermediate (51). The transformation of the initial reaction product, the allene (58) [*cf.* Scheme 4, route (*b*)]. The allene (58) could be obtained by reaction of the salt (56) with aqueous sodium hydroxide; as expected, treatment of (58) with sodium hydride in dimethyl sulphoxide gave the furan (57), confirming that the latter is formed by the reaction sequence (56) ⟶ (58) ⟶ (57). The identification of the reaction products (53), (54), (55), (57), and (58) is based upon spectroscopic data (Experimental section) which were readily interpreted by analogy with the data previously obtained for compounds derived from the propynyl salts (5) and (23).

The observation that the bicyclic salts (52) and (56) rearrange under conditions comparable to those used for the salt (48) contrasts with the inhibition of the rearrangements of the analogous cinnamyl salts (41a and c), and is inconsistent with a substantial requirement for π-bonding in the transition states of the rearrangement reactions (52) ⟶ (55) and (56) ⟶ (58). The simplest explanation is that the rearrangement reactions of the bicyclic systems (52) and (56) occur in two stages and involve betaines, analogous to (47), as intermediates.



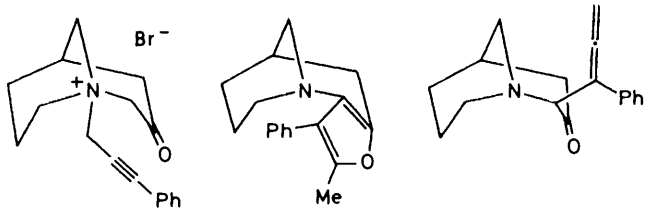
(50) (51) (52)



(53) (54) (55)

azabicyclo[3.2.1]octane derivative (52) did, however, undergo a clean rearrangement on treatment with sodium hydride in dimethyl sulphoxide at room temperature to give a good yield (76%) of a 1 : 1 mixture of the dienamines (53) and (54). The rearrangement proceeds as readily as for the isoquinoline derivative (48) but the expected reaction product, the allene (55), evidently undergoes base catalysed isomerisation under the reaction conditions used [*cf.* Scheme 4, route (*a*)]. The allene (55) could be obtained when the reaction was conducted in a two-phase system (dimethyl sulphoxide–ether) to prevent the isomerisation (55) ⟶ (53) + (54). The azabicyclo[3.3.1]nonane derivative (56) also rearranged cleanly under similar reaction conditions (sodium hydride in dimethyl sulphoxide at room temperature) to give the furan derivative (57) in nearly quantitative yield. This product (57) also represents a base catalysed

This strongly suggests that other propynylammonium ylides, for example (6), rearrange by a similar pathway. Thus the study of the bicyclic salts (52) and (56) provides



(56) (57) (58)

a mechanistic conclusion similar to that derived earlier in this paper from the isolation of the cyclisation product (11) from the ylide (6). This conclusion has obvious

implications for the apparent [3,2] sigmatropic rearrangements of analogous ylidic and anionic systems, but although it indicates the possibility of a two-stage mechanism it does not exclude a concerted sigmatropic process when this is geometrically or electronically favoured. It is also possible to envisage a range of reaction mechanisms lying between the two-stage mechanism and the fully concerted mechanism (*cf.* ref. 13 and Scheme 5).

The differing modes of base catalysed rearrangement of the allenes (55) and (58) is remarkable [*cf.* pathways (*a*) and (*b*) of Scheme 4]. Formation of the dimethylaminofurans (17) and (36) is in both cases a thermal reaction believed to involve intramolecular addition of an enol to a triple bond; the reaction (58) ⟶ (57) presumably involves the addition of an enolate anion to a triple bond but this is equally acceptable as a mechanism. The stability of the furan (57), as compared with the furans (17) and (36), is presumably in part a consequence of the lack of conjugation between the furan system and the dialkylamino-substituent when the latter is at the bridgehead of a bicyclic system. The base catalysed rearrangement of the allene (55) to the dienamines (53) and (54) is typical of reactions observed for the acyclic allenes (23b and c). The dienamines (53) and (54) are unable to undergo further base catalysed reactions because the dialkylamino-substituent is at the bridgehead position. There is no obvious reason why the enolate anions derived from the allenes (55) and (58) should react in different ways. We note, however, that the double bond of the dienyl system in (53) and (54) is exocyclic to a five-membered ring and the double bond in (57) is endocyclic in a six-membered ring. These relationships are reminiscent of a generalisation [28] made some time ago, to which there are, however, many exceptions.[29]

EXPERIMENTAL

For general directions see Part 1.[2b]

Reaction between Dimethylphenacyl-(3-phenylprop-2-ynyl)-ammonium Bromide (5) *and Aqueous Sodium Hydroxide. Formation of 2-Dimethylamino-1,3-diphenylpenta-3,4-dien-1-one* (7) *and 2-Benzoyl-1,1-dimethyl-3-phenyl-Δ³-pyrrolin-1-io-2-ide* (11).—Cold aqueous sodium hydroxide (28%, 25 ml) was added to a stirred solution of the salt (5) (7.2 g) in distilled water (1 200 ml) at 0 °C. The mixture was kept at 0 °C for 9 h, filtered, and the residue washed with water to give a mixture of the allene (7) and the ylide (11). The mixture was washed with ether to give the *ylide* (11) (1.4 g), m.p. 80 °C, as the ether-insoluble product (Found: $M^{+\bullet}$, 277.1458. $C_{19}H_{19}NO$ requires *M*, 277.1467); $\nu_{max.}$ 1 575 and 1 520 cm^{-1}; τ 2.82—3.20 (m, 10 aryl-H), AX_2 system, τ_A 5.27, τ_X 5.79 [J_{AX} 2 Hz, $\overset{+}{N}C(H_X)_2CH_A$], and 6.32 (s, $\overset{+}{N}Me_2$). The ether-soluble allene (7) was obtained by evaporation at 20 °C as a gum (3.6 g) identical with a sample previously obtained [5b] by rearrangement of the salt (5) using aqueous sodium carbonate.

The ylide (11) (2.8 g) reacted with cold aqueous hydrobromic acid (48%, 900 mg) in tetrahydrofuran (30 ml) to give *2-benzoyl-1,1-dimethyl-3-phenyl-Δ³-pyrrolinium bromide* (12) as a gum, precipitated by the addition of ether, which slowly crystallised. The salt was obtained as plates, m.p. 174—175 °C (2.2 g) by crystallisation from methanol–ether (Found: C, 63.4; H, 5.7; N, 3.8; Br, 22.3. $C_{19}H_{20}BrNO$ requires C, 63.7; H, 5.6; N, 3.9; Br, 22.3%); $\nu_{max.}$ 1 645 and 1 595 cm^{-1}; τ 2.35 (dd, *J* 2, 8 Hz, 2 *ortho*-H of PhCO), 2.48—2.90 (m, 8 aryl-H), A_2X_2 system, τ_A 5.61, τ_X 6.34 [J_{AX} 7 Hz, $\overset{+}{N}C(H_A)_2C(H_X)_2$], and 6.27 (s, $\overset{+}{N}Me_2$). The ylide (11) was regenerated by treatment of the salt (12) with aqueous sodium hydroxide.

Action of Heat on the Ylide (11). *Formation of 5-Hydroxy-2,5-diphenylcyclopent-2-en-1-one* (13).—The ylide (11) (2.5 g) was refluxed in benzene for 6 h; the solvent was evaporated and the residue purified by chromatography (silica gel, chloroform–benzene) to give the *cyclopentenone* (13) (800 mg) which crystallised from light petroleum as prisms, m.p. 112 °C (Found: C, 81.3; H, 5.7. $C_{17}H_{14}O_2$ requires C, 81.6; H, 5.7%); $\lambda_{max.}$ 229 (ε 16 600) and 264 nm (ε 3 875); $\nu_{max.}$ 3 540 and 1 715 cm^{-1}; τ, AX_2 system, τ_A 2.18, τ_X 6.97 [J_{AX} 3 Hz, CH_A–$C(H_X)_2$], 2.30—2.89 (m, 10 aryl-H), and 6.71 (br s, OH).

Action of Heat on the Allene (7). *Formation of 4-Dimethylamino-2-methyl-3,5-diphenylfuran* (17).—The allene (7) (9 g) was heated at 55 °C (N_2 atmosphere) for 9 h to give the furan (17) (9 g) (Found: $M^{+\bullet}$, 277. $C_{19}H_{19}NO$ requires *M*, 277); $\nu_{max.}$ 1 620, 1 580, and 1 560 cm^{-1}; τ 1.98—2.82 (m, 10 aryl-H), 7.23 (s, NMe_2), and 7.89 (s, CMe). The furan (17) was kept in chloroform (20 ml) at 20 °C for 12 h in the presence of light and air. The product was diluted with ether and the solution extracted with hydrochloric acid (2N, 3 × 150 ml), washed with water, dried, and evaporated. The hydrochloric acid extracts were made basic (2N NaOH) and extracted with ether (3 × 200 ml). The ether extract was washed with water, dried, and evaporated to give a brown oil (7.2 g) which was separated into its components by chromatography on silica. (*i*) Elution with benzene gave a viscous oil identified as *5-methyl-2,4-diphenylfuran-3(2H)-one* (18) (1.75 g) (Found: $M^{+\bullet}$, 250.0093. $C_{17}H_{14}O_2$ requires *M*, 250.0 094); $\lambda_{max.}$ 252 nm (ε 11 500); $\nu_{max.}$ 1 755 cm^{-1}; τ 2.44—2.86 (m, 10 aryl-H), 4.33 (s, C-2-H), and 8.10 (s, CMe). (*ii*) Elution with chloroform–benzene (1 : 1) gave *4-benzoyl-4-dimethylamino-3-phenylbut-3-en-2-one* as a mixture of *E*- (19) and *Z*- (20) isomers (3.5 g). These isomers, A and B, were separated by crystallisation of the mixture (300 mg) from light petroleum. Isomer A [(19) or (20)] (100 mg) was obtained as needles, m.p. 94 °C (Found: C, 77.9; H, 6.6; N, 4.8%; $M^{+\bullet}$, 293. $C_{19}H_{19}NO_2$ requires C, 77.8; H, 6.5; N, 4.8%; *M*, 293); $\lambda_{max.}$ 252 (ε 19 400) and 278 nm (ε 9 500); $\nu_{max.}$ 1 660 and 1 625 cm^{-1}; τ 2.14 (dd, *J* 2, 7.5 Hz, 2 *ortho*-H of PhCO), 2.47—2.74 (m, 8 aryl-H), 7.28 (br s, NMe_2), and 7.98 (s, COMe). Isomer B [(20) or (19)] (50 mg) was obtained as needles, m.p. 103—104 °C (Found: C, 77.5; H, 6.35; N, 4.6%; $M^{+\bullet}$, 293); $\lambda_{max.}$ 244 (ε 16 000) and 280 nm (ε 5 100); $\nu_{max.}$ 1 655 and 1 620 cm^{-1}; τ 2.19 (dd, *J* 2,7.5 Hz, 2 *ortho*-H of PhCO), 2.45—2.98 (m, 8 aryl-H), 6.97 (s, NMe), 7.06 (s, NMe), and 7.96 (s, COMe). The non-basic reaction products (1.37 g) were separated by chromatography to give further amounts of the furanone (18) (100 mg) and the vinylogous amide [(19) and (20)] (300 mg).

Reaction of 4-Benzoyl-4-dimethylamino-3-phenylbut-3-en-2-one [(19) *or*(20)] *with Hydrochloric Acid.*—(*a*) The vinylogous amide (19) or (20) (500 mg) was refluxed for 30 min in methanol (10 ml) containing hydrochloric acid (5N, 10 ml). The solution was kept at room temperature for 18 h, diluted

with water, and extracted with ether (2 × 75 ml). The ethereal extract was dried and evaporated and the residual oil separated by preparative t.l.c. (silica gel, chloroform) to give two products. (*i*) *2-Methoxy-5-methyl-2,4-diphenylfuran-3(2H)-one* (22) (150 mg) was obtained as an oil (Found: C, 77.4; H, 6.0%; $M^{+\cdot}$, 280.1096. $C_{18}H_{16}O_3$ requires C, 77.1; H, 5.75%; *M*, 280.1099); $\lambda_{max.}$ 261 nm (ε 9 400); $\nu_{max.}$ 1 755 cm^{-1}; τ 2.47—2.90 (m, 10 aryl-H); 6.64 (s, OMe), and 8.07 (s, C=CMe). (*ii*) *2-Hydroxy-5-methyl-2,4-diphenylfuran-3(2H)-one* (21) (200 mg) crystallised as needles, m.p. 167—168 °C, from chloroform–light petroleum (Found: C, 76.9; H, 5.5%; $M^{+\cdot}$, 266. $C_{17}H_{14}O_3$ requires C, 76.7; H, 5.3%; *M*, 266); $\lambda_{max.}$ 258 nm (ε 9 700); $\nu_{max.}$ 3 510, 3 250, and 1 755 cm^{-1}; τ 2.47—2.90 (m, 10 aryl-H), 5.66 (br s, OH), and 8.02 (s, C=CMe).

(*b*) The vinylogous amide (19) or (20) (300 mg) was refluxed in hydrochloric acid (5N, 10 ml) for 1 h and the solution kept at room temperature for 4 h. Extraction with ether gave 2-hydroxy-5-methyl-2,4-diphenylfuran-3(2H)-one (21) (210 mg).

Conversion of 5-Methyl-2,4-diphenylfuran-3(2H)-one (18) *into 2-Methoxy-5-methyl-2,4-diphenylfuran-3(2H)-one* (22).—Bromine (600 mg) was added dropwise to a stirred solution of the dihydrofuran derivative (18) (750 mg) in dry carbon tetrachloride (25 ml) and the resulting solution left for a further 8 h. The solvent was removed by evaporation and the residue heated under reflux with methanol (25 ml) for 4 h. Evaporation and purification of the residue by preparative t.l.c. gave 2-methoxy-5-methyl-2,4-diphenylfuran-3(2*H*)-one (22) (350 mg), identical with a sample obtained by methanolysis of the vinylogous amide (19) or (20).

(3,3-Dimethyl-2-oxobutyl)dimethyl-(3-phenylprop-2-ynyl)ammonium Bromide (23a).—Dimethyl-(3-phenylprop-2-ynyl)amine (8 g) and 1-bromo-3,3-dimethylbutan-2-one (7.5 g) in methyl cyanide (30 ml) gave the *salt* (23a) (12 g, 71%) which crystallised from methanol–ether as prisms, m.p. 158—159 °C (Found: C, 60.4; H, 7.2; N, 4.1; Br, 23.6. $C_{17}H_{24}BrNO$ requires C, 60.1; H, 7.2; N, 4.2; Br, 23.7%); $\nu_{max.}$ 1 710 cm^{-1}; τ 2.53–2.69 (m, C_6H_5), 4.35 (s, $COCH_2\overset{+}{N}$), 4.75 (s, $C{\equiv}CCH_2\overset{+}{N}$), 6.30 (s, $\overset{+}{N}Me_2$), and 8.73 (s, CMe_3).

Reaction between (3,3-Dimethyl-2-oxobutyl)dimethyl-(3-phenylprop-2-ynyl)ammonium Bromide (23a) *and Aqueous Sodium Hydroxide. Formation of 4-Dimethylamino-3-phenyl-4-pivaloylbuta-1,2-diene* (24a).—Cold aqueous sodium hydroxide (42%, 7 ml) was added to a stirred solution of the salt (23a) (2.0 g) in water (50 ml) at 0 °C. The solution was kept at 0 °C for 5h and the precipitated *amine* (24a) (1.25 g) collected by filtration (Found: $M^{+\cdot}$, 257. $C_{17}H_{23}NO$ requires *M*, 257); $\nu_{max.}$ 1 940 and 1 700 cm^{-1}; τ 2.43—2.83 (m, Ph), 4.89—4.93 (m, $C{=}CH_2$), 5.38–5.41 (m, COCHN), 7.57 (s, NMe_2), and 8.91 (s, CMe_3). The *methiodide* crystallised from methanol–ether as prisms, m.p. 135—136 °C (Found: C, 54.2; H, 6.8; N, 3.5; I, 31.8. $C_{18}H_{26}INO$ requires C, 54.0; H, 6.8; N, 3.6; I, 31.7%); $\nu_{max.}$ 2 915 and 1 700 cm^{-1}; τ 1.99 (d, *J* 6 Hz, 2 *ortho*-H of Ph), 2.47—2.74 (m, 3 aryl-H), 3.41 (s, $\overset{+}{N}$COCHN), AB system, τ_A 4.46, τ_B 4.59 (J_{AB} 15 Hz, $C{=}C{=}CH_AH_B$), and 8.65 (s, CMe_3).

(Methoxycarbonylmethyl)dimethyl-(3-phenylprop-2-ynyl)ammonium Bromide (23b).—Methyl bromoacetate (10.1 g) and dimethyl-(3-phenylprop-2-ynyl)amine (10.0 g) in ether gave the *salt* (23b) which crystallised from ethanol–ethyl acetate as prisms (17.2 g, 86%), m.p. 155—157 °C (Found: C, 53.7; H, 5.6; N, 4.3; Br, 25.8. $C_{14}H_{18}BrNO_2$ requires C, 53.9; H, 5.8; N, 4.5; Br, 25.6%); $\nu_{max.}$ 2 270 and 1 755 cm^{-1}; τ (D_2O) 2.18—2.57 (m, C_6H_5), 5.15 (s, $CH_2\overset{+}{N}$), 5.39 (s, $CH_2\overset{+}{N}$), 6.00 (s, CO_2Me), and 6.47 (s, $\overset{+}{N}Me_2$).

Base Catalysed Rearrangement of (Methoxycarbonylmethyl)-dimethyl-(3-phenylprop-2-ynyl)ammonium Bromide (23b). *Formation of 4-Dimethylamino-4-methoxycarbonyl-3-phenylbuta-1,2-diene* (24b).—A methanolic solution of sodium methoxide, prepared from sodium (1.15 g) and methanol (20 ml), was added to a solution of salt (23b) (15.6 g) in methanol (50 ml). The mixture was left at room temperature overnight, poured into water (300 ml), and the aqueous solution extracted with ether. The ethereal extract was washed (saturated aqueous NaCl), dried, and evaporated to give the *allene* (24b) (6.2 g, 56%) as a brown oil (Found: $M^{+\cdot}$, 231. $C_{14}H_{17}NO_2$ requires *M*, 231); $\nu_{max.}$ 1 930 and 1 740 cm^{-1}; τ 2.30—2.81 (m, Ph), 4.75 (d, *J* 2 Hz, $C{=}CH_2$), 5.68 (t, *J* 2 Hz, CH=C), 6.26 (s, CO_2Me), and 7.53 (s, NMe_2). The *methiodide* had m.p. 176—177 °C (Found: C, 48.1; H, 5.3; N, 3.7; I, 33.9. $C_{15}H_{20}INO_2$ requires C, 48.3; H, 5.4; N, 3.75; I, 34.0%); $\nu_{max.}$ 1 930 and 1 745 cm^{-1}; τ ($CDCl_3$–CF_3CO_2H) 2.50 (s, Ph), 4.42 (s, $C{=}CH_2$), 4.56 (s, CH=C), 6.05 (s, CO_2Me), and 6.61 (s, $\overset{+}{N}Me_3$).

Acetonyl(dimethyl)-(3-phenylprop-2-ynyl)ammonium Chloride (23c).—Chloroacetone (18.3 g) and dimethyl-(3-phenylprop-2- ynyl)amine (20.0 g) in ether gave the *salt* (23c) (31.0 g, 99%) as prisms, m.p. 151—153 °C (Found: C, 66.9; H, 7.1; N, 5.4; Cl, 14.4. $C_{14}H_{18}ClNO$ requires C, 66.8; H, 7.2; N, 5.6; Cl, 14.1%); $\nu_{max.}$ 2 260 and 1 730 cm^{-1}; τ (D_2O) 2.10—2.58 (m, Ph), 5.20 (s, $CH_2\overset{+}{N}$), 6.50 (s, $\overset{+}{N}Me_2$), and 7.55 (s, COMe).

Reaction of Acetonyl(dimethyl)-(3-phenylprop-2-ynyl)ammonium Chloride (23c) *with Aqueous Sodium Hydroxide. Formation of 3-Dimethylamino-4-phenylhexa-4,5-dien-2-one* (24c).—Aqueous sodium hydroxide (10N, 20 ml) was added to a solution of the salt (23c) (12.6 g) in water (200 ml). The solution was left at room temperature for 30 min and the brown oil which separated was extracted with ether. The ethereal extract was dried and evaporated to give the *allene* (24c) (8.6 g, 80%) as a brown oil (Found: $M^{+\cdot}$, 215. $C_{14}H_{17}NO$ requires *M*, 215); $\nu_{max.}$ 1 940 and 1 710 cm^{-1}; τ 2.35—2.82 (m, Ph), AX_2 system, τ_A 6.08, τ_X 4.76 [J_{AX} 1 Hz, $CH_A{-}C{=}C(H_X)_2$], 7.62 (s, NMe_2), and 7.85 (s, COMe). The *methiodide* had m.p. 182 °C (decomp.) (Found: C, 50.5; H, 5.6; N, 3.8. $C_{15}H_{20}INO$ requires C, 50.4; H, 5.6; N, 3.9%); $\nu_{max.}$ 1 955, 1 918, and 1 718 cm^{-1}; τ 2.15—2.60 (m, Ph), 4.17 (s, $\overset{+}{N}$CHCO), 4.35 (s, $C{=}CH_2$), 6.60 (s, $\overset{+}{N}Me_3$), and 7.47 (s, COMe).

Dimethyl-(α-phenylphenacyl)prop-2-ynylammonium Bromide (23d).—Dimethyl(prop-2-ynyl)amine (95% aqueous solution, 2 g) and α-phenylphenacyl bromide (5.5 g) in methyl cyanide (25 ml) gave the *salt* (23d) (6.5 g, 91%) which crystallised from methanol–ether as prisms, m.p. 150—151 °C (Found: C, 63.6; H, 5.9; N, 4.0; Br, 22.15. $C_{19}H_{20}BrNO$ requires C, 63.7; H, 5.6; N, 3.9; Br, 22.3%); $\nu_{max.}$ 3 300, 2 130, and 1 675 cm^{-1}; τ 1.77 (d, *J* 7.5 Hz, 2 *ortho*-H of PhCO), 1.94 (s, $COCH\overset{+}{N}$), 2.15—2.72 (m, 8 aryl-H), ABX system, τ_A 4.84, τ_B 5.15, τ_X 6.83 (J_{AB} 16, J_{AX} 2, J_{BX} 2 Hz, $\overset{+}{N}CH_AH_BC{\equiv}CH_X$), and 6.39 (s, $\overset{+}{N}Me_2$).

Base Catalysed Rearrangement of Dimethyl-(α-phenylphenacyl)prop-2-ynylammonium Bromide (23d). *Formation of Dimethyl-[α-phenyl-α-(propa-1,2-dienyl)phenacyl]amine* (24d).—Cold (0 °C) methanolic sodium methoxide (4.5%, 25 ml)

was added to a solution of the salt (23d) (2 g) in methanol (20 ml) at 0 °C and the solution maintained at this temperature for 5 days. The solution was acidified (100 ml, 2N HCl), washed with ether, made basic (5N NaOH) and extracted with ether. The ethereal extract was washed with water, dried, and evaporated to give the *amine* (24d) (300 mg, 19%) (Found: $M^{+\bullet}$, 277.1465. $C_{19}H_{19}NO$ requires M, 277.1466); $\nu_{max.}$ 1 950 and 1 670 cm^{-1}; τ 1.87 (dd, J 2, 7.5 Hz, 2 *ortho*-H of PhCO), 2.46—2.89 (m, 8 aryl-H), ABX system, τ_A 5.48, τ_B 5.27, τ_X 4.11 (J_{AB} 11.5, J_{AX} 6.5, J_{BX} 7 Hz, $CH_X{=}C{=}CH_AH_B$), and 7.70 (s, NMe_2).

Dimethyl-(α-phenylphenacyl)-(3-phenylprop-2-ynyl)-ammonium Bromide (23e).—Dimethyl-(α-phenylphenacyl)-amine (12 g) and 3-phenylprop-2-ynyl bromide (10 g) in methyl cyanide (50 ml) gave the *salt* (23e) (18 g, 83%) as a hygroscopic solid, m.p. 147—148 °C (Found: C, 66.8; H, 6.0; N, 3.2; Br, 18.0. $C_{25}H_{24}BrNO{\cdot}H_2O$ requires C, 66.4; H, 5.8; N, 3.1; Br, 17.7%); $\nu_{max.}$ 1 680 cm^{-1}; τ 1.76 (dd, J 2, 7.5 Hz, 2 *ortho*-H of PhCO), 1.82 (s, $COCH\overset{+}{N}$), 2.11—2.75 (m, 13 aryl-H), AB system, τ_A 4.79, τ_B 4.97 (J_{AB} 16 Hz, $C{\equiv}C{-}CH_AH_B\overset{+}{N}$), 6.35 (s, $\overset{+}{N}Me$), and 6.37 (s, $\overset{+}{N}Me$).

Base Catalysed Rearrangement of Dimethyl-(α-phenylphenacyl)-(3-phenylprop-2-ynyl)ammonium Bromide (23e). *Formation of 1,2,5-Triphenylpent-4-yn-1-one* (26), *Dimethyl-[α-phenyl-α-(1-phenylpropa-1,2-dienyl)phenacyl]amine* (24e), *and Dimethyl-[α-phenyl-α-(3-phenylprop-2-ynyl)phenacyl]amine* (25).—Cold (0 °C) aqueous sodium hydroxide (20%, 50 ml) was added to a solution of the salt (23e) (8 g) in aqueous methanol (9%, 1 650 ml) at 0 °C and the solution was kept at this temperature for 12 h. The product was extracted into dichloromethane and the extract washed with water, dried, and evaporated. The residue was purified by chromatography (silica, benzene) to give three products. (*i*) *1,2,5-Triphenylpent-4-yn-1-one* (26) (400 mg, 7%) was obtained as a colourless oil (Found: $M^{+\bullet}$, 310.1351. $C_{23}H_{18}O$ requires M, 310.1358); $\nu_{max.}$ 1 680 cm^{-1}; τ 2.07 (dd, J 2, 7.5 Hz, 2 *ortho*-H of PhCO), 2.66—2.88 (m, 13 aryl-H), ABX system, τ_A 7.12, τ_B 6.79, τ_X 5.20 (J_{AB} 17, J_{AX} 8, J_{BX} 7 Hz, $COCH_X{-}CH_AH_B$). (*ii*) *Dimethyl-[α-phenyl-α(1-phenylpropa-1,2-dienyl)phenacyl]amine* (24e) (1.3 g, 20%) was obtained as an oil (Found: $M^{+\bullet}$, 353.1772. $C_{25}H_{23}NO$ requires M, 353.1780); $\nu_{max.}$ 1 940 and 1 680 cm^{-1}; τ 1.93 (dd, J 2, 7.5 Hz, 2 *ortho*-H of PhCO), 2.53—2.98 (m, 13 aryl-H), 4.85 (s, $C{=}CH_2$), and 7.77 (s, NMe_2). The *picrate* had m.p. 170—172 °C (Found: C, 63.2; H, 4.6; N, 9.1. $C_{31}H_{26}N_4O_8$ requires C, 63.9; H, 4.5; N, 9.6%). (*iii*) *Dimethyl-[α-phenyl-α-(3-phenylprop-2-ynyl)phenacyl]amine* (25) (4 g, 62%) crystallised as prisms, m.p. 111—112 °C from light petroleum (Found: C, 84.9; H, 6.9; N, 3.8%; $M^{+\bullet}$, 353.1772. $C_{25}H_{23}NO$ requires C, 85.0; H, 6.6; N, 4.0%; M, 353.1780); $\nu_{max.}$ 1 670 cm^{-1}; τ 1.94 (dd, J 2, 7.5 Hz, 2 *ortho*-H of PhCO), 2.41—2.86 (m, 13 aryl-H), AB system, τ_A 6.38, τ_B 6.67 (J_{AB} 18 Hz, $C{\equiv}CCH_AH_B$), and 7.42 (s, NMe_2).

Base Catalysed Isomerisation of 4-Dimethylamino-4-methoxycarbonyl-3-phenylbuta-1,2-diene (24b). *Formation of 4-Dimethylamino-4-methoxycarbonyl-3-phenylbuta-1,3-diene* (31a).—(*a*) Sodium methoxide in dimethyl sulphoxide [from the addition of sodium hydride (0.12 g) to methanol (1.5 ml) in dimethyl sulphoxide (5 ml)] was added to a solution of the allene (24b) (2.5 g) in dimethyl sulphoxide (3 ml). After 2 h at room temperature the mixture was poured into water (200 ml) and the product extracted into chloroform (200 ml). The chloroform extract was washed with water, dried, and evaporated to give the conjugated *diene* (31a) (2.5 g) as a brown oil; $\nu_{max.}$ 1 720 and 1 610 cm^{-1}; τ 2.35–2.98 (m, Ph), AMX system, τ_A 3.05, τ_M 4.68, τ_X 5.08 (J_{AM} 10, J_{AX} 18, J_{MX} 2 Hz, $CH_A{=}CH_MH_X$), 6.60 (s, CO_2Me), and 7.25 (s, NMe_2).

(*b*) An identical product was obtained (39% yield) by the reaction of the salt (23b) with sodium methoxide in dimethyl sulphoxide at room temperature for 1.5 h. The diene (31a), from the salt (23b) (6.2 g), was repeatedly extracted from an ethereal solution with hydrochloric acid (2N, 6 × 150 ml). The acidic extract became cloudy on standing and was extracted with ether. The ethereal extract was dried and evaporated to give *methyl 2-oxo-3-phenylpent-3-enoate* (32a) (1.1 g, 40%) as an oil, b.p. 90—93 °C at 0.05 mmHg (Found: C, 70.8; H, 5.9%; $M^{+\bullet}$, 204. $C_{12}H_{12}O_3$ requires C, 70.6; H, 5.9%; M, 204); $\nu_{max.}$ (liquid film) 1 630, 1 680, and 1 735 cm^{-1}; τ 2.30—3.08 (m, Ph), AX_3 system, τ_A 2.86, τ_X 8.09 [J_{AX} 7 Hz, $=CH_AC(H_X)_3$], and 6.09 (s, CO_2Me).

3-Hydroxy-5-methyl-4-phenylfuran-5(2H)-one (33).—A solution of methyl 2-oxo-3-phenylpent-3-enoate (32a) (1.0 g) in methanol (10 ml) and water (5 ml) containing hydrochloric acid (11N, 2 ml) was left overnight at room temperature. The product was extracted into ether to give the *lactone* (33) (0.75 g, 82%) which crystallised from benzene as prisms, m.p. 141—142 °C (Found: C, 69.6; H, 5.6%; $M^{+\bullet}$, 190. $C_{11}H_{10}O_3$ requires C, 69.5; H, 5.3%; M, 190); $\lambda_{max.}$ 287 nm (ε 25 000) (with a shift to longer wavelength on the addition of KOH); $\nu_{max.}$ 3 550 and 1 740 cm^{-1}; τ 2.26—2.75 (m, Ph), AX_3 system, τ_A 4.54, τ_X 8.41 [J_{AX} 7 Hz, $CH_A{-}C(H_X)_3$].

Reaction of 3-Dimethylamino-4-phenylhexa-4,5-dien-2-one (24c) *with Sodium Methoxide. Formation of 5-Hydroxy-5-methyl-2-phenylcyclopent-2-en-1-one* (34).—A solution of sodium methoxide in dimethyl sulphoxide [from sodium hydride (0.25 g), methanol (2 ml), and dimethyl sulphoxide (5 ml)], was added to a solution of the allene (24c) (2.0 g) in dimethyl sulphoxide (8 ml). The mixture was left at room temperature overnight, poured into water (100 ml), and the product extracted with chloroform. The chloroform extract was dried and evaporated to give the *cyclopentenone* (34) as a brown oil (0.86 g, 50%) which was purified by preparative t.l.c. and recrystallisation from hexane to give a sample, m.p. 85—87 °C (Found: C, 76.3; H, 6.3%; $M^{+\bullet}$, 188.0843. $C_{12}H_{12}O_2$ requires C, 76.6; H, 6.4%; M, 188.0837); $\lambda_{max.}$ 226 (ε 16 000) and 265 nm (ε 5 800); $\nu_{max.}$ 3 400 and 1 700 cm^{-1}; τ 2.20—2.42 (m, 2 *ortho*-H of Ph and C=CH), 2.50—2.85 (m, 3 aryl-H), 7.18 (m, CH_2 + OH), and 8.60 (s, Me).

Thermal Reaction of 3-Dimethylamino-4-phenylhexa-4,5-dien-2-one (24c). *Formation of 3-Dimethylamino-2,5-dimethyl-4-phenylfuran* (36).—The allene (24c) was unchanged when refluxed in benzene for 2 h. A solution of the allene in xylene was heated under reflux for 2 h. Evaporation of the solvent gave an unstable brown oil having an n.m.r. spectrum consistent with that expected for the furan derivative (36); τ 2.45—3.15 (m, 5 aryl-H), 7.34 (s, Me), 7.70 (s, NMe_2 and 7.76 (s, Me); the i.r. spectrum showed no bands assignable to carbonyl groups. The product decomposed to a tar on standing.

(9-Fluorenyl)dimethyl-(3-phenylprop-2-ynyl)ammonium Bromide (27).—9-Bromofluorene (10.0 g) and dimethyl-(3-phenylprop-2-ynyl)amine (6.1 g) in ether gave the *salt* (27) (11.4 g, 73%), m.p. 98–102 °C (Found : C, 70.1; H, 5.5; N, 3.2; Br, 19.2. $C_{24}H_{22}BrN{\cdot}0.5\ H_2O$ requires C, 69.7; H, 5.7; N, 3.4; Br, 19.3%); $\nu_{max.}$ 2 250 and 1 605 cm^{-1}; τ 2.03—

2.85 (m, 13 aromatic H), 3.74 (s, 9-H), 4.91 (s, CH_2-C≡C), and 7.60 (s, $\overset{+}{N}Me_2$).

Rearrangement of (9-*Fluorenyl*)*dimethyl*-(3-*phenylprop*-2-*ynyl*)*ammonium Bromide* (27). *Formation of* 9-*Dimethylamino*-9-(1-*phenylpropa*-1,2-*dienyl*)*fluorene* (28).—Methanolic sodium methoxide [prepared from sodium (0.46 g) and methanol (10 ml)] was added to a solution of the salt (27) (4.04 g) in methanol (20 ml) and the mixture refluxed for 20 min. The solution was cooled, poured into water (100 ml), and the product extracted with ether. The ethereal extract was dried and evaporated to give an orange solid (3.09 g, 95%) which was recrystallised from hexane to give the pure *allene* (28) (1.0 g, 30%) as prisms, m.p. 128—129 °C (Found: C, 88.9; H, 6.55; N, 4.1%; $M^{+\bullet}$, 323. $C_{24}H_{21}N$ requires C, 89.1; H, 6.55; N, 4.3%; *M*, 323); $\lambda_{max.}$ 273 infl. (ε 18 000), 298 infl. (6 100), and 309 nm (4 400); $\nu_{max.}$ 1 950 and 1 600 cm^{-1}; τ 2.26—3.00 (m, 13 aryl-H), 5.04 (s, C=CH_2), and 7.76 (s, NMe_2). Hydrogenation of the allene (28) (Pt catalyst, ethyl acetate, 1 atm H_2) gave 9-*dimethylamino*-9-(1-*phenylprop*-1-*enyl*)*fluorene* (40) which crystallised from hexane as prisms, m.p. 114—116 °C (Found: C, 88.1; H, 7.1; N, 4.2%; $M^{+\bullet}$, 325. $C_{24}H_{23}N$ requires C, 88.6; H, 7.1; N, 4.3%; *M*, 325); $\lambda_{max.}$ 272 (ε 15 000), 300 infl. (5 700), and 312 nm (4 600); $\nu_{max.}$ 1 600 cm^{-1}; τ 2.38—3.52 (m, 13 aryl-H), AX_3 system, τ_A 4.13, τ_X 7.55 [J_{AX} 7 Hz, C=$CH_AC(H_X)_3$], and 7.93 (s, NMe_2).

Thermal Rearrangement of 9-*Dimethylamino*-9-(1-*phenylpropa*-1,2-*dienyl*)*fluorene* (28). *Formation of* 2-*Dimethylamino*-3-(9-*fluorenylidene*)-3-*phenylpropene* (37).—The allene (28) (2.0 g) in benzene (40 ml) was refluxed for 8 h. Evaporation of the solvent gave the *fluorenylidenepropene* (37) (100%) as a yellow solid, m.p. 147—150 °C, which darkened on standing or recrystallisation from hexane (Found: $M^{+\bullet}$, 323. $C_{24}H_{21}N$ requires *M*, 323); $\lambda_{max.}$ 209 (ε 27 000), 230 (30 000), and 260 nm (22 000); $\nu_{max.}$ 1 560, 1 580, and 1 602 cm^{-1}; τ 2.30—2.98 (m, 11 aryl-H), 3.13 (td, *J* 7.5, 1.5 Hz, fluorenyl 2′-H), 3.44 (d, *J* 7.5 Hz, fluorenyl 1′-H), 5.94 (s, C=CH), 6.04 (s, C=CH), and 7.26 (s, NMe_2). This product was further characterised by reduction. Hydrogenation of (37) (Pt catalyst, ethyl acetate, 1 atm H_2) gave 9-[2-*dimethylamino*-1-*phenylpropylidene*)*fluorene* (38) which crystallised from hexane as prisms, m.p. 89—93 °C (32%) (Found: $M^{+\bullet}$, 325.1832. $C_{24}H_{23}N$ requires *M*, 325.1830); $\nu_{max.}$ 1 595 and 1 615 cm^{-1}; τ 2.20—2.98 (m, 11 aryl-H), 3.24 (td, *J* 8, 1.5 Hz, fluorenyl 2′-H), 4.20 (d, *J* 8 Hz, fluorenyl 1′-H), AX_3 system, τ_A 5.62, τ_X 8.70 [J_{AX} 7 Hz, $CH_AC(H_X)_3$], and 7.66 (s, NMe_2). Reduction of (37) with zinc dust–sulphuric acid (2N) at room temperature for 24 h gave 9-(1-*phenyl*-2-*oxopropyl*)*fluorene* (39) which crystallised from hexane as prisms, m.p. 125—126 °C (78%) (Found: C, 88.8; H, 5.9%; $M^{+\bullet}$, 298. $C_{22}H_{18}O$ requires C, 88.6; H, 6.1%; *M*, 298); $\lambda_{max.}$ 267 (ε 25 000), 276 infl. (18 000), 293 (6 900), and 304 nm (8 000); $\nu_{max.}$ 1 710 and 1 603 cm^{-1}; τ 2.22—2.96 (m, 11 aryl-H), 3.14 (td, *J* 7.5, 1.3 Hz, fluorenyl 2′-H), 3.78 (d, *J* 7.5 Hz, fluorenyl 1′-H), AB system, τ_A 5.20, τ_B 6.38 (J_{AB} 10 Hz, CH_A–CH_B), and 7.94 (s, COMe).

Benzhydryl(*dimethyl*)-(3-*phenylprop*-2-*ynyl*)*ammonium Bromide* (29).—3-Phenylprop-2-ynyl bromide (1.3 g) and benzhydryl(dimethyl)amine (1.3 g) in ether (5 ml) gave the salt (29) as a very hygroscopic crystalline solid; τ 1.87—2.84 (m, 15 aryl-H), 2.88 (s, $\overset{+}{N}CH$), 5.14 (s, $\overset{+}{N}CH_2$), and 6.55 (s, $\overset{+}{N}Me_2$). The salt was rearranged without further purification.

Base Catalysed Rearrangement of Benzhydryl(*dimethyl*)-(3-*phenylprop*-2-*ynyl*)*ammonium Bromide* (29). *Formation of* 3-*Dimethylamino*-1,4,4-*triphenylbut*-1-*yne* (30).—The salt (29) (0.41 g) was left in methanolic sodium methoxide, prepared from sodium (0.1 g) and methanol (5 ml), at 0 °C for 2 days. The crystalline product was collected by filtration and washed with methanol to give the *amine* (30) (0.15 g, 46%), which crystallised from methanol as prisms, m.p. 162—163 °C (Found: $M^{+\bullet}$, 325. $C_{24}H_{23}N$ requires *M*, 325); $\lambda_{max.}$ 207 (ε 25 000), 244 (10 000), and 255 nm (8 900); $\nu_{max.}$ 1 600 cm^{-1}; τ 2.56—2.88 (m, 15 aryl-H), AB system, τ_A 5.66, τ_B 5.82 (J_{AB} 11 Hz, CH_A–CH_B), and 7.69 (s, NMe_2). The *methiodide* had m.p. 190—191 °C (Found: C, 64.0; H, 5.7; N, 3.0. $C_{25}H_{26}IN$ requires C, 64.3; H, 5.6; N, 3.0%); τ 2.14—2.95 (m, 15 aryl-H), AB system, τ_A 3.78, τ_B 5.10 (J_{AB} 7 Hz, CH_A–CH_B), and 6.50 (s, $\overset{+}{N}Me_3$).

2-*Methyl*-2-(3-*phenylprop*-2-*ynyl*)-4-*oxo*-1,2,3,4-*tetrahydroisoquinolinium Bromide* (48).—3-Phenylprop-2-ynyl bromide and 2-methyl-2,3-dihydro-1*H*-4-isoquinolone in methyl cyanide gave the *salt* (48) (82%), m.p. 161—163 °C (Found: C, 62.5; H, 5.6; N, 3.6; Br, 21.9. $C_{19}H_{18}BrNO{\cdot}0.5H_2O$ requires C, 62.5; H, 5.2; N, 3.8; Br, 21.9%); $\nu_{max.}$ 2 220 and 1 690 cm^{-1}; τ (CF_3CO_2H) 1.73—2.78 (m, 9 aryl-H), AB system, τ_A 4.65, τ_B 4.92 (J_{AB} 15 Hz, $\overset{+}{N}CH_AH_BAr$), AB system, τ_A 5.10, τ_B 5.34 (J_{AB} 16.5 Hz, $\overset{+}{N}CH_AH_BCO$), 5.21 (s, C≡CCH_2), and 6.44 (s, $\overset{+}{N}Me$).

Base Catalysed Rearrangement of 2-*Methyl*-2-(3-*phenylprop*-2-*ynyl*)-4-*oxo*-1,2,3,4-*tetrahydroisoquinolinium Bromide* (48). *Formation of* 2-*methyl*-3-(1-*phenylpropa*-1,2-*dienyl*)-2,3-*dihydro*-1H-4-*isoquinolone* (49).—The salt (48) (500 mg) was stirred with dimethyl sulphoxide (4 ml) and sodium hydride (100 mg) at room temperature for 10 h. Excess of sodium hydride was decomposed by the addition of wet ether and the product was extracted into ether. The ethereal extract was dried and evaporated to give the *allene* (49) (330 mg, 86%) as a yellow oil (Found: $M^{+\bullet}$, 275.1303. $C_{19}H_{17}NO$ requires *M*, 275.1310); $\nu_{max.}$ 1 940 and 1 680 cm^{-1}; τ 1.95—2.87 (m, 9 aryl-H), 5.01 (s, C=C=CH_2), AB system, τ_A 5.77, τ_B 6.35 (J_{AB} 15 Hz, $ArCH_AH_BN$), 5.89 (br s, NCHCO), and 7.52 (s, NMe). The product was unstable and decomposed during attempted crystallisation.

1-(3-*Phenylprop*-2-*ynyl*)-1-*azoniabicyclo*[2.2.2]*octan*-3-*one Bromide* (50).—3-Phenylprop-2-ynyl bromide and 3-quinuclidone in methyl cyanide gave the *salt* (50) (90%) as plates, m.p. 236—238 °C (decomp.) after crystallisation from ethanol (Found: C, 59.8; H, 5.9; N, 4.3; Br, 25.1. $C_{16}H_{18}BrNO$ requires C, 60.0; H, 5.6; N, 4.4; Br, 25.0%); $\nu_{max.}$ 1 740 cm^{-1}; τ (CF_3CO_2H) 2.48—2.72 (m, 5 aryl-H), 5.42 (s, $\overset{+}{N}CH_2$-C≡C), 5.54 (s, $\overset{+}{N}CH_2CO$), 5.97–6.12 (m, $CH_2\overset{+}{N}CH_2$), 6.96—7.02 (m, CHCO), and 7.48—7.57 (m, CH_2–C–CH_2). The reaction of the salt (50) with sodium hydride in dimethyl sulphoxide at 80—90 °C for 12 h gave a complex mixture of products which was not further examined.

1-(3-*Phenylprop*-2-*ynyl*)-1-*azoniabicyclo*[3.2.1]*octan*-6-*one Bromide* (52).—3-Phenylprop-2-ynyl bromide and 1-azabicyclo[3.2.1]octan-6-one in methyl cyanide gave the *salt* (52) (88%) as plates, m.p. 206—208 °C after crystallisation from ethanol (Found: C, 59.9; H, 5.8; N, 4.4; Br, 25.3. $C_{16}H_{18}BrNO$ requires C, 60.0; H, 5.6; N, 4.4; Br, 25.0%); $\nu_{max.}$ 2 240 and 1 770 cm^{-1}; τ (CF_3CO_2H) 2.42—2.68 (m, 5 aryl-H), 5.25 (s, $NCH_2C{\equiv}C$), AB system, τ_A 5.46, τ_B 5.72 (J_{AB} 18 Hz,

$\overset{+}{N}CH_AH_BCO$), 5.62—5.98 (m, $CH_2\overset{+}{N}CH_2$), 6.74—6.78 (m, CH), and 7.79 (m, CH_2CH_2).

Base Catalysed Rearrangement of 1-(3-*Phenylprop*-2-*ynyl*)-1-*azoniabicyclo*[3.2.1]*octan*-6-*one Bromide* (52). *Formation of* cis- *and* trans-7-(1-*Phenylprop*-2-*enylidene*)-1-*azabicyclo*-[3.2.1]*octan*-6-*one*, (53) *and* (54).—A mixture of the salt (52) (600 mg) and sodium hydride (100 mg) in dimethyl sulphoxide (5 ml) was stirred at room temperature for 12 h (N_2 atmosphere). Excess of sodium hydride was decomposed by the addition of wet ether and the products were extracted into ether. The extract was dried and evaporated to give a mixture of two compounds which were separated by preparative t.l.c. (silica gel, light petroleum–ethyl acetate). The faster-running component crystallised from light petroleum as yellow rhombs, m.p. 151—152.5 °C, and was shown to be the Z-*dienone* (54) (170 mg, 38%) (Found: C, 80.1; H, 7.3; N, 5.7%; $M^{+\bullet}$, 239. $C_{16}H_{17}NO$ requires C, 80.3; H, 7.1; N, 5.9%; *M*, 239); $\nu_{max.}$ 1 700, 1 600, and 1 575 cm^{-1}; τ 2.65—2.92 (m, 5 aryl-H), ABX system, τ_A 5.04, τ_B 4.69, τ_X 1.91 (J_{AB} 2, J_{AX} 17, J_{BX} 10.5 Hz, $CH_X{=}CH_AH_B$), 6.68—7.27 (m, CH_2NCH_2), 7.53—7.58 (m, CH), and 8.10—8.68 (m, CH_2CH_2). The slower-running component crystallised from light petroleum as pale yellow rhombs, m.p. 104.5 °C, and was shown to be the E-*dienone* (53) (170 mg, 38%) (Found: C, 80.0; H, 7.2; N, 5.7%; $M^{+\bullet}$, 239); $\nu_{max.}$ 1 700, 1 595, and 1575 cm^{-1}; τ 2.66—2.99 (m, 5 aryl-H), ABX system, τ_A 4.98, τ_B 4.53, τ_X 2.87 (J_{AB} 1.5 Hz, J_{AX} 17, J_{BX} 10.5 Hz, $CH_X{=}CH_AH_B$), 6.70—7.07 (m, CH_2NCH_2), 7.68—7.72 (m, CH), and 8.05—8.61 (m, CH_2CH_2).

Base Catalysed Rearrangement of 1-(3-*Phenylprop*-2-*ynyl*)-1-*azoniabicyclo*[3.2.1]*octan*-6-*one Bromide* (52). *Formation of* 7-(1-*Phenylprop*-1,2-*dienyl*)-1-*azabicyclo*[3.2.1]*octan*-6-*one* (55).—A mixture of the salt (52) (500 mg), dimethyl sulphoxide (5 ml), anhydrous ether (10 ml), and sodium hydride (80 mg) was stirred at room temperature for 15 min (N_2 atmosphere). The ether layer was separated, washed with water, dried, and evaporated and the residual solid crystallised from light petroleum to give the *allene* (55) (157 mg, 42%) as pale yellow prisms, m.p. 106 °C (Found: C, 80.4; H, 7.4; N, 6.1%; $M^{+\bullet}$, 239. $C_{16}H_{17}NO$ requires C, 80.3; H, 7.1; N, 5.9%; *M*, 239); $\nu_{max.}$ 1 945 and 1745 cm^{-1}; τ 2.57—2.89 (m, 5 aryl-H), ABX system, τ_A 4.90, τ_B 4.94, τ_X 5.99 (J_{AB} 13.5, $J_{AX}{=}J_{BX}$ = 2.5 Hz, $CH_X{-}CPh{=}C{=}CH_AH_B$), 6.42—7.18 (m, CH_2NCH_2), 7.71—7.78 (m, CH), and 8.08—8.60 (m, CH_2CH_2).

Base Catalysed Rearrangement of 1-(3-*Phenylprop*-2-*ynyl*)-1-*azoniabicyclo*[3.3.1]*nonan*-3-*one Bromide* (56).—(a) *With aqueous sodium hydroxide. Formation of* 2-(1-*phenylpropa*-1,2-*dienyl*)-1-*azabicyclo*[3.3.1]*nonan*-3-*one* (58). An excess of aqueous sodium hydroxide (50%, 5 ml) was added to a stirred, cold solution of the salt (56) [5b] (1.0 g) in water (5 ml). The reaction mixture was left at room temperature for 10 min and the products extracted into chloroform. The chloroform extract was dried and evaporated to give a brown solid which was extracted with ether. The ether-soluble material crystallised from light petroleum to give the *allene* (58) (200 mg, 26%) as pale yellow crystals, m.p. 138—139.5 °C (Found: C, 80.5; H, 7.8; N, 5.3%; $M^{+\bullet}$, 253. $C_{17}H_{19}NO$ requires C, 80.6; H, 7.5; N, 5.5%; *M*, 253); $\nu_{max.}$ 1 950 and 1 700 cm^{-1}; τ 2.70—2.82 (m, 5 aryl-H), 4.88 (d, *J* 3 Hz, $C{=}C{=}CH_2$), 5.73 (br s, $-CH{-}CPh{=}C$), AB system, τ_A 6.65, τ_B 7.23 (AB system, J_{AB} 14 Hz, NCH_2), 6.84—7.64 (m, NCH_2CH_2 and CH_2CO), 7.79 (m, CH), and 8.19—8.78 (m, CH_2CH_2).

(b) *With sodium hydride in dimethyl sulphoxide. Formation of* 4-*methyl*-3-*phenyl*-5-*oxa*-1-*azatricyclo*[6.3.1.$0^{2,6}$]*dodeca*-2(6),3-*diene* (57).—A mixture of the salt (56) (1.0 g) and sodium hydride (150 mg) in dimethyl sulphoxide (5 ml) was stirred at room temperature for 12 h. Excess of hydride was destroyed by the addition of wet ether followed by water (10 ml). The mixture was extracted with ether and the ether solution dried and evaporated to give the *derivative* (57) (750 mg, 99%) as yellow crystals, m.p. 67—68 °C. Crystallisation from light petroleum gave yellow prisms, m.p. 68 °C (Found: C, 80.6; H, 7.7; N, 5.6%; $M^{+\bullet}$, 253. $C_{17}H_{19}NO$ requires C, 80.6; H, 7.5; N, 5.5%; *M*, 253); $\nu_{max.}$ 1 600 cm^{-1}; τ 2.38—2.77 (m, 5 aryl-H), 6.81—7.43 (m, $CH_2C{=}$ and CH_2NCH_2), 7.59 (s, Me), 7.82—7.93 (m, CH), 8.19—8.94 (m, CH_2CH_2). The furan (57) was obtained (74% yield) by stirring a mixture of the allene (58) (200 mg) and sodium hydride (50 mg) in dimethyl sulphoxide (5 ml) at room temperature for 4 h.

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