Base Catalysed Rearrangements Involving Ylide Intermediates. Part 10.† The Effects of Torsional Strain in the Transition State upon [1,2] and [3,2] Rearrangements

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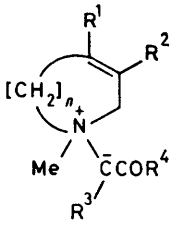
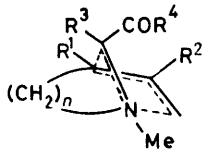
The [3,2] and [1,2] sigmatropic rearrangements of the bicyclic ammonium ylides (8), (11), and (14) are inhibited by the bicyclic framework which prevents correct orbital alignment for π-bonding in the transition state for a concerted [3,2] sigmatropic rearrangement or in the vinylogous nitroxide component of the radical pair required as an intermediate in a [1,2] sigmatropic rearrangement. The ylides (14a) and (14d), based upon the 1-azabicyclo-[3.3.1]nonane system, are the only bicyclic allylic ylides which undergo a clean [3,2] rearrangement, which involves the *exo*-transition state either exclusively (14a) or predominantly (14d).

In previous papers [1,2] of this series, the symmetry-allowed [3,2] sigmatropic rearrangement of allylic ammonium ylides has been shown to be a fast reaction at room temperature and acyclic allylic ylides are not normally isolable. In the preceding paper [3] the isolation of the



(1)



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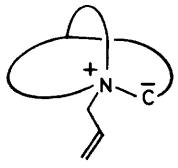

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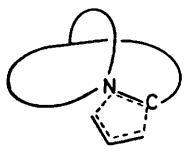

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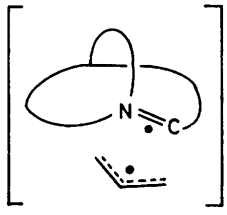


(5) ‡

allylic ammonium ylides (1) was described and in these cases the unfavourable geometry of the required [1,2,*n*] bicyclic transition states (2) significantly inhibited the [3,2] rearrangement. It was anticipated that the incorporation of the $\geq\overset{+}{N}-\overset{-}{C}<$ moiety of an allylic ammonium ylide into a position adjacent to the bridgehead of a bicyclic system, as in (3), would also inhibit a [3,2] rearrangement because of the well known difficulty associated with bridgehead π-bonding [4] in certain bicyclic systems. Thus the transition state (4) for the concerted [3,2] sigmatropic rearrangement of the allylic ammonium ylide (3) would involve a similar unfavourable situation for some of the π-bonding required [5] for a pericyclic transition state. By analogy with the reported stabilities [6-8] of various bridgehead bicyclic olefins this inhibition of the [3,2] rearrangement was expected to be most marked for systems where the corresponding bridgehead olefin is highly strained.

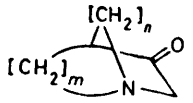
The alternative rearrangement mode for ammonium ylides is a [1,2] Stevens rearrangement, now believed to involve a radical-pair mechanism,[9] which in the case of the ylide (3) would involve the formation of the radical pair (5). The allylic component of this radical pair can achieve full resonance-stabilisation but stabilisation of the other component of the radical pair would require the π-bonding to the bridgehead nitrogen atom shown in (5).‡ Thus the geometrical restraints imposed by the bicyclic system of (3) would inhibit both the [3,2] and [1,2] rearrangement modes.

RESULTS AND DISCUSSION

The [2.2.2] bicyclic system was first examined; evidence has been reported [6] for the transient existence of bicyclo[2.2.2]oct-1-ene, but in this case the angle of twist between the adjacent *p*-orbitals of a double bond would be 90°. The aminoketone (6) was quaternised with cinnamyl bromide and benzyl bromide to give the quaternary salts (7) which were converted into the corresponding non-crystalline ylides (8) using aqueous sodium hydroxide.[10] The ylides (8) both decomposed on heating to give complex mixtures of unidentified products and we conclude that the extreme lack of orbital alignment in the transition state (4) and radical pair (5) in this system severely inhibits both the [3,2] and the [1,2] rearrangement. The [3.2.1] system was next examined since the corresponding olefin, bicyclo[3.2.1]-oct-1(7)-ene, has been reported [7] as a transient species

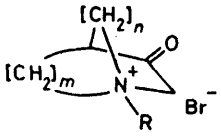
† Part 9 is the preceding paper.

‡ The $\geq\dot{\overset{\cdot\cdot}{N}}-\dot{C}<$ system is represented as shown to emphasise the π-bonding between the two centres.



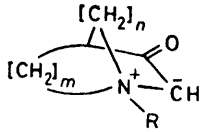
(6) $m = n = 2$

(9) $m = 3, n = 1$



(7) $m = n = 2$

(10) $m = 3, n = 1$

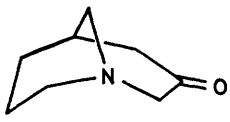


(8) $m = n = 2$

(11) $m = 3, n = 1$

a; R = (*E*)-$CH_2CH{=}CHPh$; b; R = CH_2Ph

and molecular models suggest an angle of *ca.* 60° between the adjacent *p*-orbitals of the double bond.* The aminoketone (9) was therefore quaternised with cinnamyl bromide to give the salt (10a) which yielded the ylide (11a) on treatment with aqueous sodium hydroxide.



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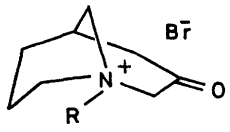

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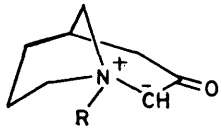


(14)

a; R = (*E*)-$CH_2CH{=}CHPh$; b; R = CH_2Ph;

c; R = $CH_2C{\equiv}CPh$; d; R = (*Z*)-$CH_2CH{=}CHPh$

The ylide (11a) was characterised by its i.r. spectrum [10] ($\nu_{max.}$ 1 580 cm^{-1}) and regeneration of the quaternary salt (10a) by reaction with hydrobromic acid. In spite of the decrease in the torsional inhibition of π-bonding in the transition state (4) for the [3.2.1] bicyclic system (11a) as compared with the [2.2.2] system (8a), the ylide (11a) failed to undergo a [3,2] rearrangement and above 80 °C gave only a complex mixture of unidentified reaction products.

The failure to observe rearrangements in these two bicyclic systems directed our attention to the [3.3.1] system since bicyclo[3.3.1]non-1-ene has been reported as an isolable, but highly reactive, olefin, and molecular models indicate an angle of *ca.* 30° between adjacent *p*-orbitals of the double bond.*

* These measurements are only of qualitative significance; molecular mechanics calculations for bridgehead olefins have been carried out (ref. 11) and they indicate that strain energy decreases in the series bicyclo[2.2.1]oct-1-ene > bicyclo[3.2.1]oct-1(7)-ene > bicyclo[3.3.1]non-1-ene.

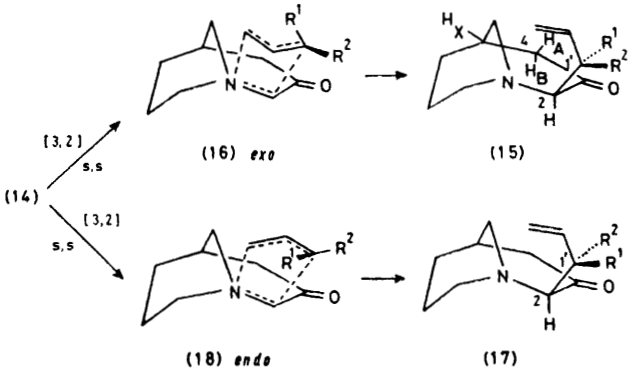
Thus the aminoketone (12) was converted into the cinnamyl and benzyl salts (13); these salts yielded the ylides (14) on treatment with aqueous sodium hydroxide. The ylides (14) were characterised by their i.r. spectra ($\nu_{max.}$ 1 575 cm^{-1}) and regeneration of the quaternary salts (13) by reaction with hydrobromic acid. The *N*-cinnamyl ylide (14a) rearranged cleanly on heating, either alone in a sealed tube at 120 °C for 5 min or in chloroform solution at 60 °C for 5 h, to give a good yield of a single diastereoisomer of the [3,2] rearrangement product (15a). The relative configuration of the chiral centres in (15a) is that expected from a suprafacial–suprafacial rearrangement involving the *exo*-transition state † (16) which appears to be significantly less sterically crowded than the *endo*-transition state (18) in a [3,2] rearrangement involving a bicyclic allylic ylide of the type (14). The n.m.r. spectrum of (15a), in the presence of $Eu(fod)_3$, was readily analysed and in particular the coupling constants (J_{AX} 6.5 Hz and $J_{BX} < 1$ Hz) for the ABX system indicated in the structural formula (15a) suggested a flattened conformation for the six-membered ring with the torsion angle H_X–C–C–H_B close to 90°. The coupling constant between $\overset{+}{N}H$ and C-2-H in the spectrum of a solution of (15a) in trifluoroacetic acid was also found to be <1 Hz, in agreement with the configuration at C-2 shown in (15).

The 1′-phenylallyl substituent at C-2 thus occupies the less hindered position *cis* to the one-atom bridge and in accord with this assignment the base-catalysed (NaOMe in MeOD) equilibration of (15a) did not produce a detectable quantity of a second diastereoisomer, although deuteriation occurred at both C-2 and C-4 during the attempted equilibration.

The stereoselective transformation (14a) ⟶ (15a), involving the *exo*-transition state for the [3,2] rearrangement, suggested that the corresponding ylide having a *cis*-cinnamyl substituent should also be examined (*cf.* ref. 3). The salt (13c) was hydrogenated to give the *cis*-cinnamyl salt (13d) and treatment of (13d) with aqueous sodium hydroxide gave the corresponding ylide (14d) ($\nu_{max.}$ 1 575 cm^{-1}). The thermal rearrangement of the ylide (14d) at 120 °C for 5 min gave a mixture of [3,2] rearrangement products, which could not be

† The terms *exo* and *endo* are used as in refs. 1 and 3 and refer to the relationship between the allylic residue and the carbonyl group.

separated, identified as a 2 : 1 mixture of the diastereoisomers (17a ≡ 15b) and (17b ≡ 15a). This identification was based upon the n.m.r. spectrum of the mixture which clearly showed signals assignable to the >CHCHPhCH=CH_2 moiety of two isomers, the minor isomer (17b) being identical with the product (15a) obtained from the *trans*-cinnamyl ylide (14a). Equilibration of the mixture of isomers (NaOMe in MeOD) did not change their ratio, indicating that the products were related as C-1′, rather than C-2, epimers. The major reaction product from the *cis*-cinnamyl ylide (14d) is therefore the aminoketone (15b ≡ 17a) which is the result of an *exo*-[3,2] rearrangement and the minor product (17b ≡ 15a) results from an *endo*-[3,2] rearrangement. The *exo* preference shown in these rearrangements is presumably the result of steric interactions between the migrating group and the bicyclic system that are unavoidable in the *endo*-transition state (18). This contrasts with the situation reported in the preceding paper of this series [3] where steric restraints of a different type lead to a preference for

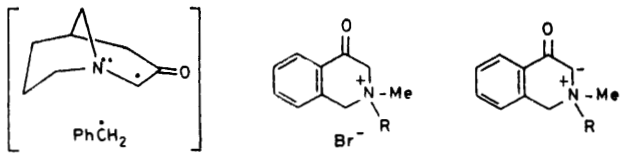


a; R^1 = H; R^2 = Ph; b; R^1 = Ph; R^2 = H

the *endo*-transition state (2). However, in general for acyclic [3,2] rearrangements [1,3,12] there is no dominating tendency for the reaction to follow either the *exo* or *endo* pathways.

The benzylammonium ylide (14b) failed to rearrange cleanly on heating and decomposed to give a complex mixture of unidentified products. Thus the geometrical restraints imposed by the [3.3.1] bicyclic system of (14b) do not permit homolysis to give the radical pair (19) required [9] as an intermediate in a Stevens [1,2] rearrangement. In particular full resonance-stabilisation of the >N̈–ĊH–Ċ=O system is prevented * by the unfavourable torsional situation about the N̈–ĊH bond. The prevention of [1,2] rearrangements by steric inhibition of resonance stabilisation of one of the participating radicals has been noted in an earlier paper of this series.[10]

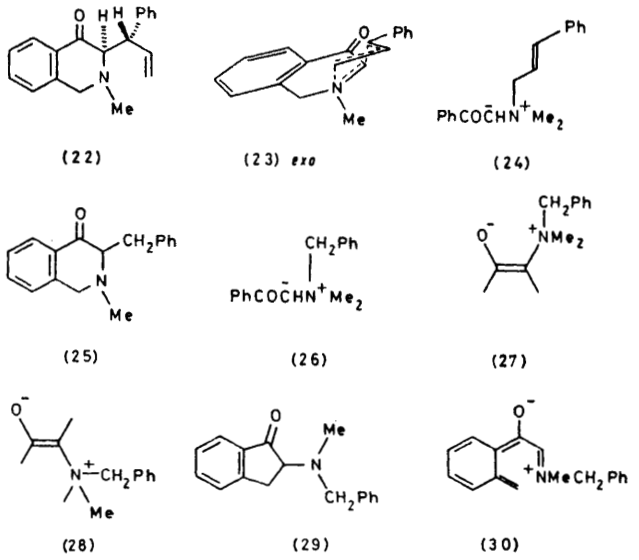
The extent to which the [3,2] rearrangement of (14a and d) is inhibited by the bicyclic system may be judged from experiments with the related ylide (21a). Thus treatment of an aqueous solution of the quaternary salt (20a) with aqueous sodium hydroxide at 0 °C, or methanolic sodium methoxide at −50 °C, gave the [3,2] rearrangement product (22). This difference in reaction temperature of >100 °C for the ylide (21a) as compared with the ylide (14a) underlines the degree to which the unfavourable orbital alignment in (16a) inhibits the



a; R = (E) - CH_2CH=CHPh; b; R = CH_2Ph

rearrangement; unfortunately it is not possible to put this difference on a more quantitative basis. The rearrangement product (22) was obtained as a single diastereoisomer in high yield (88%); on steric grounds the *exo*-transition state (23) would be preferred to the *endo*-transition state and the product (22) is therefore assigned the relative configuration that would result from the transition state (23). A strong preference for an *exo*-transition state is also shown [3] by the [3,2] rearrangement of the analogous acyclic ylide (24).

The benzylammonium salt (20b) was expected to yield a stable ylide (21b), by analogy with the formation of the stable ylide (26),[10] but when the salt (20b) was treated with aqueous sodium hydroxide at 5 °C the product (25)



of a Stevens [1,2] rearrangement was obtained. This instability of the ylide (21b) as compared with the ylide (26) is presumably a consequence of the additional stabilisation afforded to acyclic ylides, such as (26), by the maximised electrostatic attraction in the *cisoid* conformation (27), the ylide (21b) being forced to adopt

* This system, which is involved in all [1,2] Stevens rearrangements of acyl stabilised ammonium ylides, may be regarded as a vinylogue of the nitroxide [13] radical.

the *transoid* conformation (28) with a greater separation between the N^+ and O^- centres. The assignment of the structure (25) to the [1,2] rearrangement product rather than the alternative structure (29), also formed by migration of a benzylic centre, is supported by the i.r. spectrum of the product (25) ($\nu_{max.}$ 1 680 cm^{-1}) which is characteristic of an aryl-substituted ketonic carbonyl group in a six-membered ring, as in (25), rather than in a five-membered ring, as in (29). This is not unexpected in view of the ability of (21b) to adopt the conformation in which the breaking $\overset{+}{N}-CH_2Ar$ bond is correctly aligned for the formation of two fully conjugated radicals only if the homolysis involves an exocyclic bond. The alternative reaction mode, (21b) ⟶ (30) ⟶ (29), is formally a sequence of allowed electrocyclic reactions [5] but this allowed reaction pathway evidently does not compete successfully with the non-allowed pathway (21b) ⟶ (25).

EXPERIMENTAL

For general directions see Part 1.[1]

1-*Cinnamyl*-1-*azoniabicyclo*[2.2.2]*octan*-3-*one* *Bromide* (7a).—An excess of aqueous sodium hydroxide (50%) was added to a solution of 3-quinuclidone hydrochloride [14] (1 g) in water (10 ml) and the liberated amine extracted into ether. The extract was dried and evaporated and the residual solid treated with cinnamyl bromide (1.25 g) in methyl cyanide (8 ml). The precipitated quaternary salt was collected and recrystallised from ethanol to give the *salt* (7a) (91%), m.p. 217 °C (Found: C, 59.6; H, 6.3; N, 4.3; Br, 25.0. $C_{16}H_{20}BrNO$ *requires* C, 59.6; H, 6.2; N, 4.4; Br, 24.8%); $\nu_{max.}$ 1 740 cm^{-1}; τ (CF_3CO_2H) 2.38—2.66 (m, 5 aryl-H), ABX_2 system, τ_A 2.95, τ_B 3.70, τ_X 5.68 [J_{AB} 16, J_{BX} 7 Hz, $\overset{+}{N}C(H_X)_2CH_B{=}CH_APh$], 5.75 (br s, $\overset{+}{N}CH_2CO$), 6.10—6.39 (m, $CH_2\overset{+}{N}CH_2$), 7.00 (br s, CHCO), and 7.37—7.92 (m, 2 × CH_2).

1-*Benzyl*-1-*azoniabicyclo*[2.2.2]*octan*-3-*one Bromide* (7b).—This was prepared using a similar method (83%). The *salt* (7b) had m.p. 232—233 °C after crystallisation from ethanol (Found: C, 57.0; H, 6.2; N, 4.8; Br, 27.3. $C_{14}H_{18}BrNO$ requires C,56.8; H, 6.1; N, 4.7; Br, 27.0%); $\nu_{max.}$ (KBr) 1 740 cm^{-1}; τ (CF_3CO_2H) 2.46 (s, 5 aryl-H), 5.29 (s, $\overset{+}{N}CH_2$-Ph), 5.71 (s, $\overset{+}{N}CH_2CO$), 6.00—6.30 (m, $CH_2\overset{+}{N}CH_2$), 6.91—7.06 (m, CH_2CHCO), and 7.28—7.80 (m, 2 × CH_2).

1-*Cinnamyl*-3-*oxo*-1-*azoniabicyclo*[2.2.2]*octan*-2-*ide* (8a).—Excess of aqueous sodium hydroxide (50%) was slowly added to a solution of the salt (7a) (2.0 g) in water (60 ml). The reaction mixture was extracted with chloroform and the extract dried and evaporated to give the *ylide* (8a) (1.2 g, 81%) as a gum; $\nu_{max.}$ 1 580 cm^{-1}; τ (CD_3OD) 2.41—2.79 (m, 5 aryl-H), ABX_2 system, τ_A 2.96, τ_B 3.53, τ_X 5.62 [J_{AB} 16, J_{BX} 7 Hz, $\overset{+}{N}C(H_X)_2CH_B{=}CH_APh$], 3.73 (br s, $\overset{+}{N}\bar{C}HCO$), 6.20—7.03 (m, $CH_2\overset{+}{N}CH_2$), and 7.65—8.50 (m ,2 × CH_2 and CH). Treatment of the ylide (8a) with hydrobromic acid regenerated the quaternary salt (7a). Pyrolysis of the ylide (8a) at 140 °C (N_2 atmosphere) gave a brown gum from which no pure compounds could be isolated.

1-*Benzyl*-3-*oxo*-1-*azoniabicyclo*[2.2.2]*octan*-2-*ide* (8b).—A solution of the salt (7b) (1.0 g) in water (3 ml) was treated with excess of aqueous sodium hydroxide (2 ml, 50%) at 0 °C. The aqueous layer was decanted leaving the ylide (8b) as a colourless gum which was dissolved in chloroform (30 ml). The solution was dried and evaporated to give the *ylide* (8b) (445 mg, 62%) as a hygroscopic gum; $\nu_{max.}$ 1 580 cm^{-1}; τ (CD_3OD) 2.48 (s, 5 aryl-H), 5.54 (s, $\overset{+}{N}CH_2Ph$), 6.32—6.90 (m, $CH_2\overset{+}{N}CH_2$ + $\overset{+}{N}\bar{C}HCO$), and 7.65—8.42 (m, 2 × CH_2 and CH). Treatment of the ylide with aqueous hydrobromic acid and evaporation of the resulting solution regenerated the quaternary salt (7b). Pyrolysis of the ylide (8b) at 160—180 °C (N_2 atmosphere) yielded a complex mixture of products which could not be separated.

1-*Cinnamyl*-1-*azoniabicyclo*[3.2.1]*octan*-6-*one* *Bromide* (10a).—1-Azabicyclo[3.2.1]octan-6-one was obtained as a pale yellow solid by treating the corresponding hydrochloride [14] with an excess of aqueous sodium hydroxide (50%). The keto-amine (1.0 g) was treated with cinnamyl bromide (1.6 g) in methyl cyanide (10 ml) to give the *quaternary salt* (10a) which crystallised from ethanol as plates, m.p. 244—246 °C (decomp.) (2.3 g, 90%) (Found: C, 59.6; H, 6.3; N, 4.2; Br, 25.0. $C_{16}H_{20}BrNO$ requires C, 59.6; H, 6.2; N, 4.4; Br, 24.8%); $\nu_{max.}$ 1 760 cm^{-1}; τ (CF_3CO_2H) 2.36—2.73 (m, 5 aryl-H), ABX_2 system, τ_A 2.90, τ_B 3.62, τ_X 5.60 [J_{AB} 16, J_{BX} 8 Hz, $\overset{+}{N}C(H_X)_2CH_B{=}CH_A$-Ph], 5.70—6.36 (m, $CH_2\overset{+}{N}CH_2$ and $\overset{+}{N}CH_2CO$), 6.80—6.89 (m, CH), and 7.84 (br s, CH_2CH_2).

1-*Cinnamyl*-6-*oxo*-1-*azoniabicyclo*[3.2.1]*octan*-7-*ide* (11a).—This was prepared from the quaternary salt (10a) by treatment with aqueous sodium hydroxide. The *ylide* (11a) was obtained as a colourless gum (76%); $\nu_{max.}$ 1 580 cm^{-1}; τ 2.42—2.80 (m, 5 aryl-H), ABX_2 system, τ_A 3.02, τ_B 3.62, τ_X 5.84 [J_{AB} 16, J_{BX} 8 Hz, $\overset{+}{N}C(H_X)_2CH_B{=}CH_APh$], 6.24—6.92 m, $CH_2\overset{+}{N}CH_2$), 7.14—7.54 (m, CH), 7.76—8.50 (m, CH_2CH_2), and 5.72 (br s, $\overset{+}{N}\bar{C}HCO$). The quaternary salt (10a) was regenerated when the ylide (11a) was treated with hydrobromic acid. The ylide (11a) decomposed at 80 °C (N_2 atmosphere) to give a complex mixture of products which could not be purified.

1-*Cinnamyl*-1-*azoniabicyclo*[3.3.1]*nonan*-3-*one* *Bromide* (13a).—This was obtained as prisms, m.p. 225 °C (93%) after crystallisation from ethanol, by the reaction of 1-azabicyclo[3.3.1]nonan-3-one [15] with cinnamyl bromide in methyl cyanide (Found: C, 60.5; H, 6.7; N, 4.1; Br, 23.8. $C_{17}H_{22}BrNO$ requires C, 60.7; H, 6.6; N, 4.2; Br, 23.8%); $\nu_{max.}$ 1 710 cm^{-1}; τ (CF_3CO_2H) 2.42—2.69 m, 5 aryl-H), ABX_2 system, τ_A 2.90, τ_B 3.62, τ_X 5.69 [J_{AB} (16, J_{BX} 7 Hz, $\overset{+}{N}C(H_X)_2{-}CH_B{=}CH_APh$], AB system, τ_A 5.50, τ_B 6.03 (J 17 Hz, $\overset{+}{N}CN_AH_BCO$), 6.78—7.32 (m, $CHCH_2CO$), and 7.75—8.33 (m, CH_2CH_2).

1-*Benzyl*-1-*azoniabicyclo*[3.3.1]*nonan*-3-*one Bromide* (13b).—This was obtained as prisms, m.p. 209 °C (90%) after crystallisation from methanol, by the reaction of 1-azabicyclo[3.3.1]nonan-3-one with benzyl bromide in methyl cyanide (Found: C, 57.7; H, 6.6; N, 4.4; Br, 25.8. $C_{15}H_{20}BrNO$ requires C, 58.1; H, 6.5; N, 4.5; Br, 25.8%); $\nu_{max.}$ 1 700 cm^{-1}; τ (CF_3CO_2H) 2.43 (s, 5 aryl-H), 5.28 ($\overset{+}{N}CH_2Ph$), AB system, τ_A 5.54, τ_B 5.96 (J 17 Hz, $\overset{+}{N}CH_AH_BCO$), 6.06—6.35 (m, $CH_2\overset{+}{N}CH_2$), 6.98—7.33 (m, $CHCH_2CO$), and 7.80—8.28 (m, CH_2CH_2).

1-*Cinnamyl*-3-*oxo*-1-*azoniabicyclo*[3.3.1]*nonan*-2-*ide* (14a).—This was obtained as a colourless gum (87%) by treating

the salt (13a) with aqueous sodium hydroxide (Found: $M^{+\bullet}$, 255.1618. $C_{17}H_{21}NO$ requires M, 255.1623); $\nu_{max.}$ 1 575 cm^{-1}; τ 2.66—2.81 (m, 5 aryl-H), ABX_2 system, τ_A 3.09, τ_B 3.68, τ_X 5.73 [J_{AB} 16, J_{BX} 7 Hz, $\overset{+}{N}C(H_X)_2$–CH_B=CH_A–Ph], 5.30 (br s, $\overset{+}{N}\overset{-}{C}HCO$), 6.12—6.88 (m, $CH_2\overset{+}{N}CH_2$), 7.15—7.80 (m, $CHCH_2CO$), and 7.82—8.50 (m, CH_2CH_2). The quaternary salt (13a) was regenerated on treating the ylide (14a) with hydrobromic acid.

1-*Benzyl*-3-*oxo*-1-*azoniabicyclo*[3.3.1]*nonan*-2-*ide* (14b).—The salt (13b) (2.0 g) in water (5 ml) was treated with an excess of aqueous sodium hydroxide (2 ml, 50%) at 0 °C. The oily product was extracted with dichloromethane and the extract dried and evaporated to give the *ylide* (14b) as a colourless oil (1.3 g, 88%); $\nu_{max.}$ 1 575 cm^{-1}; τ 2.41—2.67 (m, 5 aryl-H), 5.44 (s, $\overset{+}{N}CH_2Ph$), 6.22—6.96 (m, $CH_2\overset{+}{N}CH_2$ and $\overset{+}{N}\overset{-}{C}HCO$), 7.56—7.96 (m, $CHCH_2CO$), and 8.20—8.38 (CH_2CH_2). The quaternary salt (13b) was regenerated when the ylide (14b) was treated with hydrobromic acid. The ylide gave a complex mixture of products on heating above 80 °C, which could not be separated.

1-(3-*Phenylprop*-2-*ynyl*)-1-*azoniabicyclo*[3.3.1]*nonan*-3-*one Bromide* (13c).—3-Phenylprop-2-ynyl bromide reacted with 1-azabicyclo[3.3.1]nonan-3-one in methyl cyanide to give the *salt* (13c) (88%) which crystallised as plates from ethanol, m.p. 247 °C (Found: C, 60.9; H, 6.2; N, 4.0; Br, 23.9. $C_{17}H_{20}BrNO$ requires C, 61.1; H, 6.0; H, 4.2; Br, 24.0%); $\nu_{max.}$ 1 720 cm^{-1}; τ (CF_3CO_2H) 2.41—2.67 (m, 5 aryl-H), 5.32 (s, $\overset{+}{N}CH_2C{\equiv}C$), AB system, τ_A 5.38, τ_B 5.68 (J 17 Hz, $\overset{+}{N}CH_AH_BCO$), 5.82—6.38 (m, $CH_2\overset{+}{N}CH_2$), 6.71—7.31 (m, $CHCH_2CO$), and 7.77—8.00 (m, CH_2CH_2).

1-cis-*Cinnamyl*-1-*azoniabicyclo*[3.3.1]*nonan*-3-*one Bromide* (13d).—The phenylpropynyl salt (13c) (8.5 g) in methanol (200 ml) was hydrogenated at atmospheric pressure using a 5% Pd–$BaSO_4$ catalyst (500 mg) until the theoretical amount of hydrogen had been taken up. The reaction mixture was filtered and evaporated and the residual solid recrystallised from ethanol–ether to give the cis-*cinnamyl salt* (13d) (7.1 g, 84%), m.p. 197—199 °C (Found: C, 60.6; H, 6.8; N, 4.0; Br, 23.9. $C_{17}H_{22}BrNO$ requires C, 60.7; H, 6.6; H, 4.2; Br, 23.8%); $\nu_{max.}$ 1 720 cm^{-1}; τ (CF_3CO_2H) 2.30—2.80 (m, 5 aryl-H), ABX_2 system, τ_A 2.75, τ_B 3.97, τ_X 5.56 [J_{AB} 12, J_{BX} 7 Hz, $\overset{+}{N}C(H_X)_2CH_B$=$CH_A$Ph], AB system, τ_A 5.70, τ_B 6.15 (J 18 Hz, $\overset{+}{N}CH_AH_BCO$), 5.91—6.54 (m, $CH_2\overset{+}{N}CH_2$), 6.75—7.34 (m, $CHCH_2CO$), and 7.70—8.32 (m, CH_2CH_2).

1-cis-*Cinnamyl*-3-*oxo*-1-*azoniabicyclo*[3.3.1]*nonan*-2-*ide* (14d).—Treatment of an aqueous solution of the *cis*-cinnamyl salt (13d) (2.0 g) with sodium hydroxide gave the *ylide* (14d) (1.3 g, 85%) as a pale brown hygroscopic gum (Found: $M^{+\bullet}$, 255.1618. $C_{17}H_{21}NO$ requires M, 255.1623); $\nu_{max.}$ 1 575 cm^{-1}; τ 2.57—2.88 (m, 5 aryl-H), ABX_2 system, τ_A 3.08, τ_B 3.94, τ_X 5.92 [J_{AB} 12, J_{BX} 7 Hz, $\overset{+}{N}C(H_X)_2CH_B$=$CH_A$Ph], 5.64 (br s, $\overset{+}{N}\overset{-}{C}HCO$), 6.54—7.01 (m, $CH_2\overset{+}{N}CH_2$), 7.40—7.76 (m, $CHCH_2CO$), and 8.06—8.48 (CH_2CH_2).

Rearrangement of 1-*Cinnamyl*-3-*oxo*-1-*azoniabicyclo*[3.3.1]-*nonan*-2-*ide* (14a). *Formation of Isomer A of* 2-(1-*Phenylallyl*)-1-*azabicyclo*[3.3.1]*nonan*-3-*one* (15a).—(a) The ylide (14a) (600 mg) was heated at 120 °C for 5 min in a sealed tube (N_2 atmosphere). The product sublimed at 120 °C/0.1 Torr to give isomer A of the *amine* (15a) as pale yellow rhombic crystals, m.p. 90—92 °C (510 mg, 85%) (Found: C, 80.0; H, 8.3; N, 5.5. $C_{17}H_{21}NO$ requires C, 80.0; H, 8.2; N, 5.5%); $\nu_{max.}$ 1 700 cm^{-1}; τ 2.63—2.95 (m, 5 aryl-H), ABMXY system, τ_A 5.05, τ_B 5.07, τ_M 4.06, τ_X 6.30, τ_Y 6.57 (J_{AM} 17, J_{BM} 9, J_{MX} 9, J_{XY} 9 Hz, $COCH_YCH_X$-$PhCH_M$=CH_AH_B), AB system, τ_A 6.79 br, τ_B 7.31 br (J 14 Hz, NCH_AH_B), 7.02—7.57 (m, NCH_2 and CH_2CO), 7.77—7.86 (m, CH_2CHCH_2), and 8.12—8.90 (m, CH_2CH_2).

(b) The ylide (14a) (500 mg) in chloroform (15 ml) was refluxed (N_2 atmosphere) for 5 h. The product was extracted into dilute hydrochloric acid, and the acid solution decolourised with charcoal, filtered, and made basic by the addition of excess of aqueous sodium hydroxide (50%, w/v). The liberated amine was extracted into chloroform and the extract dried and evaporated to give isomer A of the amine (15a) (395 mg, 79%) identical with the sample obtained using method (a).

The amine (15a) gave a *methiodide*, m.p. 231—233 °C (decomp.) (Found: C, 54.2; H, 6.0; N, 3.5; I, 32.4. $C_{18}H_{24}INO$ requires C, 54.5; H, 6.1; N, 3.5; I, 32.0%); $\nu_{max.}$ (Nujol) 1 720 cm^{-1}; τ (CF_3CO_2H) 2.42—2.64 (m, 5 aryl-H), ABMXY system, τ_A 4.50, τ_B 4.78, τ_M 4.18, τ_X 5.71, τ_Y 5.30 (J_{AB} 1.5, J_{AM} 18, J_{BM} 9, J_{MX} 9, J_{XY} *ca.* 8 Hz, $\overset{+}{N}CH_YCH_X$-$PhCH_M$=CH_AH_B), 5.36—6.38 (m, 2 × $\overset{+}{N}CH_2$), 6.88 (s, $\overset{+}{N}Me$), 6.74—7.22 (m, $CHCH_2CO$), and 7.75—8.08 (m, CH_2CH_2).

Reaction of Isomer A of 2-(1-*Phenylallyl*)-1-*azabicyclo*-[3.3.1]*nonan*-3-*one* (15a) *with Sodium Methoxide in Deuteriomethanol. Formation of the* 2,4,4-*Trideuterio-derivative*.—A solution of the amine (15a) (100 mg) in deuteriomethanol (2 ml) containing sodium methoxide (0.5M) was stirred at room temperature for 12 h. The reaction mixture was evaporated and the product extracted into ether giving the 2,4,4-trideuterio-derivative of the amine (15a) (76 mg, 74%), m.p. 90—91 °C (Found: M^+, 258. $C_{17}H_{18}D_3NO$ requires M, 258); $\nu_{max.}$ 1 700 cm^{-1}; the n.m.r. spectrum was similar to that of the undeuteriated amine but the signals at τ 6.57 (CH_YCO) and part of the signal in the range τ 7.02—7.57 (CH_2CO) were absent and the signal at τ 6.30 (d, J 9 Hz, CH_XPh) indicated deuteriation at a neighbouring CH group.

Rearrangement of 1-cis-*Cinnamyl*-3-*oxo*-1-*azoniabicyclo*-[3.3.1]*nonan*-2-*ide*. *Formation of Isomers* A *and B of* 2-(1-*Phenylallyl*)-1-*azabicyclo*[3.3.1]*nonan*-3-*one* (17b ≡ 15a) *and* (15b ≡ 17a).—The *cis*-cinnamyl ylide (14d) was heated at 120 °C for 5 min in a sealed tube. The crude product (450 mg, 45%) was shown by its n.m.r. spectrum to be a mixture of isomer A (17b ≡ 15a) and isomer B (15b ≡ 17a) of the amine in the ratio 1 : 2 (Found: $M^{+\bullet}$, 255.1263. $C_{17}H_{21}$-NO requires M, 255.1623); ABMXY system, τ_A 5.01, τ_B 4.96, τ_M 3.86, τ_X 6.30, τ_Y *ca.* 6.57 (additional ABMXY system assignable to isomer B, J_{AM} 18, J_{BM} 10, J_{MX} 8, J_{XY} *ca.* 9 Hz). The ratios of the signal intensities in the ABM region were unchanged by deuteriation (NaOMe in MeOD).

2-*Cinnamyl*-2-*methyl*-4-*oxo*-1,2,3,4-*tetrahydroisoquinolinium Bromide* (20a).—This was prepared by the reaction of 2-methyl-2,3-dihydro-1*H*-4-isoquinolone [16] with cinnamyl bromide in methyl cyanide. The *salt* (20a) (89%) had m.p. 149—150 °C after crystallisation from ethanol (Found: C, 63.4; H, 5.5; N, 3.7; Br, 22.3. $C_{19}H_{20}BrNO$ requires C, 63.7; H, 5.6; N, 3.9; Br, 22.4%); $\nu_{max.}$ 1 680 cm^{-1}; τ (CF_3CO_2H) 1.75—2.66 (m, 9 aryl-H), ABX_2 system, τ_A 2.04, τ_B 3.67, τ_X 5.58 [J_{AB} 18, J_{BX} 7 Hz, $\overset{+}{N}C(H_X)_2$–CH_A=CH_B–Ph], 4.94 (s, $\overset{+}{N}CH_2Ar$), 5.38 (s, $\overset{+}{N}CH_2CO$), and 6.60 (s, $\overset{+}{N}Me$).

2-Benzyl-2-methyl-4-oxo-1,2,3,4-tetrahydroisoquinolinium Bromide (20b) was prepared from 2-methyl-2,3-dihydro-1*H*-4-isoquinolone and benzyl bromide. The *salt* (20b) (83%) had m.p. 183 °C after crystallisation from ethanol (Found: C, 61.4; H, 5.7; N, 4.2; Br, 24.0. $C_{17}H_{18}BrNO$ requires C, 61.5; H, 5.4; N, 4.2; Br, 24.1%); $\nu_{max.}$ 1 680 cm^{-1}; τ (CF_3CO_2H) 1.62—2.53 (m, 9 aryl-H), 4.90 (s, $\overset{+}{N}CH_2$-Ar), 5.10 (s, $\overset{+}{N}CH_2Ph$), 5.32 (s, $\overset{+}{N}CH_2CO$), and 6.55 (s, $\overset{+}{N}Me$).

Base Catalysed Rearrangement of 2-Cinnamyl-2-methyl-4-oxo-1,2,3,4-tetrahydroisoquinolinium Bromide (20a). *Formation of 2-Methyl-3-(1-phenylallyl)-2,3-dihydro-1H-4-isoquinolone* (22).—Excess of aqueous sodium hydroxide (2 ml, 50%) was added to a solution of the salt (20a) (1.0 g) in water (5 ml) at 0 °C. The oil which separated slowly crystallised; the solid was collected, dried, and recrystallised from light petroleum to give the *amine* (22) (680 mg, 88%) as pale yellow prisms, m.p. 110 °C (Found: C, 82.6; H, 6.65; N, 5.0%; $M^{+\cdot}$, 277. $C_{19}H_{19}NO$ requires C, 82.3; H, 6.9; N, 5.05; *M*, 277); $\nu_{max.}$ 1 680 cm^{-1}; τ 2.00—2.94 (m, 9 aryl-H), ABMXY system, τ_A 5.28, τ_B 5.10, τ_M 4.06, τ_X 6.28, τ_Y 6.32 (J_{AB} 2, J_{AM} 17, J_{BM} 10 Hz, $CH_AH_B{=}CH_M{-}CH_X{-}CH_Y$), AB system, τ_A 5.59, τ_B 6.37 (*J* 17 Hz, CH_AH_BN), and 7.62 (s, NMe); τ (CF_3CO_2H) 1.69 (br d, *J* 8 Hz, C-5-H), 2.00—2.51 (m, 8 aryl-H), ABMXY system, τ_A 4.76, τ_B 4.96, τ_M 4.01, τ_X 6.04, τ_Y 5.29 (J_{AM} 10, J_{BM} 17, J_{MX} 8, J_{XY} 11 Hz, $CH_AH_B{=}CH_M{-}CH_X{-}CH_Y$), AB system, τ_A 4.72, τ_B 5.52 (*J* 17 Hz, $\overset{+}{N}CH_AH_B$), and 6.78 (d, *J* 5 Hz, $\overset{+}{N}HMe$).

Base Catalysed Rearrangement of 2-Benzyl-2-methyl-4-oxo-1,2,3,4-tetrahydroisoquinolinium Bromide (20b). *Formation of 3-Benzyl-2-methyl-2,3-dihydro-1H-4-isoquinolone* (25).—Excess of aqueous sodium hydroxide (2 ml, 50%) was added to a solution of the salt (20b) (1.0 g) in water (5 ml) at 5 °C. The solution was allowed to warm up to room temperature and the product extracted into dichloromethane. The extract was dried and evaporated to give the *amine* (25) (460 mg, 60%) as an oil. (Found: $M^{+\cdot}$, 251.1317. $C_{17}H_{17}NO$ requires *M*, 251.1310); $\nu_{max.}$ 1 680 cm^{-1}; τ 1.98—2.88 (m, 9 aryl-H), AB system, τ_A 5.79, τ_B 6.16 (*J* 17 Hz, NCH_2-Ar), 6.42 (t, *J* 7 Hz, $NCHCH_2$), 6.92 (d, *J* 7 Hz, $NCHCH_2Ph$), and 7.54 (s, NMe). The *methiodide* had m.p. 186 °C (Found: C, 54.7; H, 5.1; N, 3.45; I, 32.4. $C_{18}H_{20}INO$ requires C, 55.0; H, 5.1; N, 3.6; I, 32.3%); $\nu_{max.}$ 1 695 cm^{-1}; τ (CF_3CO_2H) 1.73—2.93 (m, 9 aryl-H), 4.90 (s, $\overset{+}{N}CH_2Ar$), 5.29 (dd, *J* 5, 8.5 Hz, $\overset{+}{N}CHCH_2$), 6.45 (m, $CHCH_2Ph$), 6.48 (s, $\overset{+}{N}Me$), and 6.59 (s, $\overset{+}{N}Me$).

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