Base Catalysed Rearrangements Involving Ylide Intermediates. Part 9.† The Rearrangement Reactions of Cyclic Allylic Ammonium and Sulphonium Ylides

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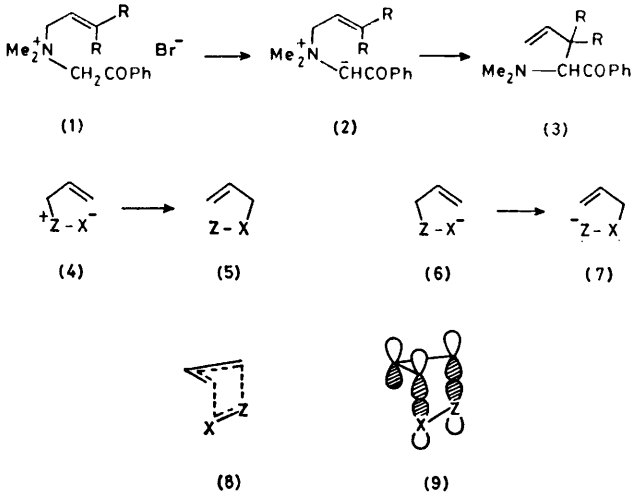
The allylic ammonium ylides (22) and (47) and sulphonium ylide (53) are isolable, usually as crystalline solids, because their [3,2] sigmatropic rearrangements are inhibited by the strain associated with the bicyclic transition state of a concerted reaction mechanism. The tetrahydropyridinium (22) and dihydrothiopyranium (29) ylides undergo a thermal [3,2] rearrangement, but the pyrrolinium ylide (47) rearranges by a [1,2], rather than a [3,2], sigmatropic pathway. The dihydrothiophenium ylide (53) does not undergo either a [1,2] or [3,2] sigmatropic rearrangement but instead reacts in a bimolecular fashion to give eventually buta-1,3-diene, 2,5-dihydrothiophen, and the heterocycle (55). The [3,2] rearrangements of the ylides (22) and (29) follow predominantly an *endo*-pathway leading to a single diastereoisomer of the products (23) and (31); this strong *endo* preference is not shown by analogous acyclic allylic ammonium ylides.

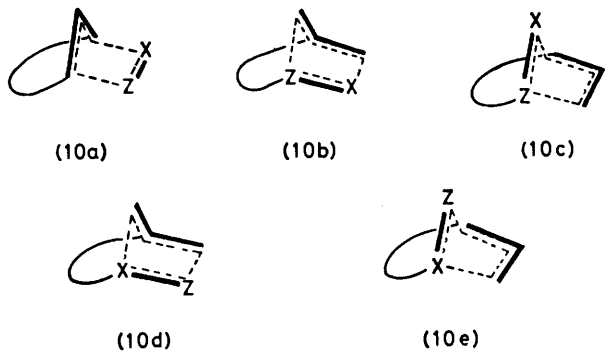
THE base catalysed rearrangement of allylic quaternary ammonium salts [*e.g.* (1) ⟶ (3)] involves the formation of an ylide (2) as an intermediate which normally rearranges rapidly, even at low temperatures, to give the product (3) of a [3,2] sigmatropic rearrangement.[1,2] This reaction is one example of the large group of [3,2] rearrangements involving ylidic [(4) ⟶ (5)] or anionic systems [(6) ⟶ (7)] which on the basis of orbital



(1) (2) (3) (4) (5) (6) (7) (8) (9)

symmetry[3] are expected to take place in a concerted suprafacial–suprafacial mode[4] involving a transition state (8), which may be viewed as a bis-homoaromatic system.[5]

In general the steric requirements of the transition state (8) are readily met by acyclic ylides [*e.g.* (2)]; this may not, however, be the case when the transition state is a bridged bicyclic system rather than monocyclic. Thus if (8) is considered to be derived from a pair of interacting π-radicals, where the π-systems are made up from individual *p*-orbitals, as shown in (9), maximum orbital overlap is achieved when the *p*-orbitals are parallel, and in particular the two partial bonds between C-1′ and Z and C-3′ and X of (8) are as near parallel as possible. The incorporation of the transition state (8) of a [3,2] sigmatropic rearrangement into a bicyclic system must involve a [1,2,*n*] system resulting in five possibilities for the location of the X and Z centres within the system as shown in the formulae (10a—e).‡ Of these five possibilities only one, *i.e.* (10a), is not associated with potential inhibition of the [3,2] rearrangement due to poor orbital overlap. This is in accord with experimental results since, for example, a number of [3,2] rearrangements of allylic sulphoxides belonging to the type (10a) have been reported[6] which proceed under conditions that are similar to those used for acyclic allylic sulphoxides. In this paper we report a study of rearrangements involving transition state (10c)[7] and recently we have reported[8] a preliminary account of rearrangements involving the transition state (10b).



(10a) (10b) (10c) (10d) (10e)

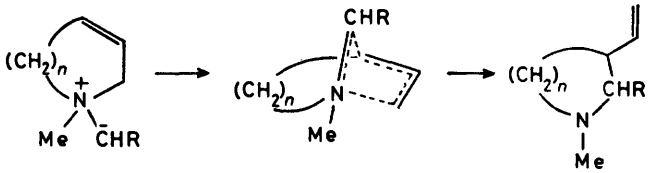
RESULTS AND DISCUSSION

The [3,2] sigmatropic rearrangement of the allylic ammonium ylides (11) requires a bicyclic transition state (12) analogous to (10c) and the reaction product (13) shows clearly that a [3,2] rearrangement has taken

† Part 8; R. W. Jemison, S. Mageswaran, W. D. Ollis, I. O. Sutherland, and Y. Thebtaranonth, *J. Chem. Soc., Perkin Trans. 1*, 1981, 1154.

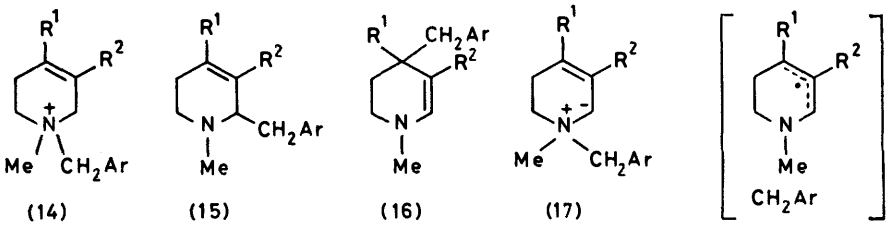
‡ These formulae indicate the σ-bonds of the five centre transition state by bold lines; the 6-electron π-bonding system is indicated by the broken lines.

place. A potential precursor (14) of an ylide analogous to (11) had been examined,[9] but in this case the products (15) and (16) were obtained suggesting initial homolysis of the endocyclic ylide (17), giving a radical pair (18), followed by recombination giving (15) and (16).

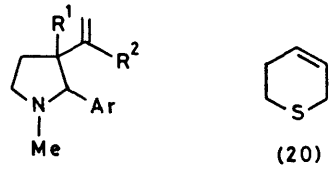


(11) (12) (13)

In one case, however, a small amount of the [3,2] rearrangement product (19) had been formed.[10,11] Reactions possibly comparable to the rearrangement (17) → (15) + (16) had also been reported [12] for the sulphonium ylide generated by the reaction of dichlorocarbene with the dihydrothiopyran (20). The phenacyl substituent of the ammonium salts (21) favours the formation of the required exocyclic ylide (11; $n = 2$, R = COPh) and accordingly the rearrangement reactions of a number of such ammonium salts (21) were investigated.



(14) (15) (16) (17) (18)



(19)

(20)

In all the cases examined (21a—f) the corresponding ylide (22) was isolated, usually as a crystalline solid, after treatment of the ammonium salt (21) with base; this contrasts with the acyclic allylic ammonium ylides [*e.g.* (2)] which normally rearrange immediately, even at low temperatures. The ylides (22) were identified by their spectroscopic properties ($\nu_{max.}$ 1 540—1 550 and 1 580—1 590 cm^{-1}, and $\overset{+}{N}\overset{-}{C}H$ signal at τ 4.43—4.80 for ylides having $R^2 = H$); on heating they rearranged in all cases, to give the pyrrolidine derivative (23) in high yield. The stereochemistry of (23) was established as *cis* by base catalysed equilibration, in cases where $R^2 = H$, to give an equilibrium mixture of the *cis*-amine (23) and the *trans*-amine (24); the equilibrium ratios established that the stereochemical assignments given in (23) and (24) are correct (Table). Thus the proportion of the *cis*-product (23) at equilibrium increased as expected with increasing size of the substituent R^4 in the series (23a—d).

TABLE

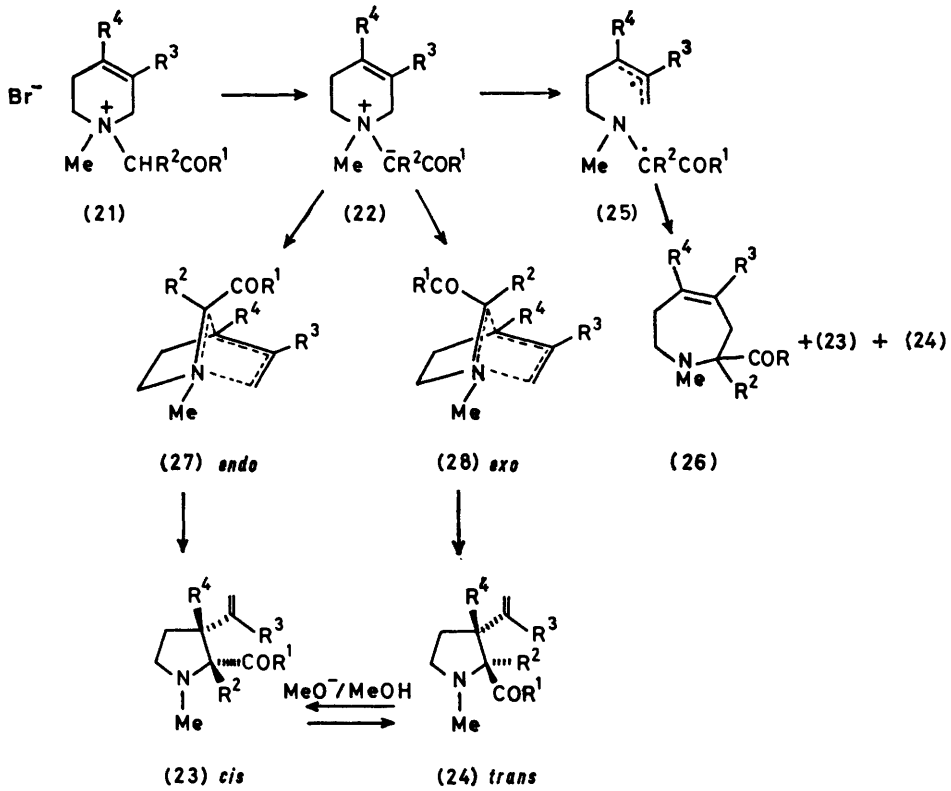
Rearrangement reaction of ylides (22) and (29)

					Product Ratio		Equilibrium Ratio [a]	
Ylide	R^1	R^2	R^3	R^4	*cis* :	*trans*	*cis* :	*trans*
(22a)	Ph	H	H	H	1	0	1	2
(22b)	Ph	H	Me	Me	1	0	4	3
(22c)	Ph	H	H	Et	1	0	5	2
(22d)	Ph	H	H	Bu^t	1	0	1 [b]	0 [b]
(22e)	Ph	Ph	H	H	1	0		
(22f)	Bu^t	H	H	H	1	0	2	3
(29)	Ph	H	H	H	25	1	1	19

[a] After base catalysed equilibration where $R^2 = H$. [b] No trace of a second isomer after equilibration.

The formation of only a single diastereoisomer (23) of the [3,2] rearrangement product of the ylides (22) was unexpected since in our earlier work using acyclic ylides [1,2] mixtures of diastereoisomers were usually obtained from appropriate [3,2] rearrangements. Nevertheless the formation of only the single reaction product (23) suggests stereo- and regio-selectivity that is consistent with a concerted mechanism for the [3,2] rearrangement (22) → (23), and inconsistent with a reaction involving an intermediate diradical (25), or a similar species resulting from bond breaking in advance of bond making, since subsequent radical coupling would be expected to give both (23) and (24) together with, possibly, (26) (see Scheme 1). This conclusion is also consistent with the observed stability of the allylic ammonium ylides (22), as compared with analogous acyclic ylides [*e.g.* (2)], since a mechanism involving prior bond-breaking [*e.g.* (22) → (25)] would not be inhibited by the restraints imposed by incorporating the allylic unit of (22) in a six-membered ring.

The [3,2] sigmatropic rearrangement of the ylide (22) can proceed by two possible transition states, one (27) having an *endo*-relationship between the acyl group COR^1 and the migrating allyl residue and the other (28) having an *exo*-relationship (Scheme 1). The form-



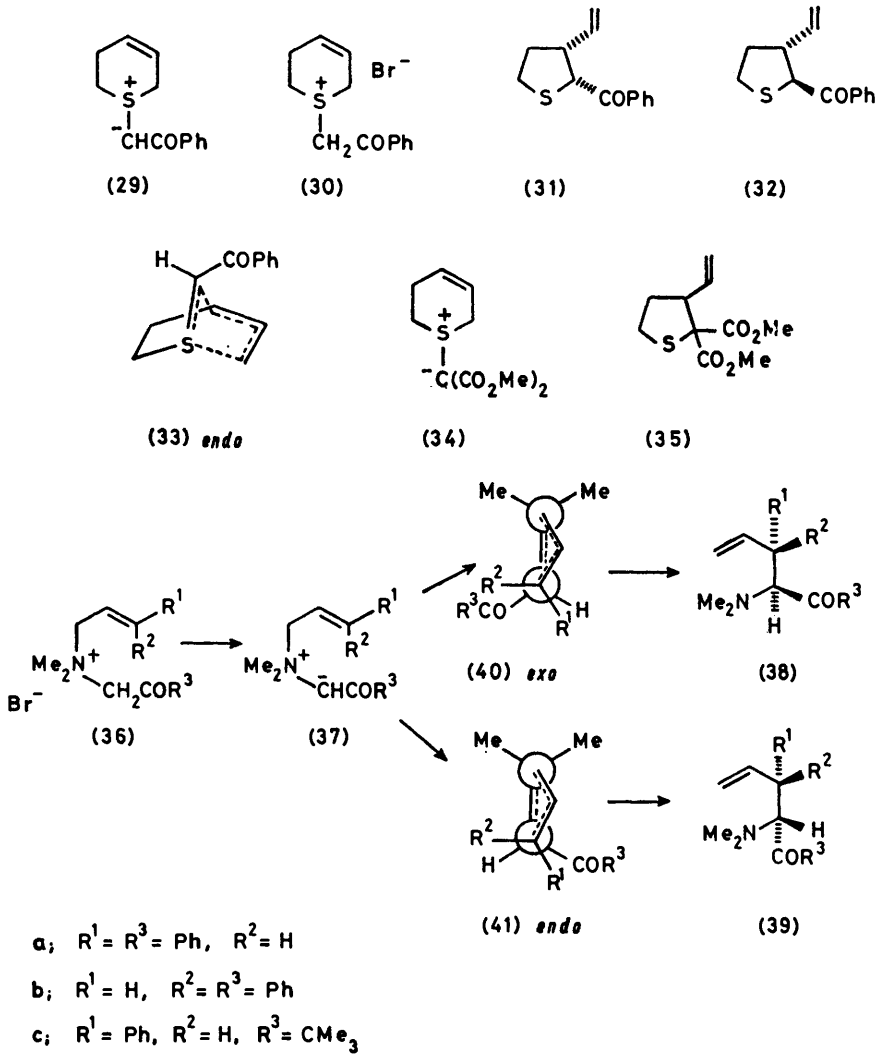
	R^1	R^2	R^3	R^4
a	Ph	H	H	H
b	Ph	H	Me	Me
c	Ph	H	H	Et
d	Ph	H	H	Bu^t
e	Ph	Ph	H	H
f	Bu^t	H	H	H

SCHEME 1

ation of the single product (23) indicates that the reaction proceeds entirely through the *endo*-transition state (27). It was therefore of interest to compare this highly stereoselective reaction of the ammonium ylides (22) with the corresponding reaction of the analogous sulphonium ylide (29). Reaction of the sulphonium salt (30) with base † gave the ylide (29) which rearranged above −5 °C to give a mixture of the *cis*-product (31) and the *trans*-product (32) in a 25 : 1 ratio. The stereochemistry of the major product (31) was established by base catalysed equilibration which gave the *cis*- (31) and *trans*- (32) tetrahydrothiophens in a 1 : 19 ratio (Table). Thus the *endo*-transition state (33) is highly preferred in this case also. The ease of [3,2] rearrangement of the sulphonium ylide (29) contrasts with the stability of the related sulphonium ylide (34), which only undergoes [3,2] rearrangement [13] to give (35) at 180 °C; but in the case of (34) the additional stability of the ylide may be associated with the two electron-withdrawing substituents at the carbanion centre.

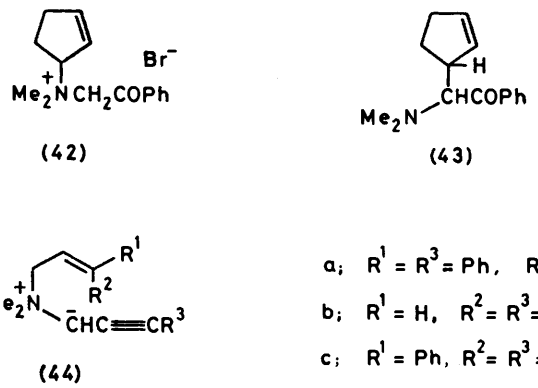
In view of this consistent preference for the *endo*-transition state, (27) or (33), in these reactions, the [3,2] rearrangements of acyclic ammonium ylides were examined further, using a two-phase system for the reaction to minimise the base catalysed equilibration of the diastereoisomeric products (see Experimental section). Under these conditions the *trans*-cinnamyl salt (36a) gave the two diastereoisomeric products (38a) and (39a) in a 5 : 1 ratio, changed to 4 : 3 by base catalysed equilibration. The *cis*-cinnamyl salt (36b) gave the same two products [(39b) ≡ (38a) and (38b) ≡ (39a)]

† The reaction was carried out in a two-phase system (water–dichloromethane) to avoid the base catalysed equilibration of the *cis*- and *trans*-isomers of the product.



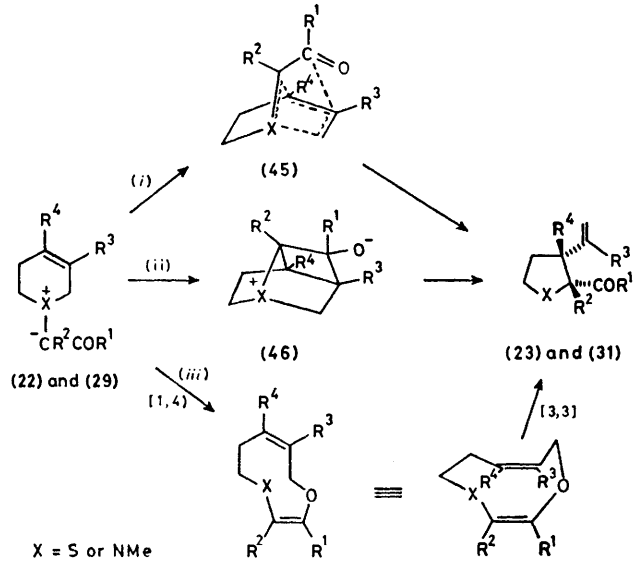
SCHEME 2

in a 2 : 1 ratio. If these two products are related to the *exo*- (40) and *endo*- (41) transition states for the rearrangement (Scheme 2) then on steric grounds the results suggest that for *trans*-cinnamyl as a migrating group the *exo*-transition state (40a) would be preferred, whereas for *cis*-cinnamyl as a migrating group the *endo*-transition state (41b) would be preferred. This conclusion is supported by the observation that for the rearrangement of the salt (36c), in which the benzoyl group of (36a) is replaced by the sterically larger pivaloyl group, the *exo*-transition state (40c) is more highly preferred giving the products (38c) and (39c) in a 9 : 1 ratio. The assignments of the diastereoisomeric structures (38) and (39) to the observed products has been based only upon a consideration of steric interactions in the transition states (40) and (41); if there were additionally a small preference for the *endo*-transition state (41), *e.g.* for electronic reasons, then the product ratio from the rearrangement of the *cis*-cinnamyl salt (36b) would be biased towards the product (39b). This appears not to be the case since the ratio (38b) : (39b) is 1 : 2 and an even higher proportion of (39b) might have been expected on steric grounds alone [*cf.* product ratios from (36a) and (36c)]. The rearrangement of the salt (42) gave the two diastereoisomeric products (43) in a 2 : 1 ratio;



again this result does not reveal a strong preference for an *endo*-transition state.

Thus the dominating preference for an *endo*-transition state in the [3,2] rearrangement of the cyclic ylides (22) and (29) is not shown by the [3,2] rearrangements of acyclic ammonium ylides. The only parallel examples of a very strong *endo*-preference are found for the [3,2] rearrangements of the acetylenic ammonium ylides (44a—c).[1] The preference for the *endo*-transition states (27) and (33) is consistent with (*i*) the secondary orbital interactions indicated by the dotted lines in (45); (*ii*) a tendency towards a betaine intermediate and consequent negative-charge stabilisation as indicated in (46); or even (*iii*) the involvement of consecutive [1,4] and [3,3] rearrangements. All these possibilities are summarised in Scheme 3; the first possibility seems to be the most likely but it is difficult to explain why such a secondary

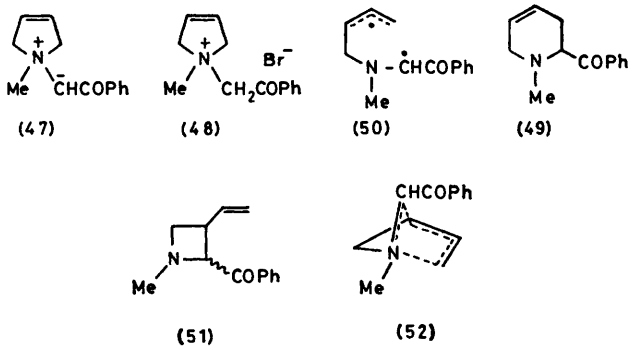


SCHEME 3

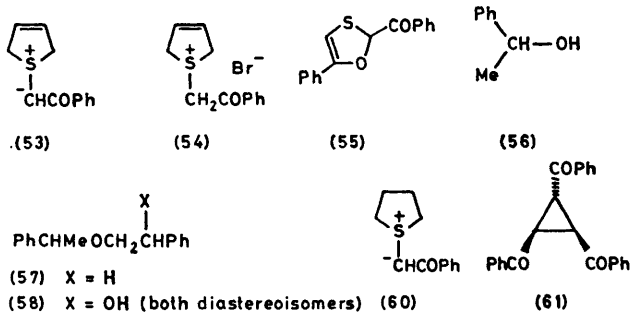
orbital interaction is more important in the cases of the strained transition states (45) from the ylides (22) and (29) than for the apparently strain-free transition states (40) and (41) derived from the acyclic ylides (37).

The pyrrolinium ylide (47), prepared by the action of base on the quaternary salt (48), was also isolated as a crystalline compound which rearranged at 80 °C; in this case, however, the rearrangement product was identified as the tetrahydropyridine derivative (49) resulting from a [1,2] rearrangement of the ylide (47). Thus this reaction takes the alternative pathway of homolysis to give the diradical (50) followed by recombination to give the observed product (49) rather than the four-membered cyclic product (51). The formation of (51) by a [3,2] rearrangement is evidently inhibited due to the strain in the required [2.1.1]bicyclic transition state (52).

The dihydrothiophenium ylide (53), prepared by the action of base on the sulphonium salt (54), also failed to undergo a [3,2] rearrangement but in this case the ylide

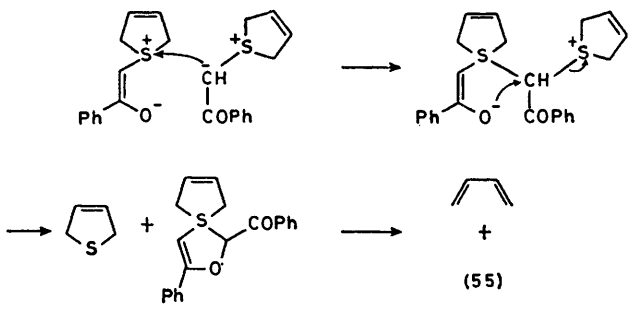


reacts by a pathway that is not available to the corresponding ammonium ylide (47). Thus the oxathiole derivative (55) was obtained when the ylide (53) was heated in benzene; the structure of (55) was assigned on the basis of molecular formula and spectroscopic properties (Experimental section) and the formation of the three reduction products (56), (57), and (58) by reaction with Raney nickel in methanol.



The formation of the product (55) was unexpected but it may be rationalised by the reaction sequence shown in Scheme 4; the other two products, butadiene and 2,5-dihydrothiophen, were identified by g.l.c. examination of the volatile reaction products.

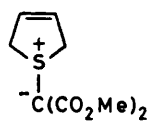
The formation of the intermediate (59) containing



SCHEME 4

tetracovalent sulphur has ample precedent [14] and a wide variety of such compounds has been recognised.[15] The mechanism shown in Scheme 4 requires an intermediate (59) capable of a cheletropic reaction to generate the

final product (55). In accord with this mechanism thermolysis of the tetrahydrothiophenium ylide (60) gave only *trans*-1,2,3-tribenzoylcyclopropane (61); the formation of the cyclopropane (61) is a common event for phenacyl ylides which are unable to undergo sigmatropic rearrangement or an alternative mode of decomposition such as that outlined in Scheme 4. The failure of the ylide (53) to undergo a [1,2] sigmatropic rearrangement contrasts with the apparent [1,2] rearrangement of the analogous ylide (62) to give the dihydrothiopyran derivative (63), which occurs spontaneously [13] when the ylide (62) is generated by the photolysis of a mixture of 2,5-dihydrothiophen and dimethyl diazomalonate.



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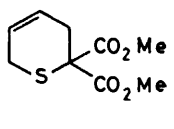

(63)

The results described in this paper show that allylic ammonium and sulphonium ylides may be isolated as relatively stable compounds when the normal ' allowed ' [3,2] rearrangement mode is inhibited by steric effects. Such inhibition provides clear evidence for steric requirements in the transition states of [3,2] sigmatropic rearrangements that are consistent with a reaction mechanism involving simultaneous making and breaking of the two σ-bonds that characterise the reaction.

EXPERIMENTAL

General directions were given in Part 1.[1]

1-Methyl-1-phenacyl-Δ³-pyrrolinium Bromide (48).—*cis*-1,4-Dichlorobut-2-ene [16] (20 g) was added dropwise to a stirred solution of methylamine in ethanol (30%, 150 ml) at 0 °C. The resulting solution was stirred for a further 12 h, made basic with dilute aqueous sodium hydroxide, and extracted with dichloromethane. The extract was dried (Na_2SO_4) and distilled; the fraction b.p. 65—80 °C (1-methyl-Δ³-pyrroline plus ethanol) reacted with phenacyl bromide (15 g) in methyl cyanide (40 ml) to give the salt (48) (15 g) which crystallised from ethanol–ether as prisms, m.p. 208 °C (Found: C, 55.0; H, 5.8; N, 4.8; Br, 28.2. $C_{13}H_{16}BrNO$ requires C, 55.3; H, 5.7; N, 5.0; Br, 28.3%); $\nu_{max.}$ 1 690 and 1 600 cm^{-1}; τ($CDCl_3$–CF_3CO_2H) 2.06 (dd, *J* 2, 8 Hz, 2 *ortho*-H of PhCO), 2.29—2.64 (m, 3 aryl-H), 4.02 (s, –CH=CH–), 4.54 (s, $COCH_2\overset{+}{N}$), τ_A 5.28, τ_B 5.46 (AB system, J_{AB} 15 Hz, $CH_AH_B\overset{+}{N}CH_AH_B$), and 6.53 (s, $\overset{+}{N}Me$).

Benzoyl-(1-methyl-Δ³-pyrrolinio)methanide (47).—Aqueous sodium hydroxide (40%, 5 ml) at 0 °C was added to a cooled (0 °C) solution of the salt (48) (1 g) in water (10 ml). The resulting solution was left at 0 °C for 12 h and extracted with dichloromethane, and the extract dried (Na_2SO_4) and evaporated. The residue was washed with ether leaving the *ylide* (47) (600 mg) m.p. 123—124 °C (Found: $M^{+\bullet}$, 201. $C_{13}H_{15}NO$ requires *M*, 201); $\nu_{max.}$ 1 580 and 1 540 cm^{-1}; τ 2.26—2.34 (m, 2 *ortho*-H of PhCO), 2.73—2.81 (m, 3 aryl-H), 4.18 (s, CH=CH), 4.43 (br s, $\bar{C}O\overset{+}{C}HN$), τ_A 4.82, τ_B 6.05 (AB system, J_{AB} 13.5 Hz, $CH_AH_B\overset{+}{N}CH_AH_B$), and 6.79 (s, $\overset{+}{N}Me$) [in $CDCl_3$–CF_3CO_2H the spectrum resembled that of the quaternary salt (48)].

1-Methyl-1-phenacyl-1,2,5,6-tetrahydropyridinium Bromide (21a).—1-Methylpyridinium iodide (25 g), aqueous sodium hydroxide (300 ml, 1N), and sodium borohydride (6 g) were stirred at room temperature for 3 h. The resulting solution was saturated with sodium chloride and extracted with ether, the extract was dried (Na_2SO_4), and the solvent evaporated to give 1-methyl-1,2,5,6-tetrahydropyridine.[17] The crude tetrahydropyridine was treated with a solution of phenacyl bromide (15 g) in methyl cyanide (50 ml) to give the *salt* (21a) which crystallised from methanol–ether as colourless prisms (21 g), m.p. 192—194 °C (Found: C, 56.5; H, 6.4; N, 4.6; Br, 26.7. $C_{14}H_{18}BrNO$ requires C, 56.8; H, 6.1; N, 4.7; Br, 27.0%); $\nu_{max.}$ 1 680, 1 590 cm^{-1}; τ(CF_3CO_2H) 2.02 (dd, *J* 2, 8 Hz, 2 *ortho*-H of PhCO), 2.22—2.58 (m, 3 aryl-H), τ_A 3.90, τ_B 4.22 (AB system, J_{AB} 10 Hz, $CH_A{=}CH_B$), 4.83 (s, $COCH_2\overset{+}{N}$), 5.67 (br, $\overset{+}{N}CH_2C{=}C$), τ_A 5.84, τ_B 6.19, τ_X 7.38 [ABX_2 system, J_{AB} 12, J_{AX} 6, J_{BX} 6 Hz, $\overset{+}{N}CH_AH_BC(H_X)_2C{=}C$], and 6.49 (s, $\overset{+}{N}Me$).

Benzoyl-(N-methyl-1,2,5,6-tetrahydropyridinio)methanide (22a).—The addition of aqueous sodium hydroxide (10 ml, 50%) to a solution of the *salt* (21a) (3 g) in water (25 ml) gave the *ylide* (22a) (1.9 g), m.p. 42—43 °C (Found: $M^{+\bullet}$, 215. $C_{14}H_{17}NO$ requires *M*, 215); $\nu_{max.}$ 1 580 and 1 540 cm^{-1}; τ 2.30—2.40 (m, 2 *ortho*-H of PhCO), 2.72—2.80 (m, 3 aryl-H), τ_A 4.12, τ_B 4.41 (AB system, J_{AB} 11 Hz, $CH_A{=}CH_B$), 4.78 (s, $\bar{C}O\overset{+}{C}HN$), τ_A 5.42, τ_B 6.76, τ_X 7.60 [ABX_2 system, J_{AB} 12, J_{AX} 6, J_{BX} 6 Hz, $\overset{+}{N}CH_AH_BC(H_X)_2C{=}C$], τ_A 5.75, τ_B 6.23 (AB system, J_{AB} 16 Hz, $\overset{+}{N}CH_AH_BC{=}C$), and 6.56 (s, $\overset{+}{N}Me$) [in $CDCl_3$–CF_3CO_2H the spectrum resembled that of the salt (21a)].

1,3,4-Trimethyl-1-phenacyl-1,2,5,6-tetrahydropyridinium Bromide (21b).—1,3,4-Trimethyl-1,2,5,6-tetrahydropyridine [9b] was prepared by the reaction of 1,3,4-trimethylpyridinium iodide (25 g) with sodium borohydride (4.5 g) in aqueous sodium hydroxide (200 ml, 1N). The crude tetrahydropyridine derivative reacted with phenacyl bromide (25 g) in methyl cyanide (75 ml) to give the *salt* (21b) (26 g) which crystallised from methanol as prisms, m.p. 194 °C (Found: C, 59.2; H, 6.7; N, 4.4; Br, 24.4. $C_{16}H_{22}BrNO$ requires C, 59.3; H, 6.8; N, 4.3; Br, 24.6%); $\nu_{max.}$ 1 675 cm^{-1}; τ(CF_3CO_2H) 2.05 (dd, *J* 2, 8 Hz, 2 *ortho*-H of PhCO), 2.23—2.58 (m, 3 aryl-H), 4.91 (s, $COCH_2\overset{+}{N}$), 5.90 (br, $\overset{+}{N}CH_2C{=}C$), 6.53 (s, $\overset{+}{N}Me$), 7.52 (br, $\overset{+}{N}CH_2CH_2C{=}C$), 8.20 (s, C=CMe), and 8.24 (s, C=CMe).

Benzoyl-(1,3,4-trimethyl-1,2,5,6-tetrahydropyridinio)-methanide (22b).—Aqueous sodium hydroxide (10 ml, 10%) was added to a solution of the salt (21b) (1.2 g) in water (20 ml) to give the *ylide* (22b) as a gum (Found: $M^{+\bullet}$, 243. $C_{16}H_{21}NO$ requires *M*, 243); $\nu_{max.}$ 1 590 and 1 550 cm^{-1}; τ 2.30—2.40 (m, 2 *ortho*-H of PhCO), 2.70—2.83 (m, 3 aryl-H), 4.83 (br s, $\bar{C}O\overset{+}{C}HN$), τ_A 5.56, τ_B 6.81, τ_X 7.77 [ABX_2 system, J_{AB} 12.5, J_{AX} 6, J_{BX} 6 Hz, $\overset{+}{N}CH_AH_BC(H_X)_2$], τ_A 6.03, τ_B 6.36 (AB system, J_{AB} 16 Hz, $\overset{+}{N}CH_A$-

$H_BC{=}C$), 6.60 (s, $\overset{+}{N}Me$), 8.36 (s, C=CMe), and 8.40 (d, *J ca.* 2 Hz, C=CMe). The ylide (22b) reacted with hydrobromic acid in aqueous methanol to give the quaternary salt (21b).

4-Ethyl-1-methyl-1-phenacyl-1,2,5,6-tetrahydropyridinium Bromide (21c).—Crude 4-ethyl-1-methyl-1,2,5,6-tetrahydropyridine, obtained from the reaction of 4-ethyl-1-methylpyridinium iodide (30 g) with sodium borohydride (6 g) in aqueous sodium hydroxide (300 ml, 1N), reacted with phenacyl bromide (25 g) to give the *salt* (21c) (35 g) which crystallised from methanol–ether as prisms, m.p. 169—170 °C (Found: C, 59.0; H, 6.9; N, 4.2; Br, 24.4. $C_{16}H_{22}BrNO$ requires C, 59.3; H, 6.8; N, 4.3; Br, 24.6%); $\nu_{max.}$ 1 680 and 1 590 cm^{-1}; τ($CDCl_3$–CF_3CO_2H) 2.01 (d, *J* 7 Hz, 2 *ortho*-H of PhCO), 2.32—2.67 (m, 3 aryl-H), τ_A 4.45, τ_B 4.66 (AB system, J_{AB} 17 Hz, $COCH_2\overset{+}{N}$), 4.66 (br s, C=CH), τ_A 5.47, τ_B 5.75 (AB system, J_{AB} 16 Hz, $\overset{+}{N}CH_AH_BC{=}C$), 5.80—6.20 (m, $\overset{+}{N}CH_2CH_2$), 6.55 (s, $\overset{+}{N}Me$), 7.62 (br, $CH_2CH_2\overset{+}{N}$), and τ_A 7.93, τ_X 8.98 [A_2X_3 system, J_{AX} 7.5 Hz, $C(H_A)_2C(H_X)_3$].

Benzoyl-(4-ethyl-1-methyl-1,2,5,6-tetrahydropyridinio)-methanide (22c).—The salt (21c) (30 g) in water (300 ml) reacted with aqueous sodium hydroxide (100 ml, 20%) to give the *ylide* (22c) (20 g), m.p. 140—141 °C; $\nu_{max.}$ 1 585 and 1 545 cm^{-1}; τ 2.30—2.40 (m, 2 *ortho*-H of PhCO), 2.70—2.83 (m, 3 aryl-H), 4.78 (br s, C=CH + $\overset{-}{C}O\overset{+}{C}HN$), τ_A 5.44, τ_B 6.75, τ_X 7.74 [ABX_2 system, J_{AB} 12, J_{AX} 6, J_{BX} 6 Hz, $\overset{+}{N}CH_AH_BC(H_X)_2$], τ_A 5.90, τ_B 6.27 (AB system, J_{AB} 17 Hz, $\overset{+}{N}CH_AH_BC{=}C$), 6.58 (s, $\overset{+}{N}Me$), and τ_A 7.99, τ_X 9.00 [A_2X_3 system, J_{AX} 7 Hz, $C(H_A)_2C(H_X)_3$]. [The n.m.r. spectrum in $CDCl_3$–CF_3CO_2H resembled that of the salt (21c)].

1-Methyl-1-phenacyl-4-t-butyl-1,2,5,6-tetrahydropyridinium Bromide (21d).—Crude 1-methyl-4-t-butyl-1,2,5,6-tetrahydropyridine, obtained from the reaction of 1-methyl-4-t-butylpyridinium iodide (17 g) with sodium borohydride (4 g) in aqueous sodium hydroxide (200 ml, 1N), reacted with phenacyl bromide (10 g) in methyl cyanide (50 ml) to give the *salt* (21d) (15 g) which crystallised from methanol–ether as prisms, m.p. 199 °C (Found: C, 61.1; H, 7.5; N, 3.8; Br, 22.4. $C_{18}H_{26}BrNO$ requires C, 61.4; H, 7.4; N, 4.0; Br, 22.8%); $\nu_{max.}$ 1 690 and 1 590 cm^{-1}; τ 1.94 (d, *J* 7.5 Hz, 2 *ortho*-H of PhCO), 2.34—2.66 (m, 3 aryl-H), τ_A 3.95, τ_B 4.25 (AB system, J_{AB} 18 Hz, $\overset{+}{N}CH_AH_BCO$), 4.63 (br s, C=CH), τ_A 5.23, τ_B 5.55 (AB system, J_{AB} 16 Hz, $\overset{+}{N}CH_AH_BC{=}C$), 5.81 (br, $\overset{+}{N}CH_2CH_2$), 6.47 (s, $\overset{+}{N}Me$), 7.59 (br, $\overset{+}{N}CH_2CH_2$), and 8.95 (s, CMe_3).

Benzoyl-(1-methyl-4-t-butyl-1,2,5,6-tetrahydropyridinio)-methanide) (22d) —An aqueous solution of the salt (21d) (3 g) reacted with aqueous sodium hydroxide (20 ml, 20%) to give the *ylide* (22d) (2 g), m.p. 152 °C (Found: $M^{+\bullet}$, 271. $C_{18}H_{25}NO$ requires *M*, 271); $\nu_{max.}$ 1 580 and 1 545 cm^{-1}; τ 2.30—2.39 (m, 2 *ortho*-H of PhCO), 2.74—2.84 (m, 3 aryl-H), 4.67 (br s, C=CH), 4.80 (br s, $\overset{-}{C}O\overset{+}{C}HN$), τ_A 5.38, τ_B 6.74, τ_X 7.65 [ABX_2 system, J_{AB} 12, J_{AX} 6, J_{BX} 6 Hz, $\overset{+}{N}CH_AH_BC(H_X)_2$], τ_A 5.84, τ_B 6.23 (AB system, J_{AB} 16 Hz, $\overset{+}{N}CH_AH_BC{=}C$), 6.55 (s, $\overset{+}{N}Me$), and 8.93 (s, CMe_3). The ylide reacted with hydrobromic acid in aqueous methanol to give the quaternary salt (21d).

1-Methyl-1-(α-phenylphenacyl)-1,2,5,6-tetrahydropyridinium Bromide (21e).—Crude 1-methyl-1,2,5,6-tetrahydropyridine, prepared from 1-methylpyridinium iodide (22 g), reacted with α-phenylphenacyl bromide [18] (19 g) in methyl cyanide (75 ml) to give the *salt* (21e) (22 g) which crystallised from methyl cyanide–ether as plates, m.p. 159—160 °C (Found: C, 64.3; H, 6.2; N, 3.95; Br, 21.4. $C_{20}H_{22}BrNO$ requires C, 64.5; H, 5.9; N, 3.8; Br, 21.5%); $\nu_{max.}$ 1 670 and 1 590 cm^{-1}; τ 1.65—1.78 (m, 2 *ortho*-H of PhCO), 1.85 (s, $COC\overset{+}{H}N$), 2.13—2.74 (m, 8 aryl-H), τ_A 3.99, τ_B 4.30 (AB system, J_{AB} 11 Hz, $CH_A{=}CH_B$), τ_A 5.10, τ_B 5.63 (AB system, J_{AB} 17 Hz, $\overset{+}{N}CH_AH_BC{=}C$), 5.87 (br, $\overset{+}{N}CH_2CH_2$), 6.52 (s, $\overset{+}{N}Me$), and 7.47 (br, $\overset{+}{N}CH_2CH_2$).

Benzoyl-(1-methyl-1,2,5,6-tetrahydropyridinio)phenyl-methanide (22e).—The salt (21e) (3 g) in water reacted with aqueous sodium hydroxide (10 ml, 50%) to give the *ylide* (22e) (2.2 g) as plates, m.p. 55—56 °C (Found: $M^{+\bullet}$, 291. $C_{20}H_{21}NO$ requires *M*, 291); $\nu_{max.}$ 1 540 cm^{-1}; τ 2.50—3.09 (m, 10 aryl-H), τ_A 4.13, τ_B 4.55 (AB system, J_{AB} 11 Hz, $CH_A{=}CH_B$), τ_A 4.95, τ_B 6.38, τ_X 7.50 [br, ABX_2 system, $\overset{+}{N}CH_AH_BC(H_X)_2$], τ_A 5.62, τ_B 6.12 (AB system, J_{AB} 16 Hz, $\overset{+}{N}CH_AH_BC{=}C$), and 6.51 (s, $\overset{+}{N}Me$).

1-(3,3-Dimethyl-2-oxobutyl)-1-methyl-1,2,5,6-tetrahydropyridinium Bromide (21f).—Crude 1-methyl-1,2,5,6-tetrahydropyridine, prepared from 1-methylpyridinium iodide (33 g), reacted with 1-bromo-3,3-dimethylbutan-2-one (17 g) in methyl cyanide (30 ml) to give the *salt* (21f) (23 g) which crystallised from methyl cyanide–ether as prisms, m.p. 176—177 °C (Found: C, 52.3; H, 8.1; N, 5.2; Br, 28.7. $C_{12}H_{22}BrNO$ requires C, 52.2; H, 8.0; N, 5.1; Br, 28.9%); $\nu_{max.}$ 1 705 cm^{-1}; τ_A 3.99, τ_B 4.29 (AB system, J_{AB} 10 Hz, $CH_A{=}CH_B$), τ_A 4.37, τ_B 4.59 (AB system, J_{AB} 18 Hz, $\overset{+}{N}CH_AH_BCO$), τ_A 5.26, τ_B 5.56 (AB system, J_{AB} 16 Hz, $\overset{+}{N}CH_AH_BC{=}C$), 5.82 (br, $\overset{+}{N}CH_2CH_2$), 6.50 (s, $\overset{+}{N}Me$), 7.52 (br, $\overset{+}{N}CH_2CH_2$), and 8.73 (s, CMe_3).

1-Methyl-1,2,5,6-tetrahydropyridinio(pivaloyl)methanide (22f).—Methanolic sodium methoxide (15 ml, 16%) at 0 °C was added to a cold (0 °C) solution of the salt (21f) (1.5 g) in methanol (10 ml). The resulting solution was kept at 0 °C for 4 days, poured into cold water, and extracted with dichloromethane. The extract was dried (Na_2SO_4) and evaporated at 20 °C, and the residue washed with ether to give the *ylide* (22f) (800 mg) as a gum; $\nu_{max.}$ 1 550 cm^{-1}; τ_A 4.09, τ_B 4.37 (AB system, J_{AB} 11 Hz, $CH_A{=}CH_B$), τ_A 5.51, τ_B 6.70, τ_X 7.62 [ABX_2 system, J_{AB} 13 Hz, J_{AX} 6 Hz, J_{BX} 6 Hz, $\overset{+}{N}CH_AH_BC(H_X)_2$], τ_A 5.80, τ_B 6.20 (AB system, J_{AB} 16 Hz, $\overset{+}{N}CH_AH_BC{=}C$), 6.62 (s, $\overset{+}{N}Me$), and 8.93 (s, CMe_3).

1-Phenacyl-2,5-dihydrothiophenium Bromide (54).—2,5-Dihydrothiophen [19] (4 g) reacted with phenacyl bromide (10 g) in methyl cyanide (50 ml) to give the *salt* (54) (10 g) which crystallised from methanol–ether as prisms, m.p. 125 °C (Found: C, 50.8; H, 4.8; S, 11.3; Br, 27.8. $C_{12}H_{13}BrOS$ requires C, 50.5; H, 4.6; S, 11.2; Br, 28.0%); $\nu_{max.}$ 1 670 cm^{-1}; τ(CF_3CO_2H) 2.01 (d, *J* 8 Hz, 2 *ortho*-H of PhCO), 2.24—2.53 (m, 3 aryl-H), 3.84 (s, CH=CH), 4.67 (s, SCH_2CO), and τ_A 5.34, τ_B 5.57 (AB system, J_{AB} 15 Hz, $CH_AH_B\overset{+}{S}CH_AH_B$).

Benzoyl-(2,5-dihydrothiophenio)methanide (53).—The salt (54) (1 g) in water (8 ml) reacted with aqueous sodium hydroxide (8 ml, 22%) to give the *ylide* (53) (680 mg) as a pale yellow solid, m.p. 93—94 °C; $\nu_{max.}$ 1 580 and 1 505

cm^{-1}; τ 2.16—2.25 (m, 2 *ortho*-H of PhCO), 2.62—2.74 (m, 3 aryl-H), 4.03 (s, CH=CH), τ_A 5.58, τ_B 6.23 (AB system, J_{AB} 14 Hz, $CH_AH_B\overset{+}{S}CH_AH_B$), and 5.63 (br s, $\overset{-}{C}O\overset{+}{C}HS$). The ylide reacted with hydrobromic acid in aqueous methanol to give the salt (54).

1-*Phenacyl*-5,6-*dihydro*-2H-*thiopyranium Bromide* (30).—5,6-Dihydro-2*H*-thiopyran [20] (6 g) reacted with phenacyl bromide (10 g) in methyl cyanide to give the *salt* (30) (12 g) which crystallised from methanol–ether as colourless prisms, m.p. 107—108 °C (Found: C, 52.3; H, 5.2; S, 10.8; Br, 26.8. $C_{13}H_{15}BrSO$ requires C, 52.2; H, 5.1; S, 10.7; Br, 26.7%); $\nu_{max.}$ 1 670 and 1 595 cm^{-1}; τ(CF_3CO_2H) 2.01 (dd, *J* 2, 8 Hz, 2 *ortho*-H of PhCO), 2.19—2.56 (m, 3 aryl-H), τ_A 5.77, τ_B 5.98 (AB system, J_{AB} 18 Hz, $\overset{+}{S}CH_AH_BC{=}C$), 6.33 (t, *J* 6 Hz, $\overset{+}{S}CH_2CH_2$), and 7.24 (br, $\overset{+}{S}CH_2CH_2$).

Reaction Between 1-*Phenacyl*-5,6-*dihydro*-2H-*thiopyranium Bromide* (30) *and Aqueous Sodium Hydroxide. Formation of* cis- *and* trans-2-*Benzoyl*-3-*vinyltetrahydrothiophen* [(31) *and* (32)].—Cold aqueous sodium hydroxide (10 ml, 10%) was added to a stirred mixture of dichloromethane (50 ml) and a solution of the salt (30) (500 mg) in water (20 ml) maintained at 0 °C. The mixture was stirred at 0 °C for a further 1 h, and the organic layer separated, dried (Na_2SO_4), and evaporated to give cis-2-*benzoyl*-3-*vinyltetrahydrothiophen* (31) (315 mg) as a brown oil (Found: C, 69.6; H, 6.4; S, 14.6. $C_{13}H_{14}OS$ requires C, 69.9; H, 6.5; S, 14.8%); $\nu_{max.}$ 1 675 and 1 595 cm^{-1}; τ 2.15 (dd, *J* 2, 8 Hz, 2 *ortho*-H of PhCO), 2.45—2.77 (m, 3 aryl-H), τ_A 5.02, τ_B 4.89, τ_X 3.96 (ABX system, J_{AB} 2, J_{BX} 16, J_{AX} 10 Hz, $CH_X{=}CH_AH_B$), 5.27 (d, *J* 6 Hz, S–CH), 6.80—7.97 (m, S–CH_2CH_2CH) [an additional doublet at τ 5.53 (*J* 6 Hz) indicated that the compound was contaminated with a small amount of the corresponding *trans*-isomer (32), *cis* : *trans* ratio 25 : 1]. *cis*-2-Benzoyl-3-vinyltetrahydrothiophen (31) (800 mg) was equilibrated with the *trans*-isomer (32) in methanolic sodium methoxide (10 ml, 11.5%) at room temperature for 18 h. The resulting solution was acidified (150 ml, 2N HCl) and the products extracted into ether to give a mixture of the *trans*- (32) (SCH doublet at τ 5.53) and *cis*- (31) (SCH doublet at τ 5.27) isomers in the ratio 19 : 1.

Thermal Rearrangements of Ammonium Ylides (22) *and* (47).—*Benzoyl*-(1-*methyl*-Δ^3-*pyrrolinio*)*methanide* (47). *Formation of* 6-*benzoyl*-1-*methyl*-1,2,5,6-*tetrahydropyridine* (49). The ylide (47) (500 mg) was refluxed in benzene for 3 h. Filtration and evaporation of the solvent gave 6-*benzoyl*-1-*methyl*-1,2,5,6-*tetrahydropyridine* (49) (450 mg) as an oil (Found: $M^{+\bullet}$, 201.1149. $C_{13}H_{15}NO$ requires *M*, 201.1154); $\nu_{max.}$ 1 680 cm^{-1}; τ 1.92 (dd, *J* 2, 7 Hz, 2 *ortho*-H of PhCO), 2.44—2.67 (m, 3 aryl-H), 4.26 (s, HC=CH), 5.90 (dd, *J* 6, 7 Hz, NCHCO), τ_A 6.51, τ_B 6.85 (AB system, J_{AB} 18 Hz, $NCH_AH_BC{=}C$), 7.49—7.65 (m, CH_2CHCO), and 7.65 (s, NMe). The *methiodide* crystallised from methanol–ether as plates, m.p. 162—164 °C (Found: C, 49.0; H, 5.4; N, 4.0; I, 36.7. $C_{14}H_{18}INO$ requires C, 49.0; H, 5.3; N, 4.1; I, 37.0%); $\nu_{max.}$ 1 690 and 1 595 cm^{-1}; τ(CF_3CO_2H) 1.92 (d, *J* 7 Hz, 2 *ortho*-H of PhCO), 2.19—2.55 (m, 3 aryl-H), τ_A 3.92, τ_B 4.11 (AB system, J_{AB} 10 Hz, $CH_A{=}CH_B$), τ_A 6.93, τ_B 7.33, τ_X 4.35 (ABX system, J_{AB} 19.5, J_{AX} 6, J_{BX} 6.5 Hz, $NCH_XCH_AH_BC{=}C$), 5.60 (s, $\overset{+}{N}CH_2$), 6.45 (s, $\overset{+}{N}Me$), and 6.63 (s, $\overset{+}{N}Me$).

Benzoyl-(1-*methyl*-1,2,5,6-*tetrahydropyridinio*)*methanide* (22a). *Formation of* cis-2-*benzoyl*-1-*methyl*-3-*vinylpyrrolidine* (23a). The ylide (22a) (1.0 g) was heated under reflux in benzene for 45 min. Filtration and evaporation of the solvent gave the cis-*pyrrolidine derivative* (23a) (900 mg) as an oil (Found: $M^{+\bullet}$, 215. $C_{14}H_{17}NO$ requires *M*, 215); $\nu_{max.}$ 1 680 cm^{-1}; τ 2.09 (dd, *J* 2, 8 Hz, 2 *ortho*-H of PhCO), 2.48—2.75 (3 aryl-H), τ_A 5.37, τ_B 5.34, τ_X 4.41 (ABX of ABXY system, J_{AB} 2, J_{AX} 16.5, J_{BX} 11 Hz, $CH_AH_B{=}CH_X$), 6.05 (d, *J* 8.5 Hz, NCHCO), 6.41—7.16 (m, $CHCH_2CH_2N$), 7.49—8.50 (m, $CHCH_2CH_2N$), and 7.66 (s, NMe). The *picrate* had m.p. 152—153 °C (Found: C, 53.8; H, 5.0; N, 12.6. $C_{20}H_{20}N_4O_8$ requires C, 54.05; H, 4.5; N, 12.6%).

The *cis*-pyrrolidine derivative (23a) was equilibrated with the *trans*-isomer (24a) in methanolic sodium methoxide (20 ml, 6%) at room temperature for 18 h. The product was a mixture of the *cis*- (23a) (NCHCO doublet at τ 6.07) and *trans*- (24a) (NCHCO doublet at τ 6.40) isomers in a ratio of 1 : 2.

Benzoyl-(1,3,4-*trimethyl*-1,2,5,6-*tetrahydropyridinio*)*methanide* (22b). *Formation of* cis-2-*benzoyl*-1,3-*dimethyl*-3-(α-*methylvinyl*)*pyrrolidine* (23b). The ylide (22b) (900 mg) was refluxed in benzene for 1 h. Filtration and evaporation of the solvent gave the cis-*amine* (23b) (810 mg) (Found: $M^{+\bullet}$, 243. $C_{16}H_{21}NO$ requires *M*, 243); $\nu_{max.}$ 1 680 cm^{-1}; τ 2.20 (dd, *J* 2, 7 Hz, 2 *ortho*-H of PhCO), 2.54—2.76 (m, 3 aryl-H), 4.44 (s, C=CH), 4.50 (s, C=CH), 6.06 (s, NCHCO), 6.77—8.58 (m, NCH_2CH_2), 7.69 (s, NMe), 8.48 (s, C=CMe), and 8.73 (s, CMe). The *picrate* had m.p. 167—168 °C (Found: C, 56.1; H, 5.5; N, 11.75. $C_{22}H_{24}N_4O_8$ requires C, 55.9; H, 5.12; N, 11.9%).

Equilibration of the *cis*- (23b) and *trans*- (24b) isomers gave a mixture of the *cis*- (CMe at τ 8.43 and 8.70) and *trans*- (CMe at τ 8.11 and 9.00) isomers in a 3 : 2 ratio.

Benzoyl-(4-*ethyl*-1-*methyl*-1,2,5,6-*tetrahydropyridinio*)*methanide* (22c). *Formation of* cis-2-*benzoyl*-3-*ethyl*-1-*methyl*-3-*vinylpyrrolidine* (23c). The ylide (22c) (8.0 g) was refluxed in benzene (250 ml) for 2 h. Filtration and evaporation of the solvent gave the cis-*amine* (23c) (7.5 g) as an oil; $\nu_{max.}$ 1 680 cm^{-1}; τ 2.10 (dd, *J* 2.5, 7.5 Hz, 2 *ortho*-H of PhCO), 2.50—2.70 (m, 3 aryl-H), τ_A 5.18, τ_B 5.08, τ_X 4.47 (ABX system, J_{AB} 1, J_{AX} 17.5, J_{BX} 11 Hz, $CH_X{=}CH_AH_B$), 6.20 (s, NCH), 6.67—8.31 (m, NCH_2CH_2), 7.68 (s, NMe), and τ_A 8.41, τ_X 9.17 [A_2X_3 system, J_{AX} 8 Hz, $C(H_A)_2C(H_X)_3$]. The *picrate* had m.p. 140—143 °C (Found: C, 56.0; H, 5.1; N, 12.1. $C_{22}H_{24}N_4O_8$ requires C, 55.9; H, 5.1; N, 11.9%).

Equilibration of the *cis*- (23c) and *trans*- (24c) isomers gave a mixture of the *cis* (CH_X at τ 4.44) and *trans* (CH_X at τ 4.18) isomers in the ratio *ca.* 2 : 1.

Benzoyl-(1-*methyl*-4-*t*-*butyl*-1,2,5,6-*tetrahydropyridinio*)*methanide* (22d). *Formation of* cis-2-*benzoyl*-1-*methyl*-3-*t*-*butyl*-3-*vinylpyrrolidine* (23d). The ylide (22d) (500 mg) was refluxed in benzene (50 ml) for 3 h. Filtration and evaporation of the solvent gave the cis-*amine* (23d) (330 mg) as an oil (Found: $M^{+\bullet}$, 271.1932. $C_{18}H_{25}NO$ requires *M*, 271.1936); $\nu_{max.}$ 1 675 cm^{-1}; τ 1.95 (dd, *J* 2, 7 Hz, 2 *ortho*-H of PhCO), 2.52—2.76 (m, 3 aryl-H), τ_A 4.97, τ_B 4.97, τ_X 4.21 (ABX system, J_{AX} 17, J_{BX} 10.5 Hz, $CH_X{=}CH_AH_B$), 5.93 (s, NCH), 6.70—8.20 (m, NCH_2CH_2), 7.79 (s, NMe), and 9.10 (s, CMe_3). The *methiodide* had m.p. 186—187 °C (Found: C, 55.2; H, 7.1; N, 3.2; I, 30.9. $C_{19}H_{28}INO$ requires C, 55.2; H, 6.8; N, 3.4; I, 30.7%); $\nu_{max.}$ 1 670 and 1 590 cm^{-1}; τ 1.61 (dd, *J* 2, 7.5 Hz, 2 *ortho*-H of PhCO), 2.20—2.50 (m, 3 aryl-H), τ_A 4.68, τ_B 4.53, τ_X 3.74 (ABX system, J_{AX} 18, J_{BX} 11 Hz, $CH_X{=}CH_AH_B$),

4.39 (s, $\overset{+}{N}CH$), 5.43—5.79 (m, $\overset{+}{N}CH_2$), 6.10 (s, NMe), 6.64 (s, $\overset{+}{N}Me$), 7.38 (t, *J* 8 Hz, $\overset{+}{N}CH_2CH_2$), and 9.06 (s, CMe_3).

Equilibration of the *cis*- (23d) and *trans*- (24d) isomers of the amine gave a product in which only the *cis*-isomer could be detected.

1-*Methyl*-1,2,5,6-*tetrahydropyridinio*(*pivaloyl*)*methanide* (22e). *Formation of* cis-1-*methyl*-2-*pivaloyl*-3-*vinylpyrrolidine* (23e). The ylide (22e) (500 mg) was heated under reflux in benzene (50 ml) for 4 h. Filtration and evaporation gave the cis-*amine* (23e) (420 mg) as an oil (Found: $M^{+\bullet}$, 195. $C_{12}H_{21}NO$ requires *M*, 195); $\nu_{max.}$ 1 700 cm^{-1}; τ_A 5.16, τ_B 5.13, τ_X 4.32 (ABX system, J_{AB} 2, J_{AX} 17, J_{BX} 10 Hz, $CH_X{=}CH_AH_B$), 6.51 (d, *J* 8.5 Hz, NCHCO), 6.76—8.48 (m, NCH_2CH_2CH), 7.80 (s, NMe), and 8.89 (s, CMe_3). The *picrate* had m.p. 138—139 °C (Found: C, 51.1; H, 5.9; N, 13.4. $C_{18}H_{24}N_4O_8$ requires C, 50.9; H, 5.8; N, 13.2%).

Equilibration of the *cis*- (23e) and *trans*- (24e) isomers of the amine gave a mixture of the *cis*- (NMe at τ 7.80) and *trans*- (NMe at τ 7.70) amines in the ratio 1 : 1.

Benzoyl-(2,5-*dihydrothiophenio*)*methanide* (53). *Formation of* 2-*Benzoyl*-5-*phenyl*-2H-1,3-*oxathiole* (55).—The ylide (53) (500 mg) was refluxed in benzene (50 ml) for 1 h. Filtration and evaporation gave the *oxathiole* derivative (55) (300 mg) which crystallised from light petroleum as yellow prisms, m.p. 94—95 °C (Found: C, 71.7; H, 4.8; S, 12.0; $M^{+\bullet}$, 268.0559. $C_{16}H_{12}SO_2$ requires C, 71.6; H, 4.5; S, 11.9%; *M*, 268.0558); $\lambda_{max.}$ 241 (ε 18 500), 295 (ε 7 950), 313 (ε 8 300), and 402 nm (ε 1 500); $\nu_{max.}$ 1 695 and 1 595 cm^{-1}; τ 2.08 (dd, *J* 2, 7.5 Hz, 2 *ortho*-H of PhCO), 2.37—2.76 (m, 8 aryl-H), 2.99 (s, C=CH–S), and 4.17 (s, OCHS).

The oxathiole (55) (1.1 g) was refluxed with Raney nickel (from 15 g Ni–Al alloy) in methanol for 15 h. The mixture was filtered, the solvent evaporated, and the residue chromatographed (silica gel–$CHCl_3$) to give products identified as: (*i*) 1-phenylethanol (56) (300 mg); (*ii*) 1,4-diphenyl-3-oxapentane (57) (75 mg) (Found: $M^{+\bullet}$, 226.1358. $C_{16}H_{18}O$ requires *M*, 226.1358); τ 2.72—2.82 (m, 2 × Ph), 5.62 (q, *J* 7 Hz, OC*H*Me), 6.52 (t, *J* 7.5 Hz, OCH_2CH_2), 7.14 (t, *J* 7.5 Hz, OCH_2CH_2), and 8.58 (d, *J* 7 Hz, CH*Me*); and (*iii*) both diastereoisomers of 1,4-diphenyl-1-hydroxy-3-oxapentane (58) (200 mg) (Found: $M^{+\bullet}$, 242.1309. $C_{16}H_{18}O_2$ requires *M*, 242.1307); $\nu_{max.}$ 3 510 cm^{-1}; τ 2.60—2.80 (m, 2 × Ph), 5.16 (t, *J* 8.5 Hz, $HOCHCH_2$, isomer A) 5.20 (t, *J* 8.5 Hz, $HOCHCH_2$, isomer B), 5.55 (q, *J* 6.5 Hz, OC*H*Me, isomer A), 5.60 (q, *J* 6.5 Hz, OC*H*Me, isomer B), 6.46—6.82 (m, OCH_2), 7.09 (br s, OH), and 8.53 (d, *J* 6.5 Hz, CH*Me*).

Base Catalysed Rearrangement of trans-*Cinnamyldimethylphenacylammonium Bromide* (36a). *Formation of Diastereoisomers A and B of* 2-*Dimethylamino*-1,3-*diphenylpent*-4-*en*-1-*one* [(38a) *and* (39a)].—Cold aqueous sodium hydroxide (20 ml, 2%) was added to a stirred solution of the salt (36a) (500 mg) in chloroform (30 ml) at 0 °C and the mixture stirred for 5 min. The organic layer was separated, dried (Na_2SO_4), and evaporated. The n.m.r. spectrum of the residue indicated that it was a mixture of diastereoisomers A (38a) (NMe_2 at τ 7.60) and B (39a) (NMe_2 at τ 7.80) of the [3,2] rearrangement product in a 5 : 1 ratio (*cf.* ref. 2).

cis-*Cinnamyldimethylphenacylammonium Bromide* (36b).—Dimethylphenacyl-(3-phenylprop-2-ynyl)ammonium bromide [2] (3.6 g) in methanol (50 ml) and a Pd–$BaSO_4$ catalyst (5%, 500 mg) were stirred in an atmosphere of hydrogen until the acetylenic salt had been reduced (H_2 uptake *ca.* 300 ml). The mixture was filtered and the filtrate evaporated; repeated crystallisation of the residue from methanol–ether gave the cis-*cinnamyl salt* (36b) (1.0 g), m.p. 146—147 °C (Found: C, 63.4; H, 6.4; N, 3.7; Br, 22.0. $C_{19}H_{22}BrNO$ requires C, 63.3; H, 6.15; N, 3.9; Br, 22.2%); $\nu_{max.}$ 1 685 cm^{-1}; τ 2.09 (d, *J* 7 Hz, 2 *ortho*-H of PhCO), 2.41—2.94 (m, 8 aryl-H), τ_A 3.03, τ_B 4.01, τ_X 5.15 [ABX_2 system, J_{AB} 12, J_{BX} 7.5 Hz, $CH_A{=}CH_BC(H_X)_2$], 4.26 (s, $COCH_2\overset{+}{N}$), and 6.44 (s, $\overset{+}{N}Me_2$).

Base Catalysed Rearrangement of cis-*Cinnamyldimethylphenacylammonium Bromide. Formation of Diastereoisomers A and B of* 2-*Dimethylamino*-1,3-*diphenylpent*-4-*en*-1-*one* [(39b) *and* (38b)].—Cold aqueous sodium hydroxide (25 ml, 1%) was added to a stirred solution of the *cis*-cinnamyl salt (36b) (230 mg) in chloroform (50 ml) at 0 °C and the mixture stirred at 0 °C for 5 min. The n.m.r. spectrum of the product indicated that it was a mixture of diastereoisomers A (39b≡38a) (NMe_2 at τ 7.60) and B (38b≡39a) (NMe_2 at τ 7.80) of the [3,2] rearrangement product in the ratio 2 : 1.

trans-*Cinnamyldimethyl*-(3,3-*dimethyl*-2-*oxobutyl*)-*ammonium Bromide* (36c).—*trans*-Cinnamyldimethylamine (8 g) and 1-bromo-3,3-dimethylbutan-2-one (9 g) in methyl cyanide (50 ml) gave the salt (36c) (13.5 g) which crystallised from methanol–ether as prisms, m.p. 180—181 °C (Found: C, 59.9; H, 7.7; N, 4.0; Br, 23.3. $C_{17}H_{26}BrNO$ requires C, 60.0; H, 7.7; N, 4.1; Br, 23.5%); $\nu_{max.}$ 1 710 cm^{-1}; τ 2.50—2.80 (m, Ph), τ_A 3.09, τ_B 3.65, τ_X 5.25 [ABX_2 system, J_{AB} 16, J_{BX} 7.5 Hz, $CH_A{=}CH_BC(H_X)_2$], 4.59 (s, $COCH_2\overset{+}{N}$), 6.44 (s, $\overset{+}{N}Me_2$), and 8.79 (s, CMe_3).

Base Catalysed Rearrangement of trans-*Cinnamyldimethyl*-(3,3-*dimethyl*-2-*oxobutyl*)*ammonium Bromide* (36c). *Formation of Diastereoisomers A and B of* 4-*Dimethylamino*-2,2-*dimethyl*-5-*phenylhept*-6-*en*-3-*one* [(38c) *and* (39c)].—Cold aqueous sodium hydroxide (50 ml, 4%) was added to a stirred mixture of the salt (36c) (700 mg) in water (15 ml) and ether (150 ml) and the mixture stirred for 1 h. The ether layer was separated, dried (Na_2SO_4), and evaporated to give a mixture (400 mg) of the diastereoisomers A and B of the amine, (38c) and (39c), in the ratio 9 : 1 (Found: $M^{+\bullet}$, 259.1884. $C_{17}H_{25}ON$ requires *M*, 259.1936); $\nu_{max.}$ 1 690 cm^{-1}; τ (CF_3CO_2H) 2.68—2.82 (m, Ph), 3.71 (dt, *J* 17, 10 Hz, CH–C*H*=CH_2), 4.46 (d, *J* 17 Hz, C*H*H=CH), 4.48 (d, *J* 10 Hz, CH*H*=CH), 4.79 (dd, *J* 3, 10 Hz, CHC*H*-CH), 6.08 (t, *J* 10 Hz, $Me_2\overset{+}{N}CHCH$), 6.82 (d, *J* 5 Hz, $\overset{+}{N}HMe$), 6.95 (d, *J* 5 Hz, $\overset{+}{N}HMe$), 8.86 (s, CMe_3, diastereoisomer B), and 9.12 (s, CMe_3, diastereoisomer A). The *picrate* had m.p. 166—167 °C (Found: C, 56.1; H, 6.0; N, 11.3. $C_{23}H_{28}N_4O_8$ requires C, 56.55; H, 5.8; N, 11.5%).

Cyclopent-2-*enyldimethylphenacylammonium Bromide* (42).—*NN*-Dimethylcyclopent-2-enylamine (9.8 g) and phenacyl bromide (17.5 g) in methyl cyanide (35 ml) gave the *salt* (42) (21 g) which crystallised from methanol–ether as prisms, m.p. 145—146 °C (Found: C, 58.1; H, 6.3; N, 4.3; Br, 25.7. $C_{15}H_{20}BrNO$ requires C, 58.1; H, 6.5; N, 4.5; Br, 25.8%); $\nu_{max.}$ 1 690 cm^{-1}; τ 2.01 (dd, *J* 2, 8 Hz, 2 *ortho*-H of PhCO), 2.20—2.54 (m, 3 aryl-H), 3.29—3.36 (m, CH=C), 3.97—4.08 (m, C=CH), 4.64—4.81 (m, $CH\overset{+}{N}$), 4.93 (s, $COCH_2\overset{+}{N}$), 6.62 (s, $\overset{+}{N}Me_2$), and 7.30—7.67 (m, CH_2CH_2).

Base Catalysed Rearrangement of Cyclopent-2-*enyldimethylphenacylammonium Bromide* (42). *Formation of* α-

(*Cyclopent-2-enyl*)-α-(*dimethylamino*)*acetophenone* (43).—Cold aqueous sodium hydroxide (25 ml, 2%) was added to a stirred solution of the salt (42) (600 mg) in chloroform at 0 °C. The mixture was stirred for 3 min at 0 °C, and the chloroform layer separated, dried, and evaporated to give the *amine* (43) (300 mg) as a mixture of two diastereoisomers A and B in the ratio 1 : 2; $\nu_{max.}$ 1 680 cm^{-1}; τ 2.13 (m, 2 *ortho*-H of PhCO), 2.52—2.84 (m, 3 aryl-H), 4.16—4.38 (m, CH=CH of isomer A + C=CH of isomer B), 4.67 (dq, *J* 6, 2 Hz, HC=C*H*CH_2 of isomer B), 6.02 (d, *J* 10 Hz, NC*H*CO of isomer A), 6.10 (d, *J* 10 Hz, NC*H*CO of isomer B), 6.50—6.90 (br m, CH–C=C), 7.40—8.80 (m, CH_2CH_2C=), and 7.66 (s, NMe_2) (the ratio of diastereoisomers was changed to 1 : 1 by equilibration). The *methiodide* had m.p. 194—195 °C (Found: C, 51.9; H, 6.2; N, 3.7; I, 34.6. $C_{16}H_{22}INO$ requires C, 51.8; H, 6.0; N, 3.8; I, 34.2%).

1-*Phenacyltetrahydrothiophenium Bromide*.—Tetrahydrothiophen (10 g) and phenacyl bromide (12 g) in methyl cyanide (15 ml) gave the salt (14 g) which crystallised from methyl cyanide–ether as prisms, m.p. 117—118 °C (lit.,[21] 119—120 °C); $\nu_{max.}$ 1 670 and 1 595 cm^{-1}; τ(CF_3CO_2H) 2.00 (d, *J* 8 Hz, 2 *ortho*-H of PhCO), 2.21—2.58 (m, 3 aryl-H), 4.61 (s, $COCH_2\overset{+}{S}$), 6.02—6.43 (m, $CH_2\overset{+}{S}CH_2$), and 7.29—7.77 (m, CH_2CH_2).

Benzoyl(*tetrahydrothiophenio*)*methanide* (60).—Addition of aqueous sodium hydroxide (25 ml, 32%) to a solution of 1-phenacyltetrahydrothiophenium bromide (7 g) in water (80 ml) gave the ylide (60) (4.2 g), m.p. 85—87 °C (lit.[22] 82—85 °C) (Found: $M^{+\bullet}$, 206.0761. Calc. for $C_{12}H_{14}OS$: *M*, 206.0766); $\nu_{max.}$ 1 580 cm^{-1}; τ 2.20—2.30 (m, 2 *ortho*-H of PhCO), 2.69—2.77 (m, 3 aryl-H), 5.73 (br s, $\overset{-}{C}H\overset{+}{S}$), τ_A 6.58, τ_B 6.97, τ_X 7.44, τ_Y 8.14 (AA'BB'XX'YY' system, J_{AB} 12, J_{AX} 6.5, J_{AY} 6.5, J_{BX} 6, J_{BY} 6 Hz, $CH_2CH_2CH_2CH_2$). The ylide (60) (1.2 g) was refluxed in benzene for 24 h; evaporation and washing the residue with ether gave *trans*-1,2,3-tribenzoylcyclopropane (61) (400 mg) as the ether-insoluble product.

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