Concertedness in [2,3] Anionic Sigmatropic Rearrangements

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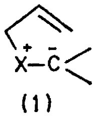
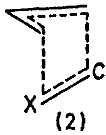
Summary The relative rates of the [2,3] sigmatropic rearrangement of the six-membered cyclic allylic ylides (**4a**—**e**) in comparison to acyclic counterparts provide positive evidence for bonding in the transition state consistent with a concerted reaction mechanism; the five-membered allylic ylides (**6a** and **b**) rearrange by different processes.

The transition state for the [2,3] sigmatropic rearrangement of ammonium ylides and related systems (**1**) is generally believed[1] to have the stereochemistry shown in formula (**2**). On the basis of the retardation of reaction rate in bicyclic ammonium ylides[2] it is possible to discount a reaction mechanism involving a betaine intermediate [*e.g.* (**3**)], but this result does not provide positive proof of transition-state bonding since, for example, a diradical transition state would be destabilised by analogous steric influences. A more direct proof of bonding requirements in the transition state is available from the study of the rearrangement reactions of the cyclic allylic ylides (**4**) and (**6**).†


(1)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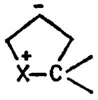
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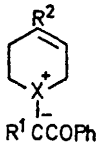
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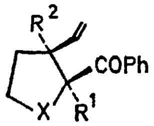
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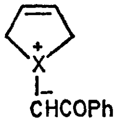
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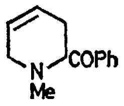
(7)

In (4) and (5)
a; X = NMe, $R^1 = R^2 = H$
b; X = NMe, $R^1 = H, R^2 = Et$
c; X = NMe, $R^1 = H, R^2 = CMe_3$
d; X = NMe, $R^1 = Ph, R^2 = H$
e; X = S, $R^1 = R^2 = H$

a; X = NMe
b; X = S

The six-membered cyclic ylides (**4a**—**d**) rearranged in boiling benzene to give the corresponding *cis*-2-benzoyl-3-vinylpyrrolidines (**5a**—**d**). The *cis*-stereochemistry of these products was established by equilibration experiments using methanolic sodium methoxide; both (**5a**) and (**5b**) gave some *trans*-isomer under these conditions [equilibrium ratios *cis*:*trans*; (**5a**), 1:2, (**5b**) 2:1] but (**5c**) did not give a second isomer. These results are only consistent with a *cis*-relationship between the benzoyl and vinyl substituents and an analogous stereochemistry is assigned to (**5d**). The corresponding six-membered sulphonium ylide (**4e**) rearranged at 0° to give almost entirely the *cis*-tetrahydrothiophen derivative (**5e**) together with a little of the *trans*-isomer (25:1 ratio); again the *cis*-stereochemistry is consistent with the equilibrium ratio of diastereomers (*cis*: *trans*, 1:19). The *cis*-stereochemistry of the products (**5**)

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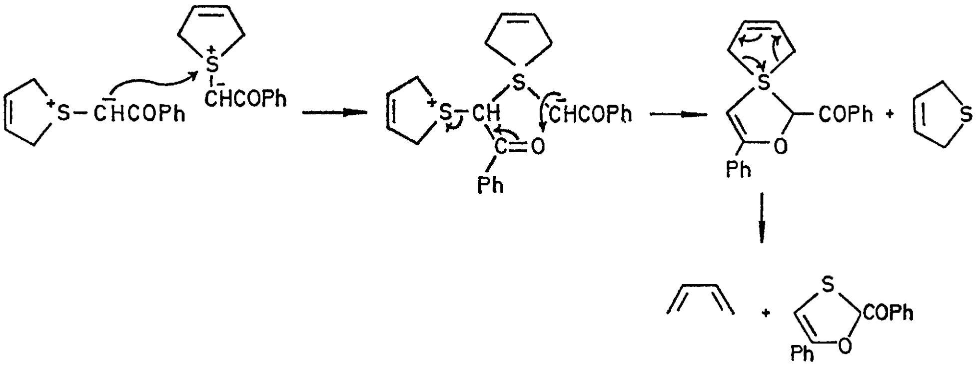
† All these ylides, except (**4e**), are crystalline compounds, prepared by the reaction of the corresponding onium salts with aqueous sodium hydroxide at 0°. All were characterised by their spectroscopic properties, mass spectra and by regeneration of quaternary salts on treatment with acid.

is difficult to explain, since diastereomer ratios for the products of [2,3] rearrangements may usually be accounted for[1] by considering steric interactions in the transition state. This is not the case for the reactions (**4**) → (**5**) and this point is being further investigated.‡

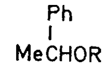


(8)

Scheme

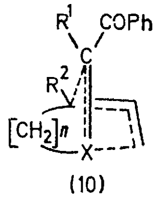
The five-membered cyclic ylide (**6a**) rearranges in boiling benzene to give only the tetrahydropyridine derivative (**7**), the product of a [1,2] rearrangement. The dihydrothiophen derivative (**6b**), in boiling benzene, undergoes a more complex reaction to give the thioxolen derivative (**8**), 2,5-dihydrothiophen, and buta-1,3-diene, the structure (**8**) being based upon spectroscopic data and reduction with Raney nickel to give the products (**9a**—**c**). The formation of (**8**) may be rationalised as shown in the Scheme, and analogous reactions involving tetracovalent sulphur intermediates have been reported.[3]

It is evident from these results that the rates of the [2,3] rearrangements of the ylides (**4**) are considerably retarded as compared with acyclic ylides. This is consistent with the bonded transition state (**10**) in which the π-system must suffer considerable twisting distortion, and this would not be the case for a mechanism in which the two participating π-electron systems were not bonded together. The results obtained in this study are therefore complementary to those described in our earlier papers,[2] and together they provide positive evidence for a bonded transition state and a concerted [2,3] sigmatropic process.


$\overset{\text{Ph}}{\text{MeCHOR}}$

(9)

a; R = H
b; R = CH_2CH_2Ph
c; R = CH_2CHOH Ph



(10)

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‡ Possibilities include secondary orbital interactions or an alternative reaction pathway of consecutive [1,4] and [3,3] rearrangements. The observed reaction temperature (80°) is therefore the minimum required for the [2,3] rearrangement of the ylides (**4a**—**d**).

[1] V. Rautenstrauch, *Chem. Comm.*, 1970, 526; J. E. Baldwin and J. E. Patrick, *J. Amer. Chem. Soc.*, 1971, **93**, 3556; B. M. Trost and R. F. Hammen, *J. Amer. Chem. Soc.*, 1973, **95**, 963.

[2] S. Mageswaran, W. D. Ollis, I. O. Sutherland, and Y. Thebtaranonth, *Chem. Comm.*, 1971, 1494; W. D. Ollis, I. O. Sutherland, and Y. Thebtaranonth, following communication.

[3] B. M. Trost, R. LaRochelle, and R. C. Atkins, *J. Amer. Chem. Soc.*, 1969, **91**, 2175; B. M. Trost, W. L. Schinski, and I. B. Mantz, *ibid.*, p. 4320; B. M. Trost, W. L. Schinski, F. Chen, and I. B. Mantz, *ibid.*, 1971, **93**, 676; B. M. Trost and S. D. Ziman, *ibid.*, 3825.