Stereochemistry of the Thermal Electrocyclic Ring Opening of α-Cyano-*cis*-stilbene Oxide

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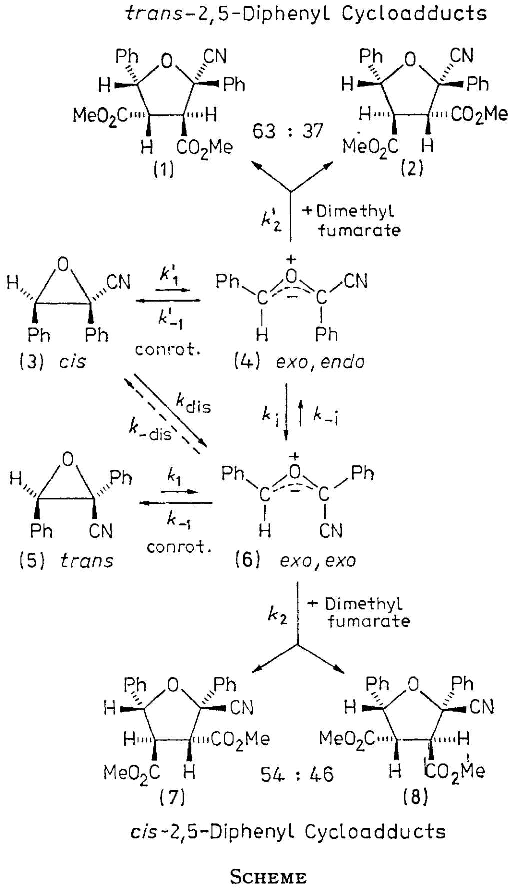
Summary Whereas α-cyano-*trans*-stilbene oxide undergoes conrotatory ring opening to a carbonyl ylide which combines stereospecifically with dimethyl fumarate, the *cis*-oxiran produces mixtures of stereospecific and non-stereospecific cycloadducts depending on the dimethyl fumarate concentration; a geometrical isomerisation of

the carbonyl ylide formed by conrotation and, probably, a disrotatory ring opening of the oxiran are responsible for the nonstereospecific course.

α-CYANO-*trans*-STILBENE OXIDE (**5**) combines at 130 °C *via* the *exo,exo*-diphenyl-substituted carbonyl ylide (**6**) with dimethyl fumarate to give the *cis*-2,5-diphenyl cycloadducts (**7**) and (**8**) exclusively.[1] In contrast, the stereomixed cycloaddition of the *cis*-oxiran (**3**) in molten dimethyl fumarate at 140 °C produces 43% of the *trans*-2,5-diphenyl adducts (**1**) and (**2**) in addition to 57% of (**7**) and (**8**)[1] (Scheme). Whereas the electrocyclic reaction (**5**) ⇌ (**6**) obeys clearly the orbital symmetry-allowed conrotation, the assumption of the same steric course for (**3**) would imply that the *exo,endo*-diphenyl substituted carbonyl ylide (**4**) is only partially trapped by fumaric ester (k'_2D and k_i of similar magnitude, D = concentration of the intercepting dimethyl fumarate); the competing isomerisation (**4**) → (**6**) is followed by cyclo-addition to give (**7**) + (**8**). The *endo* phenyl group in (**4**) causes van der Waals strain and steric inhibition of resonance, thus giving the *exo,exo* isomer (**6**) an energetic advantage.



SCHEME

We present evidence that at least *two reaction paths* are responsible for the formation of the nonstereospecific products (**7**) and (**8**) from (**3**).

In the reaction of the *cis*-oxiran (**3**) through the *exo,endo* carbonyl ylide (**4**), the direct cycloaddition to dimethyl fumarate to give stereospecifically *trans* adducts (**1**) + (**2**) is a *second-order* process, whereas the formation of the *cis* adducts (**7**) + (**8**) should be of *first order*, independent of the excess concentration of the dipolarophile ($k_2D >> k_{-i}$); the product-determining step is the rotation (**4**) → (**6**) followed by a fast 1,3-dipolar cycloaddition.

$$\frac{cis\text{-2,5-Diphenyl cycloadducts}}{trans\text{-2,5-Diphenyl cycloadducts}} = \frac{k_i}{k_2'}\frac{1}{D} \qquad (1)$$

We treated the *cis*-oxiran (**3**) with variable concentrations of fumaric ester in *o*-dichlorobenzene at three temperatures. After removal of the excess of dimethyl fumarate, the *cis*:*trans* ratio of the cycloadducts can be determined by n.m.r. analysis without separation of the mixture.

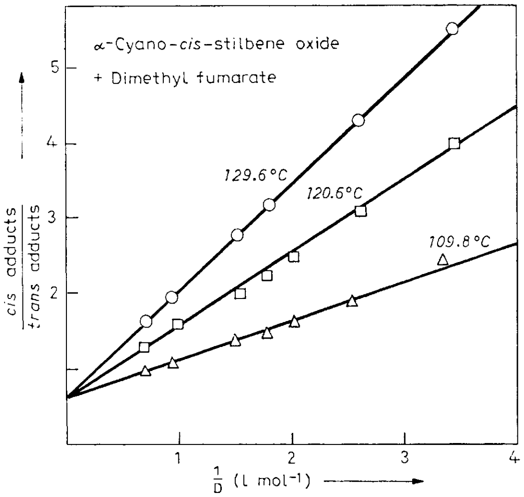


FIGURE 1. Reaction of 0·041 mol l^{-1} *cis*-oxiran (**3**) with 0·30—1·42 mol l^{-1} dimethyl fumarate in *o*-dichlorobenzene. Dependence of cycloadduct ratio, [(**7**) + (**8**)]/[(**1**) + (**2**)], on reciprocal concentration of fumaric ester.

The linear relations in Figure 1 prove that second-order formation of (**1**) + (**2**) and first-order formation of (**7**) + (**8**) are indeed competing processes of an intermediate. However, the straight lines do not go through the origin as required by equation (1), but rather cut the ordinate at a value of 0·56. Even the fictitious, infinitely high concentration of dimethyl fumarate ($1/D = 0$) traps only 64% of (**4**), whereas 36% of (**4**) escapes and furnishes 36% of (**7**) + (**8**); 36/64 = 0·56. The conclusion is imperative: only 64% of the total material becomes exposed to the competition of unimolecular isomerisation and bimolecular cycloaddition. The remaining 36% of the nonstereospecific *cis* adducts must be formed in a second pathway for which several possibilities are considered.

(A) If the transition-state energy of the ring opening (**3**) → (**4**) exceeds the barrier height of the rotation (**4**) → (**6**), it is conceivable that 36% of (**4**) is 'rotationally excited,' passes adiabatically the rotational barrier, and ends up as the favoured *exo,exo* carbonyl ylide (**6**) ('overshooting').†

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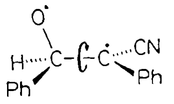
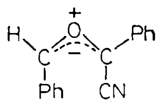
† This possibility was suggested by Professor John D. Roberts, California Institute of Technology, to R.H. in June 1975.



(9)



(10) *endo, exo*

(B) CO bond dissociation of (**3**), rotation about the CC bond of (**9**), and recyclisation should lead to the *trans*-oxiran (**5**). Apart from the higher bond energy of σ C–O compared with σ C–C, the intermediate (**9**) is lacking the octet stabilisation of the carbonyl ylide.

(C) Besides the 64% conversion (**3**) → (**4**), another conrotatory electrocyclic process furnishing the *endo,exo* carbonyl ylide (**10**) could take place to the extent of 36%. If (**10**) is not interceptable by dimethyl fumarate (a more active dipolarophile was not found), but undergoes fast rotation to the *exo,exo* isomer (**6**), then this route to the *cis*-diphenyl adducts (**7**) + (**8**) would by-pass (**4**).‡ Considering the stronger van der Waals overlap of Ph and CN as *endo* substituents in (**10**), compared with Ph and H in (**4**), a **36**: **64** ratio of (**10**) and (**4**) from (**3**) is unlikely.

(D) The most probable second pathway from (**3**) to (**6**) appears to be direct *disrotatory* ring opening. Steady-state treatment of the supplemented kinetic system of the Scheme provides equation (2) which is still a linear function, but one with an intercept given by k_{dis}/k'_1. This ratio amounts to 0·56, *i.e.*, the symmetry-allowed conrotation is not even twice as fast as the symmetry-forbidden disrotation.

$$\frac{cis\text{ Adducts}}{trans\text{ Adducts}} = \frac{k_{\mathrm{dis}}}{k'_1} + \frac{k_1k'_1 + k_{\mathrm{dis}}k_{-1} + k_1k_{\mathrm{dis}}}{k'_1k'_2}\,\frac{1}{D} \qquad (2)$$

On the other hand, the ring opening of the *trans*-oxiran (**5**) occurs by conrotation exclusively. The *cis*-oxiran (**3**) partially suffers disrotation, because it leads to a more stable carbonyl ylide than that arising from conrotation. We visualize a fairer comparison of orbital symmetry-allowed and -forbidden pathways on considering the formation of one and the same carbonyl ylide (**6**) from the *trans*-oxiran (**5**) by conrotation and from the *cis*-oxiran (**3**) by disrotation. The transition states of ring opening should structurally be more closely related to the high-energy intermediates than to the oxirans.

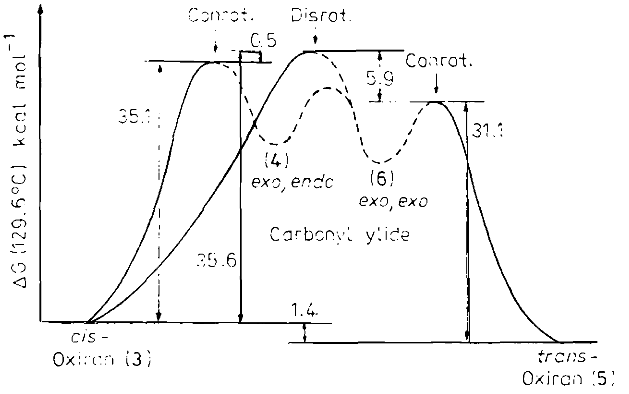


Figure 2

Activation free energies[2] are combined with the stereochemical dichotomy in Figure 2 and afford 5·9 kcal mol^{-1} as the energy difference of the two transition states leading to (**6**); this corresponds to a rate ratio of **1600**: 1 for allowed and forbidden processes, a somewhat smaller ratio than found for other electrocyclic reactions.[3] The nature of the symmetry-forbidden process, concerted or stepwise, has not been established, either here or in any other case. Two structurally constrained bicyclic oxirans undergo thermal disrotation at 100 °C.[4]

(*Received*, *7th February* 1977; *Com.* 112.)

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‡ We dealt with path (C) in internal discussions, but took it more seriously when Professor Frank B. Mallory, Bryn Mawr College, U.S.A., independently drew our attention to it in June 1975. Mechanism (C) is still not strictly refuted.

[1] A. Dahmen, H. Hamberger, R. Huisgen, and V. Markowski, *Chem. Comm.*, 1971, 1191.

[2] V. Markowski and R. Huisgen, preceding communication.

[3] G. A. Doorakian and H. H. Freedman, *J. Amer. Chem. Soc.*, 1968, **90**, 5310, 6896; A. Dahmen and R. Huisgen, *Tetrahedron Letters*, 1969, 1465; R. Huisgen, *Chimica e Industria*, 1969, **51**, 963; L. M. Stephenson and J. I. Brauman, *Accounts Chem. Res.*, 1974, **7**, 65.

[4] E. F. Ullmann and J. E. Milks, *J. Amer. Chem. Soc.*, 1964, **86**, 3814; E. F. Ullmann and W. A. Henderson, *ibid.*, 1966, **88**, 4942; D. R. Arnold and L. A. Karnischky, *ibid.*, 1970, **92**, 1404.