Conrotatory Ring Opening of Cyanostilbene Oxides to Carbonyl Ylides

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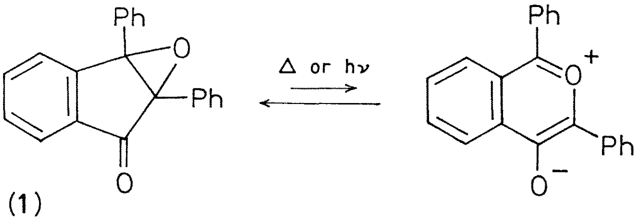
Summary The structure of the cycloadducts from 2-cyano-*trans*-stilbene oxide with acetylenic and olefinic dipolarophiles confirm the electrocyclic C–C ring scission of the oxiran while the cycloadditions of 3 cyano-*trans*- and *cis*-stilbene oxide to dimethyl fumarate establish the conrotatory course.

WOODWARD and HOFFMANN[1] predicted thermal conrotation and photochemical disrotation for the conversion of cyclopropyl anions into allyl anions. Both predictions have been verified for derivatives of isoelectronic aziridine.[2]



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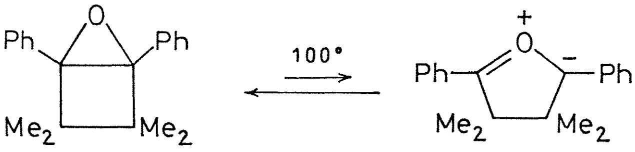
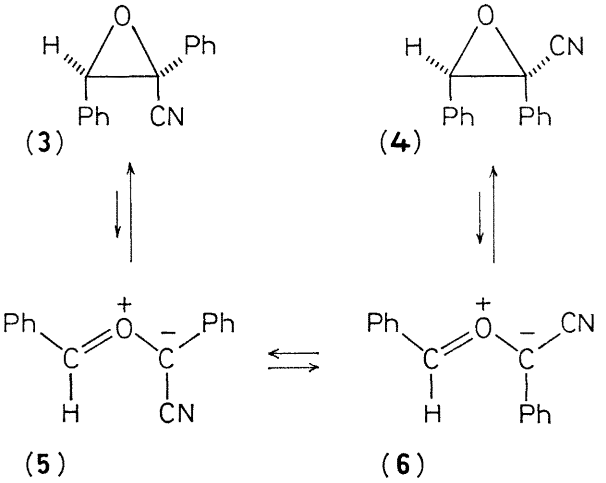


(2)

The ring-opened species is an azomethine ylide, a hetero-allyl anion, which undergoes 1,3-dipolar cycloadditions; the investigation of such cycloadducts indicated the steric course of aziridine ring opening.

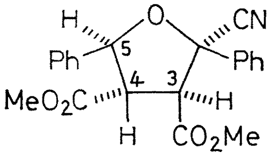
Oxiran is also isoelectronic with cyclopropyl anion. Nevertheless, it is not without interest to establish *conrotation* also for the thermal equilibration of oxirans with small concentrations of carbonyl ylides.[3] The only examples described which might allow a decision on the mode of opening are the orbital symmetry-forbidden ring-openings of (1)[4] and (2).[5]



(3) (4) (5) (6)

We report on the behaviour of the cyanostilbene oxides (3) and (4). The product of interaction of desyl chloride and KCN[6] was separated by fractional crystallisation into (3) and (4). Configurations are assigned by conversion into the known carboxamido-*trans*- and -*cis*-stilbene oxide.[7] At 160° the equilibrium mixture contains 83% of (3) and 17% of (4).

Heating of cyano-*trans*-stilbene oxide (3) with an excess of dimethyl fumarate (45 h, 130°) gave 99% of a mixture of two 1:1-adducts which consisted of 54% of (7) and 46% (8) according to n.m.r. analysis. These two adducts can be derived from the two possible orientation complexes for concerted addition of the carbonyl ylide (5) to the dipolarophile. The corresponding reaction of cyano-*cis*-stilbene oxide (4) with dimethyl fumarate afforded the tetrahydrofurans (9) and (10) which are derived from the carbonyl ylide (6), in addition to (7) and (8). The four adducts were separated by thick-layer chromatography and fractional crystallisation; they were characterised by elemental analyses and spectra. Kinetic control of the cycloaddition is established by the thermostability of the adducts at 150°.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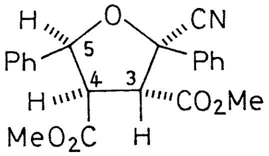
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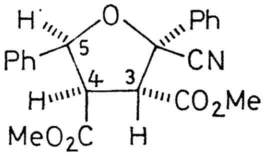
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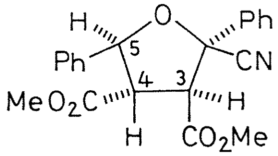
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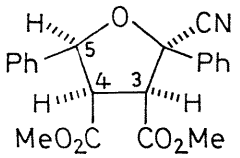
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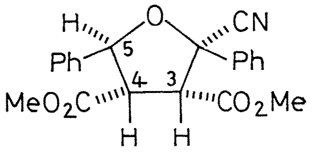

(12)

The products suggest a conrotatory opening of the oxiran ring in (3) and (4). In the case of the ylide (6), dimethyl fumarate as a dipolarophile is just active enough to suppress partially the stereoisomerisation to the sterically favoured isomer (5) in which both phenyls are *exo*-located. The geometrical isomerisation (6) → (5) should have a higher temperature coefficient than the 1,3-dipolar cycloaddition of (6) because concerted additions of this type are marked by large negative entropies of activation.[8] Indeed, the part of the reaction of (4) which goes *via* (6) → (5) to (7) and (8) decreases with the lowering of temperature (Table 1) from 57 to 31%.

TABLE 1

Reaction of the oxirans (3) *and* (4) *with dimethyl fumarate*

Oxiran	% Reacted (conditions)	Composition of the cycloadduct in % (7)	(8)	(9)	(10)
		via (5)		*via* (6)	
(3)	99 (45 h, 130°)	54	46		
(4)	95 (120 h, 140°)	33	24	27	16
(4)	80 (130 h, 130°)	29	20	32	19
(4)	87 (14 d, 120°)	26	18	35	21
(4)	26 (30 d, 100°)	18	13	44	25

The assignment of configurations for adducts (7)—(10) rests on the *trans*-relationship of the ester groups in 3- and 4-positions; the structure of *cis*–*trans*-isomeric olefinic dipolarophiles is always retained in 1,3-dipolar cycloadditions.[8] The corresponding *cis*-3,4-diesters (11) and (12) which were wanted for spectral comparison were prepared from (3) and dimethyl maleate (45 h, 310°, 99% yield, ratio 65:35). N.m.r. spectra (CDCl$_3$, 60 MHz) of the ring protons of (7)—(12) are of the ABM type. Use of the computer program LAME allowed the calculation of chemical shifts and coupling constants from the observed line positions by iteration. The values are listed in Table 2.

The most useful criterion for assigning configurations is that the ester methyl singlet moves to higher fields under the influence of a *cis*-phenyl group. The high τ values of 3-H and 4-H in the presence of a *cis-vic* phenyl group are equally characteristic. This is in accordance with known substituent effects in five-membered rings.[9] The conformational mobility of tetrahydrofurans deprives the coupling constants of their diagnostic value; *trans*-couplings can reach larger values than are found for *cis-vic* ring protons.

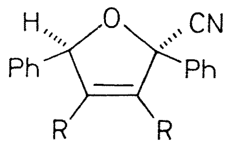
Some further cycloadditions of the oxiran (3) confirm the C–C ring opening to give the azomethine ylide (5) as reactive species.

After heating (3) with an excess of acetylene in cyclohexanone (24 h, 170°), 2,5-diphenylfuran (15) was isolated in 73% yield and found to be identical with an authentic sample. Compound (15) was obviously formed by loss of HCN from the primary adduct (13). The reaction of (3) with dimethyl acetylenedicarboxylate (60 h, 120°) allowed the isolation of the 2,5-dihydrofuran derivative (14) in 37% yield.

TABLE 2

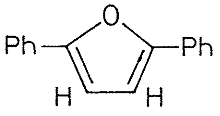
N.m.r. data (CDCl$_3$, 60 *MHz*) *of the tetrahydrofuran derivatives* (7)—(12)

Cycloadduct	τ 3-CO$_2$Me	4-CO$_2$Me	3-H	4-H	5-H	$J_{3,4}$	$J_{4,5}$	$J_{3,5}$
(7)	6·87	6·21	5·70	6·12	4·48	6·72 t	8·91 t	−0·17
(8)	6·28	6·93	5·95	5·92	4·37	7·07 t	8·29 c	−0·14
(9)	6·60	6·73	5·62	6·02	4·10	10·59 c	9·02 c	−0·41
(10)	6·37	6·45	6·10	6·16	4·67	11·24 t	10·14 t	−0·71
(11)	6·78	6·83	5·96	6·01	4·38	8·48 c	8·52 c	−0·74
(12)	6·19	6·29	6·26	6·55	4·28	10·34 c	8·33 t	−0·52



(13) R = H

(14) R = CO_2Me



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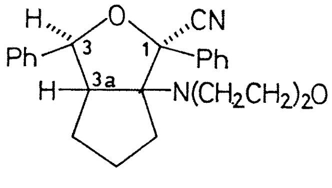

(16)

Cycloadditions of the carbonyl ylide derived from (3) to electron-deficient or electron-rich C–C double bonds also occurred smoothly (Table 3). The phenyl groups occupy *cis*-positions in all the adducts, as established by their n.m.r. spectra. The direction of addition to 1-morpholinocyclopentene is shown by the doublet at τ 4·32 for 3-H in (16) ($J_{3,3a}$ 7·6).

TABLE 3

*Cycloadditions of cyano-*trans*-stilbene oxide* (3) *to* C–C *double bonds*

Dipolarophile	Conditions	Adduct M.p.	Adduct % Yield
Norbornene	48 h, 120°	171—173°	80
Dimethyl fumarate	45 h, 130°	78—82° 108·5—110°	99
Dimethyl maleate	45 h, 130°	109—112° 138·5—140°	99
1-Pyrrolidinocyclopentene	36 h, 110°	146—147°	45
1-Morpholinocyclopentene	100 h, 110°	190—193°	29
N-Phenylmaleimide	48 h, 130°	168·5—169·5° 158—159°	76

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