Cycloadditions of a Carbonyl Ylide from 2,3-Dicyano-2,3-diphenyloxiran

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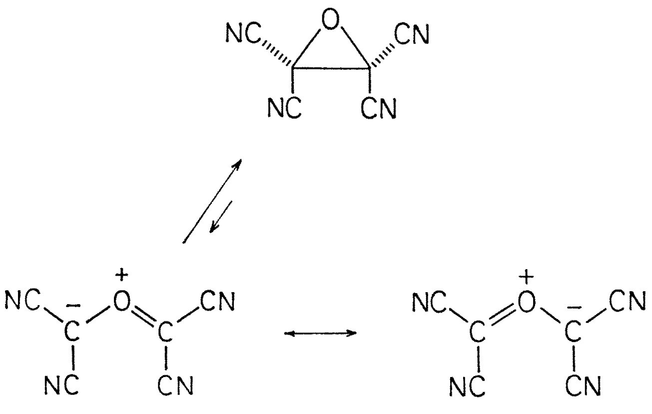
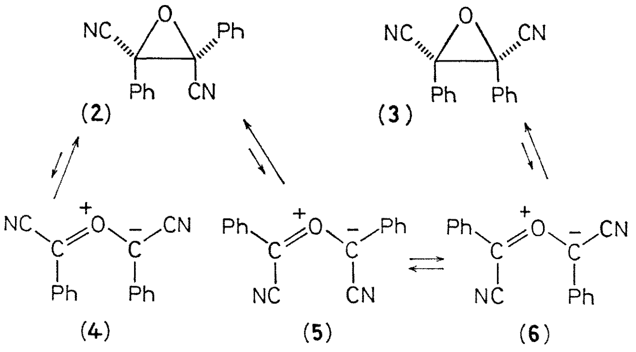
Summary *trans*- and *cis*-Dicyanostilbene oxides establish an equilibrium at 100—120° *via* carbonyl ylides, the carbonyl ylide intermediate is a 1,3-dipole and undergoes cycloadditions with a variety of acetylenic and olefinic dipolarophiles

LINN *et al* [1-3] discovered the cycloadditions of tetracyanoethylene oxide to olefins, acetylenes, and aromatic compounds The active reagent which had been considered to be a hybrid of biradical and zwitterionic species[3] must now be regarded as a carbonyl ylide (1),[4] an octet-stabilised 1,3-dipole Electrocyclic opening of the oxiran ring does not need such an excessive stabilisation of negative charge as is provided by the four cyano-groups in (1)



(1)

trans-2,3-Dicyano-2,3-diphenyloxiran (2)[5] epimerises at 100° in dioxan to the *cis*-isomer (3) until an 85 5 14 5 equilibrium is reached, the first-order reaction has $t_{\frac{1}{2}} = 87$ min at 100°, as measured by n m r spectroscopy Further measurements at 110 and 120° gave $\Delta H^{\ddagger} = 27$ 2 kcal mol^{-1} and $\Delta S^{\ddagger} = -8$ e u for the net process (2) → (3) The *cis*-oxiran (3) was isolated,† dipole moments (benzene, 25°) of 0 87 D for (2) and 6 5 D for (3) established the structures A configurational assignment of (2) recently published[6] proved erroneous



SCHEME

The expectation that the isomerisation of the oxirans proceeded *via* the carbonyl ylides (5) and (6) was confirmed by their 1,3-dipolar activity in undergoing cycloadditions at temperatures > 100° Heating (2) with acetylene in cyclohexanone gave 91% of the crystalline 2 5-dihydrofuran derivative (7), the singlet at τ 3 56 ($CDCl_3$) for the 3- and 4-H proved that C–C ring scission of the oxiran had occurred. The action of methanolic HCl converted (7) into 97% of (8) which possessed equivalent ester methyls at τ 6 22 ($CDCl_3$) The corresponding dicarboxylic acid (9) lost carbon dioxide and hydrogen at 230° to yield 2,5-diphenylfuran (12, 84%) which was shown identical with an authentic specimen The smooth conversion of (9) into the anhydride (13) by

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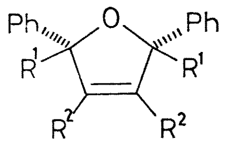
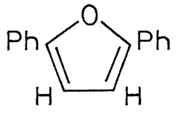
† Satisfactory C,H,N analyses and osmometric molecular weights were obtained for all new compounds described here

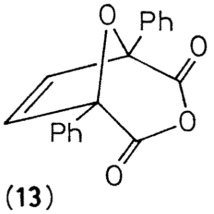
dicyclohexylcarbodi-imide at 20° is consistent with *cis*-carboxyl functions.



	R¹	R²
(**7**)	CN	H
(**8**)	CO_2Me	H
(**9**)	CO_2H	H
(**10**)	CN	CO_2Me
(**11**)	CO_2Me	CO_2Me

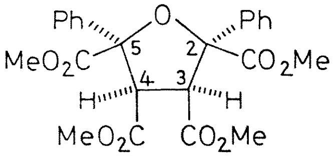


(**12**)

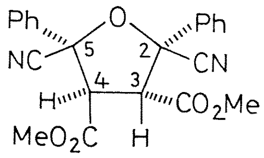


(**13**)

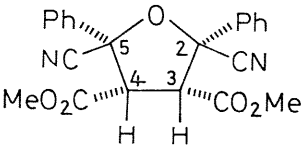
Dimethyl acetylenedicarboxylate combined with (2) in 12 h at 135° to give 84% of the adduct (10). The tetracarboxylic ester (11) obtained from (10) by the action of HCl in boiling methanol provided (14) on catalytic hydrogenation. Pairs of identical ester groups in the ^{1}H n.m.r. spectrum at τ 6·18 and 6·22 suggest structure (14) which has a plane of symmetry and probably is an all-*cis*-tetraester. Thus, the primary adduct (10) must contain *cis*-cyano-groups.



(**14**)



(**15**)



(**16**)

The reaction of (2) with dimethyl fumarate (24 h, 130°) gave 85% of (15); its configuration is established by the n.m.r. spectrum ($CDCl_3$) with signals for 4-CO_2CH_3 at τ 6·25, 3-CO_2CH_3 at 6·72 and an AB-spectrum for 3- and 4-H at 5·25 and 5·75 ($J_{3,4}$ 10·5 Hz). On the other hand, the dimethyl maleate adduct (16)[‡] showed a singlet at τ 5·50 for 3- and 4-H; the high τ-value of 6·66 for the singlet of 3- and 4-CO_2CH_3 is explained by a *cis*-relationship of ester groups and phenyls in (16).

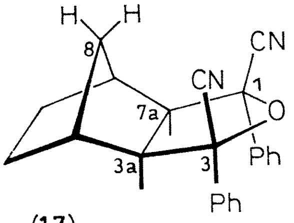
Thus, the four dipolarophiles so far mentioned combined with the *cis*-dicyanocarbonyl ylide (5) to give the adducts (7), (10), (15), and (16). The preference of (5) over the geometrical isomer (4) in the Scheme is the result of the lower van der Waals strain in (5) (bulky groups in *exo*-position) in analogy with our studies on disubstituted azomethine ylides from aziridines.[7]

An important finding is that the *cis*-oxiran (3) reacted with the four dipolarophiles mentioned to yield the same cycloadducts with *cis*-cyano-groups in the 2- and 5-positions. Thus, isomerisation of the *trans*-dicyano-substituted carbonyl ylide (6) to the *cis*-form (5) appears to precede the 1,3-dipolar cycloaddition. The assumption of a *conrotatory* opening of the oxiran ring in the Scheme is based on analogy with the behaviour of the monocyanostilbene oxides described in the following communication. Conrotation has been established rigorously for the aziridine → azomethine ylide conversion;[8] there also the isomerisation of the azomethine ylide can be faster than cycloadditions to less active dipolarophiles.[9]

The oxirans (2) and (3) combine *via* the carbonyl ylide (5) with a variety of acetylenic and olefinic dipolarophiles. The synthetic potential of this route to 2,5-dihydrofurans and tetrahydrofurans is high, since not only do the electron-deficient double and triple bonds of $\alpha\beta$-unsaturated carboxylic esters react, but also the electron-rich double bonds of vinyl ethers and enamines, giving rise to high yields of adducts (Table). The dihydro- and tetrahydro-furans were characterised by analyses and spectra.

Cycloadditions with 2,3-*dicyano*-trans-*stilbene oxide*

Dipolarophile	M.p. 2,5-Dihydrofurans	Yield (%)
Acetylene	109—110°	91
Diphenylacetylene	181—181·5°	80
Ethyl phenylpropiolate	140·5—141°	76
Methyl methylpropiolate	171—172°	64
Dimethyl acetylenedicarboxylate	159·5—160°	84
	Tetrahydrofurans	
Norbornene	302—304°	88
Norbornadiene	255—257°	89
trans-Stilbene	168—169°	84
1,1-Diphenylethylene	261—262°	23
Methyl cinnamate[‡]	185—185·5°	80
Dimethyl fumarate	133—134°	85
Dimethyl maleate[‡]	144—146°	65
Butyl vinyl ether	liquid	58
cis-β-Methoxystyrene	164—165°	75
2,3-Dihydrofuran	143—145° 190—191°	82
2,3-Dihydro-4*H*-pyran	170—171°	97
1-Pyrrolidinocyclopentene ..	210—212°	89
1-Morpholinocyclopentene ..	226—228°	81



(**17**)

In the tricyclic adduct (17) obtained with norbornene, 3a- and 7a-H show up as a 2H doublet at τ 6·76 in the n.m.r.

[‡] Experimental by Dipl. Chem. V. Markowski.

($CDCl_3$); J 1·2 Hz is probably due to coupling with *anti*-8-H.[10] The equivalence of 3a-H and 7a-H and their lack of coupling with the bridgehead protons show that the *exo*-adduct has a plane of symmetry. The sterically more favourable "two-planes orientation complex"[4,11] should lead to structure (17) with cyano-groups pointing upwards.

In their studies on the photolysis of phenyl-substituted oxirans to carbenes + carbonyl compounds, Griffin *et al.*[12] recently reported the discovery of a coloured intermediate to which a carbonyl ylide structure was assigned.[13] We found no evidence for postulating a thermal fragmentation, even at 200°, of either (2) or many other oxirans we have investigated. Therefore, it appears likely that the carbonyl ylide in Griffin's matrix experiments undergo *photo*-fragmentation.

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