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1,3-DIPOLAR CYCLOADDITIONS OF CARBONYL YLIDES TO THIOCARBONYL AND CARBONYL COMPOUNDS

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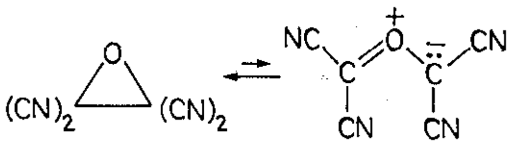
Dedicated to Ken'ichi Takeda on the Occasion of His Seventieth Birthday

α,β-Dicyanostilbene oxide at 120° undergoes electrocyclic ring opening to a carbonyl ylide which can be trapped by cycloaddition to the CS double bond of O-methyl thiobenzoate, methyl dithiobenzoate and dimethyl trithiocarbonate to produce 1,3-oxathiolanes. The carbonyl ylide combines with diethyl mesoxalate to give a 1,3-dioxolane. The corresponding carbonyl ylide from α-cyanostilbene oxide affords a 1,3-dioxolane which suffers cycloreversion and renewed cycloadditon to give 2-phenyl-1,3-dioxolane-4,4,5,5-tetracarboxylic ester.

The thermal equilibration of tetracyanoethylene oxide (1)[1] with the open-chain carbonyl ylide 2[2] constitutes the first example of the electrocyclic opening of the oxirane ring; carbonyl ylides were predicted in 1960 to be a class of reactive 1,3-dipoles.[3] Experiments with α-cyano-*cis*- and *trans*-stilbene oxide established the conrotatory ring opening.[4] Although the cycloadditions of carbonyl ylides to CC double and triple bonds are amply documented, little is known concerning the behavior of hetero-multiple bonds as dipolarophiles. The additions of 2 to benzylideneaniline [5] and of 3 to benzonitrile [6] were followed



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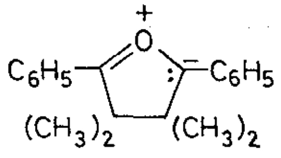

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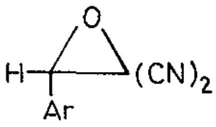

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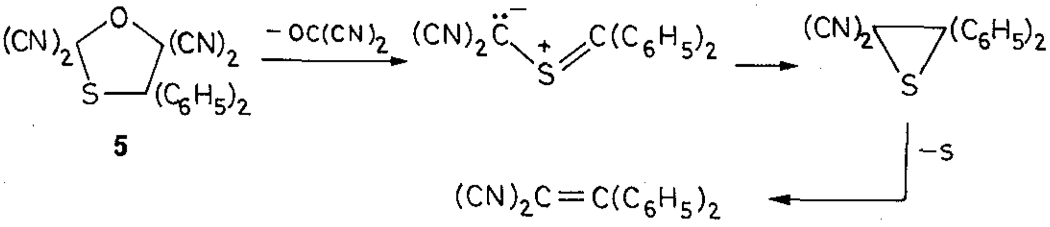
by cycloreversion. However, the reactions of 4 *via* carbonyl ylides with aromatic aldehydes and arylidenearylamines produced stable 1,3-dioxolanes [7] and oxazolidines,[8] respectively. The only reaction with a CS double bond described to date is the formation of 6 from 1 and thiobenzophenone, probably *via* 5.[9]



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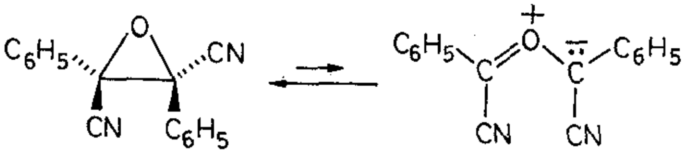
Additions of the carbonyl ylide 8 to thiocarbonyl compounds yielded stable 1,3-oxathiolanes. On heating α,β-dicyano-*trans*-stilbene oxide [10,11] with *O*-methyl thiobenzoate at 120°C for 3 days, we obtained 65 % of the cycloadducts 9 (mp 169.5-171°C) and 11 (mp 166-168°C) in a 72:28 ratio; dicyano-cis-stilbene oxide provided the same cis-dicyano adducts in the same yield in agreement with earlier experience.[11] Analogously, 7 combined via 8 with methyl dithiobenzoate to furnish 63 % of the adducts 10 (mp 166-168°C) and 12 (mp 173-175°C) in the ratio 40:60. The yield of 13 (mp 138.5-140.5°C) from 7 and dimethyl trithiocarbonate reached only 27 %.



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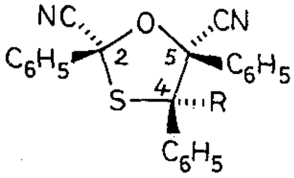
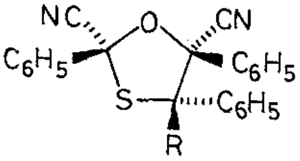
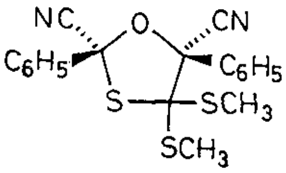




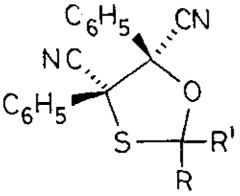


9 R = OCH_3 **11**

10 R = SCH_3 **12**

13

The structural assignments rest on nmr and mass spectra. The methoxy singlet in 9 appears at τ 6.36 and is shifted to 6.90 in 11 under the shielding influence of the cis-vic. phenyl. Correspondingly, the thiomethyl singlets at τ 7.82 for 10 and at 8.20 for 12 reveal the trans-vic. and cis-vic. relation to the 5-phenyl. In 13 the two SCH_3 signals occur at τ 7.55 and 8.32. The cis relation of the nitrile groups in positions 2 and 5 was established unequivocally for the dihydrofurans and tetrahydrofurans resulting from cycloadditions to CC double and triple bonds;[11] the cis-carbonyl ylide 8 is energetically favored over its trans-isomer.



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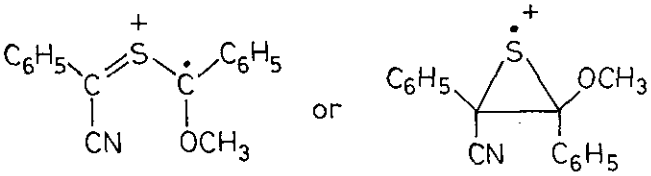
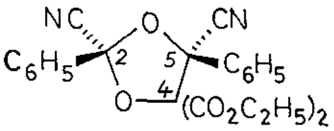


15 m/e = 267

The mass spectra show a higher degree of consistency with 9-13 rather than the positional isomers 14 which could stem from a nucleophilic CO cleavage of the oxirane 7 by the thione function. Without going into detail, it may be mentioned that in the spectrum of 9 the benzoyl cation is the base peak and that $C_6H_5-CCN^+$ (m/e 115) and 15 occur with relative intensities of 60 % each. The cation of 7 or 8 (m/e 246) appears as a 58 % peak.



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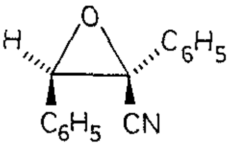

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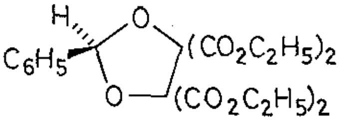

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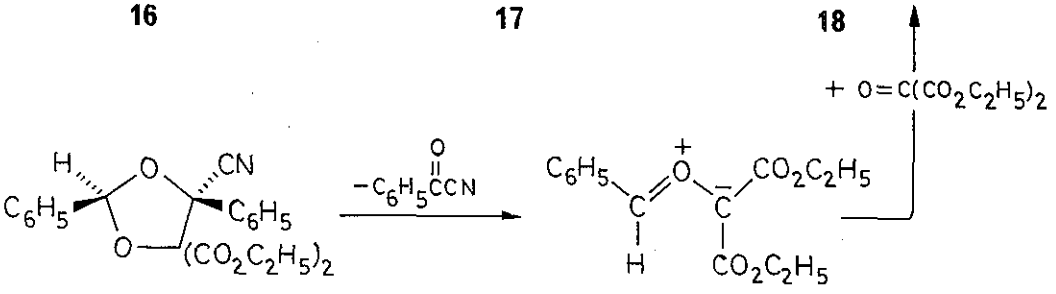

19 **20**

Heating α,β-dicyano-trans- or -cis-stilbene oxide with diethyl mesoxalate at 180° afforded via 8 the 1,3-dioxolane 16 (bp 180°C/0.001 Torr) in 70 % yield. The methyl triplets of the ester ethyls are found in the nmr spectrum at τ 8.56 and 9.25 disclosing again the trans-and cis relation to the 5-phenyl. Both sets of CH_2 contain diastereotopic protons; whereas the low field CH_2 appears as quadruplet at τ 5.48, the shielded CH_2 at 6.14 shows additional splitting.

α-Cyano-trans-stilbene oxide (17) and excess of diethyl mesoxalate furnished in 72 hr at 180°C 45 % of the 1:2 product 18 (bp 155-160°C/0.001 Torr). The nmr spectrum confirmed the pairwise equivalence of the four ethoxycarbonyl groups in structure 18. How is 18 formed? The slow reaction at 120°C (16 days) produced 25 % 1:1-adduct 19 (mp 108.5-110°C), some oxirane still remaining unchanged. The addition direction was established by acid hydrolysis of the 1,3-dioxolane 19 which gave 80 % benzaldehyde as 2,4-dinitrophenylhydrazone. 19 was converted to 18 (52 %) by heating with diethyl mesoxalate for 80 hr at 180°C. The 1,3-dipolar cycloreversion of 19 to benzoyl cyanide and a new carbonyl ylide 20 which undergoes a further 1,3-cycloaddition with a second mole of diethyl mesoxalate offers an attractive mechanistic pathway.

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