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DISROTATORY PHOTOCONVERSION OF CIS,TRANS ISOMERIC OXIRANES TO CARBONYL YLIDES

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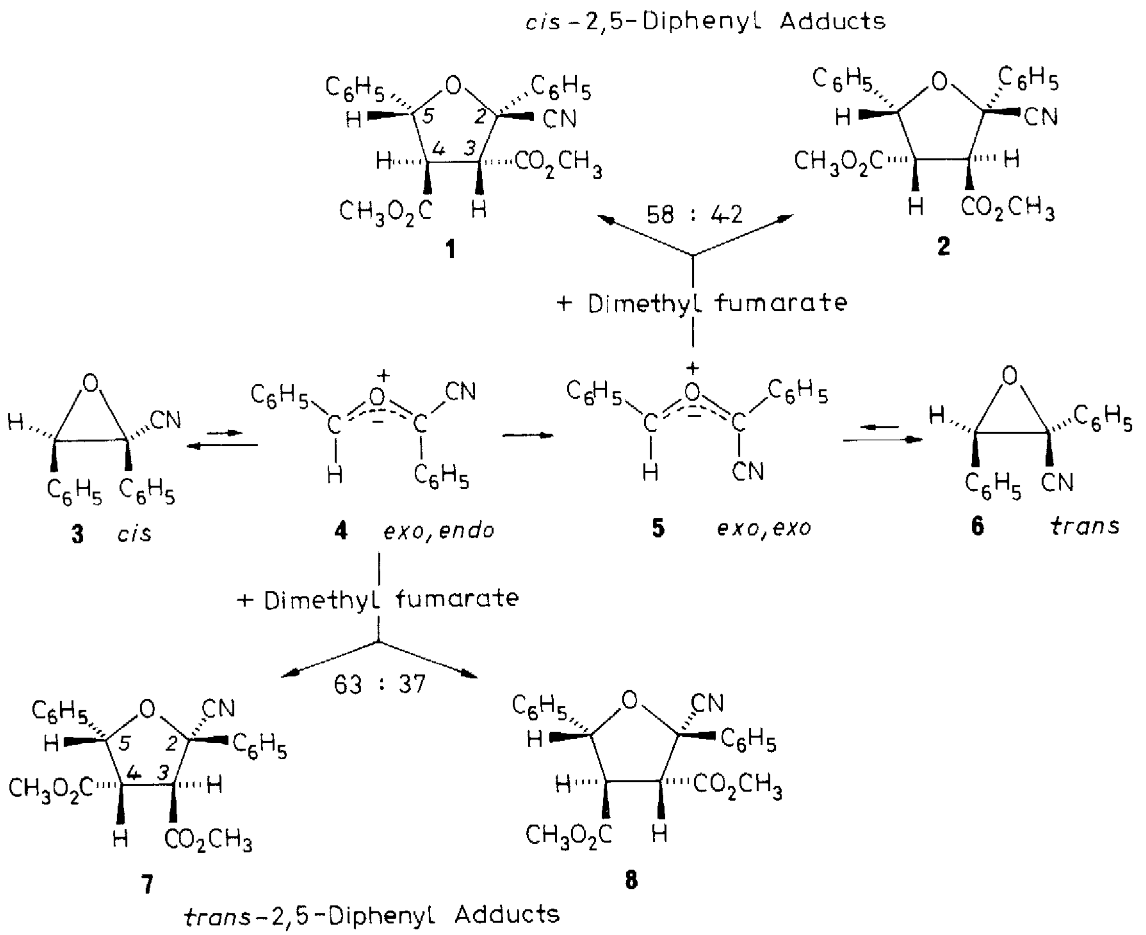
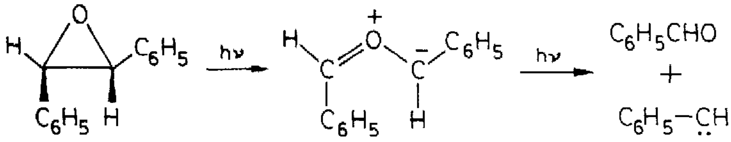
Recent papers of Griffin et al.[1] and of Lee[2] on the interception of photogenerated carbonyl ylides by 1,3-dipolar cycloaddition prompted us to report photochemical experiments which we carried out in 1972.[3,4]



α-Cyano-*cis*- and -*trans*-stilbene oxide (3 and 6) had served as models to demonstrate the at least preferential conrotation in the *thermal* electrocyclic ring opening oxirane ⟶ carbonyl ylide.[5] The cyano-*trans*-diphenyloxirane (6) produced in molten dimethyl fumarate at 130°C the carbonyl ylide 5 which was trapped to yield 99 % of the tetrahydrofuran adducts 1 and 2. The structural retention of 1,3-dipole and dipolarophile in the concerted cycloaddition[6] allowed us to infer from the cis disposed phenyls in 1 and 2 the exo,exo configuration 5 of the reactive intermediate. The cis oxirane 3 reacted with dimethyl fumarate at 140°C to give 42 % of the cycloadducts 7 and 8 besides 53 % of 1 and 2. The four cycloadducts were separated by tlc and structurally elucidated by nmr. It was assumed that the isomerization of the exo,endo diphenyl-substituted carbonyl ylide 4 to the energetically favored exo,exo form 5 competes with the interception by the dipolarophile. This tentative explanation found confirmation in the temperature dependence of the competition ratio.[5]



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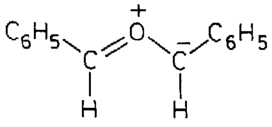

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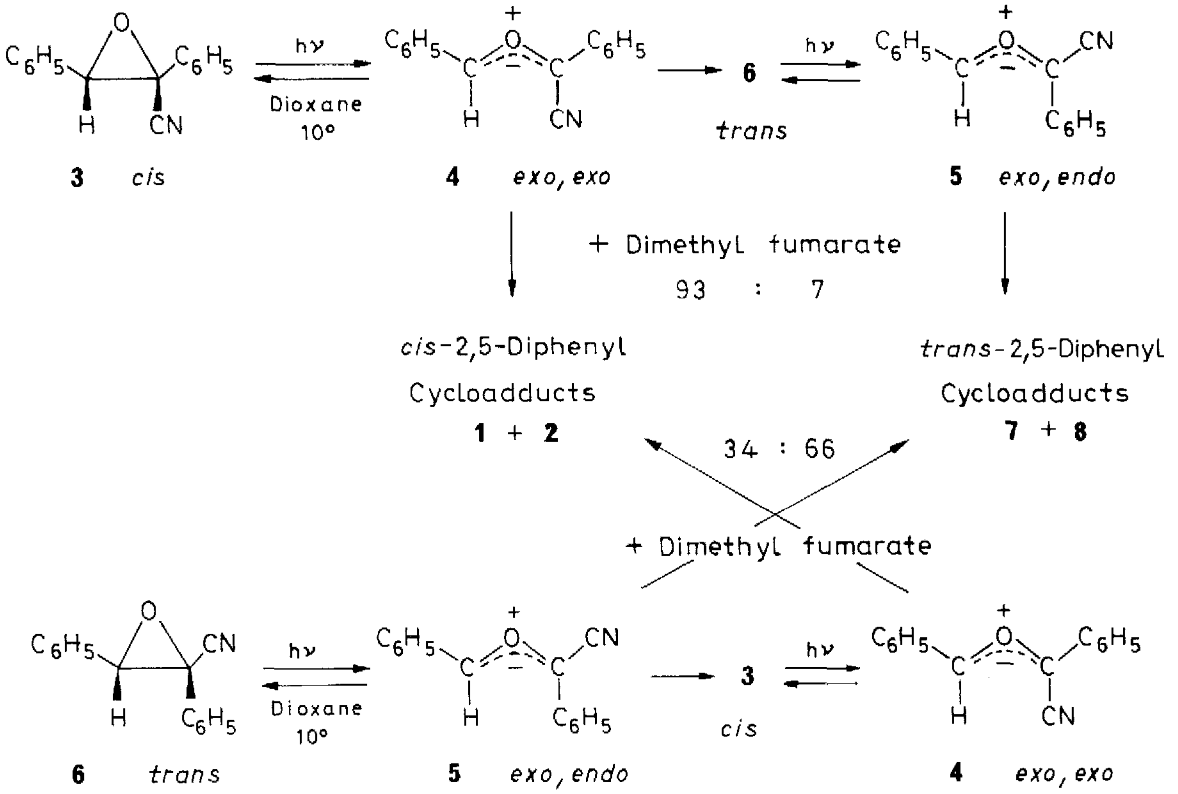
Griffin et al.[7] observed a photofragmentation of vic.-diaryloxiranes into carbonyl compound + carbene. Photochromism at 77°K suggested that two successive one-photon processes are involved. The colored intermediate was initially ascribed to a C-O ring-opened diradical;[8] later Do-Minh, Trozzolo and Griffin[9] preferred the carbonyl ylides 9 and 10 (λ_{max} 490 and 510 nm) for the products of the matrix irradiation of *trans*- and *cis*-stilbene oxide.

The α-cyanostilbene oxides 3 and 6 allowed us to establish the intermediacy of carbonyl ylides in the photocleavage. We irradiated the trans oxirane 6 (0.45 m) in dioxane at 10°C in the presence of dimethyl fumarate (0.69 m) with a low-pressure mercury arc and separated the products by tlc on silica gel (ether/petroleum ether 1 : 2). The reisolated oxirane (14 %) consisted of 6 and 3 in a 85 : 15 ratio. The second zone contained the *cis*-2,5-diphenyl adducts 1 and 2 (16 %) in the ratio 59 : 41 (nmr analysis) *vs*. 58 : 42 in the thermal reaction. The *trans*-diphenyl adducts (30 %), found in the third zone, comprised 7 and 8 in a 66 : 34 ratio (63 : 37 in the thermal process of 3 at 140°C).



Correspondingly, the irradiation of the cis oxirane 3 furnished 58 % cycloadducts, based on 46 % conversion. Nmr analysis revealed a 93 : 7 ratio of cis- and trans-2,5-diphenyl cycloadducts.

Thus, the major cycloadduct in each of the two photolyses suggests disrotatory electrocyclic ring opening as predicted by Woodward and Hoffmann[10] for the first excited state of the isoelectronic cyclopropyl anion. Virtually identical ratios of 1 : 2 and 7 : 8 in thermal and photochemical cycloadditions leave no doubt that the carbonyl ylide is intercepted in its singlet ground state. Disrotation might even be the sole path of photochemical ring opening. Why does the observed stereoselectivity amount to only 66 % and 93 %, respectively ?

1. The kinetics of the thermal cycloadditions of 3 and 6 demonstrate that the conrotatory recyclization of the carbonyl ylides competes with their interception by dimethyl fumarate.[3] The sequence of disrotatory photochemical ring-opening and conrotatory cyclization constitutes a cis,trans isomerization of the oxirane which was indeed observed. Renewed photocleavage affords the other isomer of the carbonyl ylide.

2. Part of the exo,endo carbonyl ylide **5** will escape by rotation to the exo,exo isomer **4** – as in the thermal reaction[5] – and thus change stereochemistry.

3. Photochemical cis,trans isomerization of the carbonyl ylides is conceivable.

Lee[2] observed on irradiation of *cis*- and *trans*-stilbene oxide in acetonitrile in the presence of methyl acrylate 89 % stereoselectivity in adduct formation, whereas the triplet sensitized reaction provided the same adduct mixture from both stilbene oxides. Griffin et al.[1] irradiated 1-phenyl-2,2-dicyanooxirane in benzene and intercepted the carbonyl ylide with *cis*- and *trans*-2-butene; retention of dipolarophile configuration is the only possible conclusion. Cyclic carbonyl ylides generated thermally and photochemically from 2,3-diphenylinden-3-one oxide[11] and from 1,2-diphenyl-3,3,4,4-tetramethylcyclobutene oxide[12] were also trapped by cycloadditions; the steric constraint permits disrotation only.

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