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FLASH PHOTOLYSIS OF α-CYANO-CIS- AND -TRANS-STILBENE OXIDE; ENERGY PROFILE OF CIS,TRANS ISOMERIZATION VIA CARBONYL YLIDES

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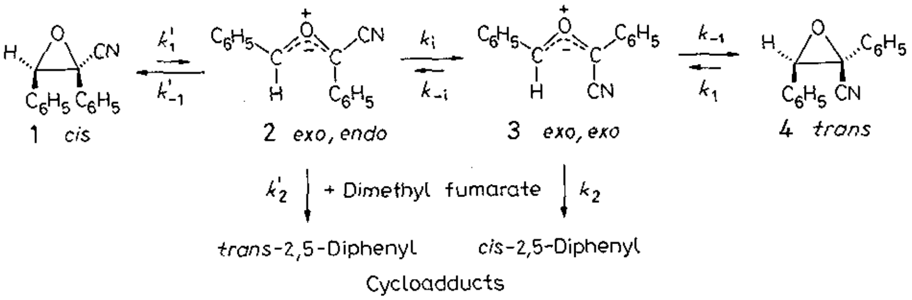
The enlightening concept of orbital control refined our ideas of the reaction event. This paper is dedicated to R. B. WOODWARD on the occasion of his sixtieth birthday

Flash photolysis of the title compounds in the matrix at −196°C produces blue and red colors which disappear with half-reaction times of 5.0 and 0.25 sec. The colors are attributed to cis,trans isomeric carbonyl ylides which decay via thermal recyclization. An ensemble of kinetic data provides estimates of upper and lower bounds for the recyclization and rotational barriers of the carbonyl ylides at 129.6°C.

α-Cyano-cis- and -trans-stilbene oxide (1 and 4) equilibrate at 160°C via the carbonyl ylides 2 and 3 which can be intercepted by 1,3-dipolar cycloadditions to suitable dipolarophiles.[1] The combination of kinetic[2] and stereochemical[3] data affords the tentative energy profile of Fig. 1. While 3 results from conrotatory ring opening of 4 and adds to dimethyl fumarate with retention of configuration, the non-stereospecific portion



in the reaction of 1 with fumaric ester arises from two mechanisms : a. concurrent rotation 2 → 3 ; b. a conversion of 1 to 3 which by-passes 2 and probably corresponds to the direct disrotatory ring opening.[3] The dashed lines in Fig. 1 reflect the uncertainty in regard to the depths of the energy troughs of 2 and 3.[3]

The photofragmentation of 4 into benzaldehyde + phenylcyanocarbene[4] is probably a sequence of two photochemical steps. *Irradiation of stilbene oxides at -196°C produces bright colors which were ascribed to carbonyl ylides.*[5] The action of light on 1 and 4 in dioxane at 10°C in the presence of dimethyl fumarate yields the same cycloadducts which result from thermal experiments, but now disrotatory ring opening constitutes the main - if not the only - reaction path.[6] Flash photolysis should produce a concentration of the carbonyl ylides sufficiently high to measure spectroscopically the rate ot their thermal conversion to the oxiranes.

In an isopentane/ether (6:1) matrix of the cis-oxirane 1 at -196°C a 25 Joule argon flash creates an intensely blue color with an *absorption maximum at 600 nm*, whereas the *trans-oxirane* gives rise to a deep-red color, λ_{max} 550 nm. The assignment of structures 3 and 2 to the colored species conforms with the evidence for disrotation from the photocycloaddition experiments ;[6] furthermore, the absorption of 2 at shorter waves is the ex-

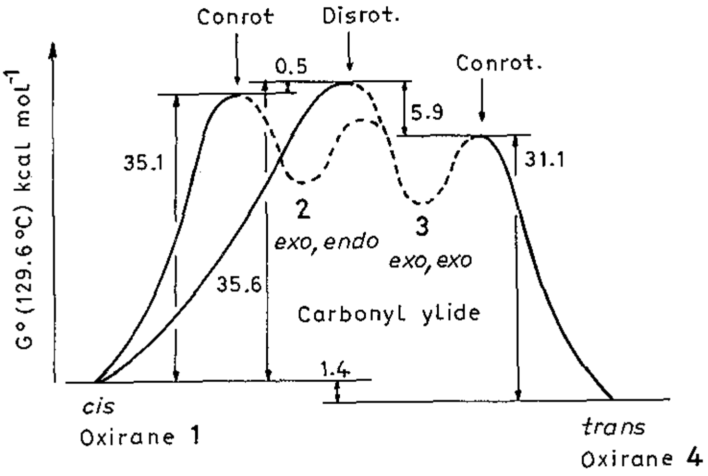


Figure 1. Free energy profile for the thermal cis,trans isomerization of α-cyano-stilbene oxide in o-dichlorobenzene at 129.6°C [3]

pected consequence of steric hindrance of resonance caused by the endo-phenyl.

The rate of disappearence of the colored species, ascribed to the thermal electrocyclic ring closures 3 → 4 and 2 → 1, is followed photometrically using the light of a xenon lamp. The first order rate constants (Fig. 2) turn out to be virtually independent of the wave-length (580, 590 and 600 nm for 3 ; 540 and 560 nm for 2). The half-reaction times at -196°C amount to 5.0 sec for 3 and to 0.25 sec for 2, corresponding to $\Delta G^{\ddagger} =$ 4.6 and 4.1 kcal/mol. Flashing of dioxane solutions of the oxiranes 1 and 4 at 25°C does not result in a detectable change of the light absorption, even if the spectrum is taken 10^{-6} sec after the flash. The assumption of half-reaction times of $< 0.5 \quad 10^{-6}$ sec at 25°C accords with $\Delta G^{\ddagger} < 12.5$ kcal/mol.

The preliminary flash photolysis investigation requires supplementary measurements : cyclization rates at various temperatures to obtain Eyring parameters and the proof that the

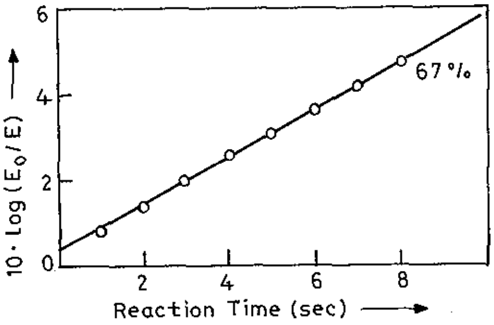
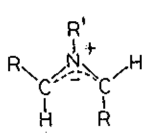


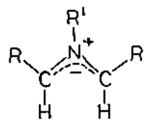
Figure 2. Kinetics of recyclization of carbonyl ylide $\underline{2}$ at -196°C

xenon light causes no disturbance. The relative rates of thermal cyclization at -196°C, $\underline{2}$ *faster than* $\underline{3}$, do not harmonize with the conclusions of Fig. 3 discussed below, but this may simply be due to the difficulties of having to compare reactions in the matrix and in the fluid medium, and to extrapolate over a temperature range of more than 300°.

The certitude that the photochromism of the oxiranes is attributable to carbonyl ylide formation, stems from the analogous behavior of aziridines.[7,8] The deep-yellow color produced on irradiation of dimethyl 1(p-methoxyphenyl)aziridine-2,3-dicarboxylate must belong to the azomethine ylide, the 1,3-dipoles $\underline{5}$ and $\underline{7}$, because fumaric ester as a potent dipolarophile effects sudden decolorization.



	R	R'	
5	CO_2CH_3	$C_6H_4OCH_3$-*p*	7
6	C_6H_5	C_6H_5	8



Assuming the correctness of the reaction scheme of Figure 1, a collection of kinetic data allows one to estimate upper and lower bounds for the individual rate constants at 129.6°C. The clue to the upper limits is offered by the following consideration. 1,3-Dipolar cycloadditions possess activation entropies of -22 to -35 e.u. Assumption of $\Delta S^{\ddagger} =$ -22 e.u. and $\Delta H^{\ddagger} \geqslant 0$ kcal/mol for the additions of $\underline{2}$ and $\underline{3}$ to dimethyl fumarate affords $k_2', k_2 \leqslant 4.3\ 10^8$ L $mol^{-1} sec^{-1}$. From the experimental $k_{-1}/k_2 = 0.37$ [2] one deduces $k_{-1} \leqslant 1.5\times10^{8}$ sec^{-1} for the recyclization of carbonyl ylide 3, whereas the experimental $k_i/k_2' = 0.93$ [3] leads to $k_i \leqslant 3.9\times10^{8}$ sec^{-1}. The cycloaddition of 4 via 3 to dimethyl fumarate (0.3 M) proceeds stereospecifically within the analytical limit of 2 %;[2] i.e., $k_2D/k_{-i} \geqslant 49$ (D = fumarate concentration). Thus, k_{-i} must be $\leqslant 2.6\times10^{6}$ sec^{-1}.

The key finding for the lower rate limits lies in the values $k_{-1}, k_{-1}' \geqslant 1.4\ 10^{6}$ sec^{-1} for the cyclization of 2 and 3 at 25°C (and even more so at 129.6°C) as well as $k_i \geqslant 1.4\times10^{6}$ sec^{-1}, because $k_i \geqslant k_{-1}'$.[3] Similar rate relations as above provide $k_2' \geqslant 4.5\times10^{6}$ and $k_2 \geqslant 3.7\times10^{7}$ L mol^{-1}sec^{-1} in addition to $k_{-i} \geqslant 1.4\times10^{5}$ sec^{-1}.

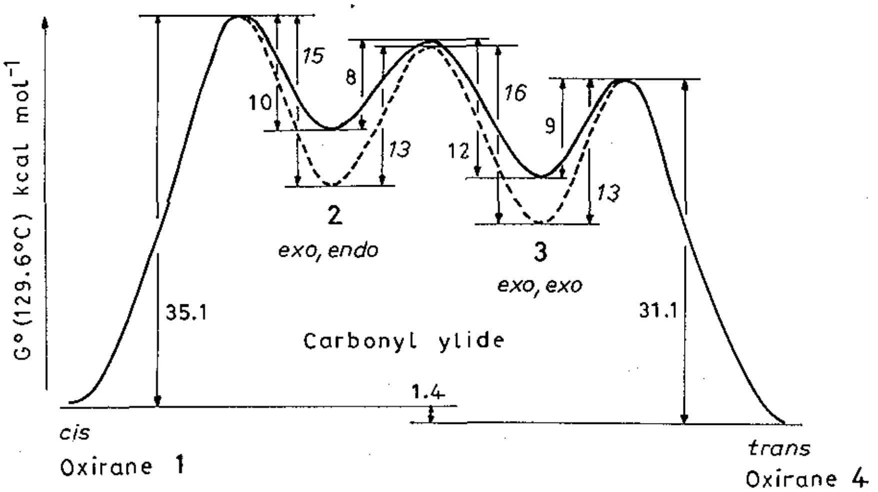


Figure 3. Lower (——) and upper limits (----) for the depths of the energy troughs of the carbonyl ylides 2 and 3 at 129.6°C ; the disrotatory ring opening 1 → 3 has been omitted for the sake of clarity.

The corresponding free energies at 129.6°C are listed in Fig. 3 and leave no doubt that the carbonyl ylides are high-energy intermediates. Spectroscopic evidence for their occurence in the thermal equilibrium with the oxiranes 1 and 4 is hardly conceivable, because $\Delta G^{o}(129.6^{o}C) \approx 20$ kcal/mol amounts to only one carbonyl ylide per 10^{11} oxirane molecules. Due to the endo-phenyl interaction, the energy level of the exo,endo-diphenylcarbonyl ylide 2 lies 3 - 4 kcal/mol above that of the exo,exo isomer 3. Cis,trans isomerization is achieved via rotational barriers between 8 and 16 kcal/mol. The small barrier between 2 and 3 is responsible for the lack of stereoselectivity in the 1,3-dipolar cycloaddition of 2 and dimethyl fumarate.[1,3] When one considers that the allyl anion type resonance of the carbonyl ylide system has to be sacrificed during rotation, the energy demand is modest. The azomethine ylides 5 - 8 with a similar substitution pattern exhibit barriers to rotation of 22 - 25 kcal/mol, arguing for a larger resonance energy.[7,8]

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