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PHOTOISOMERIZATION OF CIS AND TRANS 2,3-DICARBOMETHOXY-SPIRO-CYCLOPROPANE-1,9'-FLUORENE(1)

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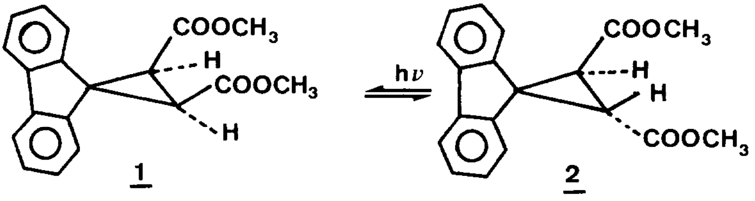
Substituted cyclopropane derivatives are known to rearrange or isomerize thermally(2) as well as photochemically(3,4). One of the first examples of a light-induced stereoisomerization has been uncovered in 1963 by Von Doering and Jones(5) in their study of the interconversion of *cis* and *trans* 2,3-dimethyl-spiro-cyclopropane-1,9'-fluorene ; the authors have yet restricted their investigation to the structural characterization of these compounds and to the determination of the photostationary state composition. In recent years a growing interest in the photoisomerization of cyclopropane type molecules has been noted(6,7,8) and different mechanisms most of them invoking a trimethylene diradical, have been proposed(9,10). During an investigation on the reactivity of such short lived radical intermediates in oligomeric and polymeric environment, we have determined the kinetics of the light-induced isomerization of *cis* and *trans* 2,3-dicarbomethoxy-spiro-cyclopropane-1,9'-fluorene 1 and 2. New quantitative and mechanistic informations have thus been obtained suggesting that the triplet state is the reactive species.



Pure *cis* and *trans* isomers have been prepared according to the method described earlier(11). The two stereoisomers exhibit similar absorption spectra in the region 230-310 nm. Neither fluorescence nor phosphorescence have been observed by conventional methods, in contrast with 9,9-disubstituted fluorene compounds(12). The NMR spectrum of the *cis*-derivative shows the methylester protons as a singlet at δ 3.77 while the cyclopropyl protons appear at 3.08. The corresponding spectrum of the *trans*-derivative is similar, methylester and cyclopropyl protons appearing at δ 3.70 and 3.52 respectively. The area ratios for those signals are also in agreement with structure 1 and 2(13). Consequently, the ratio of the two photoisomers in irradiated solutions has been determined by NMR spectroscopy using a calibration curve, rather than by gas-liquid chromatography in order to avoid any thermal isomerization resulting from analytical procedures(14). Photolyses have been carried out in argon saturated methylene chloride solutions using a quartz cell on an optical bench equipped with a Philips (HPK) 125 W mercury lamp. An aqueous solution of $NiSO_4$ + $CoSO_4$ has been used to select the 250-350 nm wavelength range.

Unsensitized photoisomerization

Cis 2,3-dicarbomethoxy-spiro-cyclopropane-1,9'fluorene 1 irradiated in deaerated methylene chloride solution (7.10^{-2} M) converts easily into the *trans* isomer 2, while the reverse isomerization yields 3% of 1 at the most. Thus the photostationary state, reached only after extended irradiation of either 1 or 2, complies with a *trans*/*cis* ratio of 32 (97% *trans* - 3% *cis*). A decade ago, Von Doering and Jones(5) calculated a *trans* to *cis* ratio of 1.74 at the photostationary state for the photoisomerization of *cis* and *trans* 2,3-dimethyl-spiro-cyclopropane-1,9'-fluorene in cyclohexane solution. With knowledge of this work, isomerization of 1 has also been carried out in deaerated cyclohexane solution, thus avoiding a possible solvent effect, but again, practically complete *cis* → *trans* conversion has been observed. The discrepancy of those results could be partly related to a steric effect of the cyclopropane substituents influencing the competitive cyclization reactions of the presumed biradical intermediate resulting from opening of the cyclopropane ring. A possible contribution of a dipole-dipole effect will be evaluated in connection with our NMR study on various spiro-cyclopropane derivatives(13).

The quantum yield of the isomerization process, determined by ferrioxalate actinometry, appears to be quite low ($\Phi_{c\to t}$=0.0095) and independent of the wavelength of excitation in the 250-310 nm range. Irradiation of 1 in aerated solution affords isomerization but with a slightly decreased quantum yield ($\Phi_{c\to t}$=0.0088). The small influence of oxygen suggests that the lifetime of the reactive excited state must be in the order of a few tens of nanoseconds. After 60 hours of irradiating the *cis* isomer 1 ($2x10^{-2}$ Einstein) and a *trans*/*cis* ratio of 2.7, 87% of the starting material has been isolated as *cis* or *trans* isomer. The mass balance deficiency increased with further irradiation and is attributed to the formation of a polymeric material accumulating at the light-exposed wall of the irradiation cell and causing a yellow coloration of the solution upon prolonged photolysis. A similar mass balance deficiency has also been observed after the same period of irradiation of the *trans* isomer 2 although no significant *trans* → *cis* isomerization occured. We conclude that there are at least two competing processes for the presumed biradical intermediate, cyclization by intramolecular recombination and polymer formation, possibly after a rearrangement.

Sensitized photoisomerization

For determination of the reactive state, photolysis of 1 was carried out in deaerated methylene chloride solution containing 10^{-2} M of various triplet sensitizers (the $7\text{x}10^{-2}$ M concentration of 1 ensures a practically complete capture of the sensitizer triplets). Direct excitation of 1 is avoided by means of a glass filter (Corning CS-7-60) isolating the 330-380 nm region.

When acetophenone is used as sensitizer, isomerization of 1 to 2 proceeds rapidly to reach a photostationary state composition of 98% *trans* - 2% *cis* for about $1.3\text{x}10^{-3}$ Einstein absorbed. No appreciable sensitized isomerization of 2 to 1 has been detected. The initial quantum yield is close to unity implying that the sensitized conversion of 1 to 2 proceeds via the triplet state of the spiro compound which is quantitatively deactivated towards an intermediate allowing the formation of the *trans* isomer. Isomerization quantum yields are also close to unity for benzophenone or thioxanthone sensitizations while no isomerization of 1 to 2 has been observed in the presence of fluorenone or 2-3 butanedione, even after extended irradiation ($4\text{x}10^{-3}$ Einstein). With 2-naphthol or 4-phenylacetophenone as sensitizers, photoisomerization occurs with lower quantum yields thus suggesting a less efficient T-T energy transfer. In relating the triplet energies of the sensitizers (E_T) with the corresponding quantum yields of the isomerization of 1 to 2 ($\Phi_{c\rightarrow t}$), Table 1, the triplet energy of 1 can be estimated to be ∿60 kcal/mole, a value significantly lower than the triplet energy of fluorene (E_T=68 kcal/mole)$^{(15)}$.

TABLE 1 : Sensitized *cis* → *trans* photoisomerization of 2,3-carbomethoxy-spirocyclopropane-1,9'-fluorene.

Sensitizer	E_T kcal/mole	$\Phi_{c\rightarrow t}$
Fluorenone	53.3	0
2,3 Butanedione	56.3	0
2 Naphthol	60.3	0.05
4 Phenyl-acetophenone	61.1	0.57
Thioxanthone	65.5	0.99
Benzophenone	68.6	0.97
Acetophenone	73.6	1.05

Quenching of the unsensitized isomerization

In order to elucidate the mechanism of the direct isomerization, the *cis* isomer 1 has been irradiated under 1.6 atmosphere of pure oxygen or in the presence of 6×10^{-2} M *cis* pentadiene. The quantum yield of isomerization ($\Phi_{c\rightarrow t}$) has been found to be reduced to 0.005 and 0.0017 respectively. It thus appears that both unsensitized and sensitized photoisomerizations of 1 proceed mainly by the triplet excited state, the lifetime of which can be estimated to be ∿ 15 ns.

Confirmation of the triplet mechanism has been searched by photolysing 1 in the presence of xenon which has been shown to be an efficient heavy atom catalyst for $^1S\rightarrow T$ transitions in aromatic hydrocarbons in solution(16). An increase of ∿ 10% for the isomerization quantum yield has been observed under 1.5 atmosphere of pure xenon. The lack of a substantial heavy atom effect in the direct photoisomerization of 1 may be due both to the expected short lifetime of the ^1S singlet state and to the relatively low concentration of dissolved xenon (3.10^{-2} M)(17) in our experiment.

Comparing the quantum yields of sensitized and unsensitized photoisomerizations, we deduce that the low conversion yield observed on direct excitation results from an inefficient intersystem crossing process ($\Phi_{ISC}\sim0.01$). Since no fluorescence of 1 has been observed, internal conversion appears as the major deactivation pathway of the excited singlet state of this spirocyclopropane derivative. Formation and characterization of the presumed biradical intermediate are currently under investigation.

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