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EFFICIENCY FOR SOLID-STATE PHOTOCYCLIZATION OF 2,4,6-TRIISOPROPYLBENZOPHENONES

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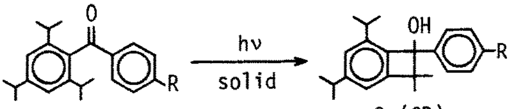
Summary: Quantum yields for photocyclization of 2,4,6-triisopropylbenzophenones in the solid state were estimated by using an usual merry-go-round apparatus. The results suggest that the π,π^* excited state is responsible for the reaction.

Techniques such as sensitization and quenching experiments and quantum yield measurements, which are normally employed by organic photochemists in an attempt to study photoreaction mechanisms in solution, are seldom used for investigation of solid-state photoreactions. This is probably due to difficulties encountered not only in doing these experiments but also in interpreting the obtained experimental results. Recently Scheffer and Trotter have demonstrated the utility of triplet sensitization for investigating reaction mechanisms of organic crystals.[1] Since quantum yield estimations in solids require special precautions and apparatus, such attempts were done only sporadically.[2] We wish to report here and in the subsequent paper that quantum yields for some solid-state photoreactions can be conveniently estimated by the usual merry-go-round method and that the results may be used to discuss the reaction mechanisms.

Photocyclization of 2,4,6-triisopropylbenzophenones 1 into the corresponding benzocyclobutanols (CB) 2 in solution phase was already studied by us in great details.[3] Now we have found that this transformation occurs also in the solid state. Each sample of crystalline 1a - 1g (100 - 200 mg) was placed between two Pyrex plates and irradiated with a 400-W high pressure mercury lamp under a nitrogen atmosphere at 0 °C for several hours. As summarized in Table I, CB 2a - 2f were produced in quantitative yields. For 1g no reaction was observed. The colorless crystals of 1a and 1d turned into colorless transparent glass as the reaction proceeded, whereas those of 1b, 1c, and 1f remained to be colorless crystals even after complete conversions. The crystalline appearance also lasted for 1e, but a trace amount of yellow byproduct(s) was formed on the crystal surface.



1   2 (CB)   (1)

Efficiency for CB formation was measured as follows. A weighed sample of 1 (0.05 mmole) in a 180 x 17 mm Pyrex tube was dissolved by addition of a small amount of ether (∿ 0.5 mL). The outside of the tube was heated with a hair dryer to evaporate the solvent. By this manipulation the interior wall of the tube was coated with a crystalline film, the top of which was adjusted as precisely as possible to be about 2 cm from the bottom. After complete

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Table I. Photocyclization of **1** in the Solid State.

reactant	R	mp, °C	preparative[a] irrad time,h	preparative[a] conv,%	Φ_{CB}(solid)[b]	Φ_{CB}(soln)[c]
1a	OMe	111-112	2	100	0.56	0.48
1b	t-Bu	120-121	2	100	0.20	0.38
1c	Me	87-87.5	2	100	0.48	0.42
1d	H	97-99	4	100	0.13	0.52
1e	Cl	92-94	8	89	0.072	0.51
1f	CF_3	89-91	8	100	0.011	0.30
1g	CO_2Me	142-143	10	no reaction	∿0.001	0.13

[a] Yields of CB **2a** - **2f** are 100 % from NMR and TLC. [b] Quantum yield for CB formation (**1** → **2**) in the solid state. [c] Quantum yield for CB formation (**1** → **2**) in benzene solution (ref. 3b). The values are reestimated by using trans-cis photoisomerization of trans-stilbene as actinometer.

evaporation and degassing at 10^{-2} mmHg, the film was irradiated on a merry-go-round apparatus at 15 °C through a potassium chromate filter (313 nm). The reactions were stopped at a small conversion (< 7.5 %) and CB formed was analyzed by HPLC (silica gel column (Finesil 5), hexane - ethyl acetate eluent).

The efficiency for CB formation was not dependent on the initial amount of **1** used (either 0.05, 0.1, or 0.2 mmole) and the conversion increased linearly with the irradiation time until 15 %. This assures that all the incident light is absorbed by **1** under these conditions. The quantity of photon absorbed by the film was estimated by parallel photolysis of the benzene solution of **1d** (Φ_{CB} = 0.52[3]), i.e., different reflections of light from the crystal and solution surfaces were neglected. The values for the quantum yield of CB formation in the solid state Φ_{CB}(solid) thus determined are summarized in Table I, together with the previously obtained quantum yields in benzene solution Φ_{CB}(soln).[3] The results for Φ_{CB}(solid) were reproducible to usually ±5 % on repeated runs.[4] Table I clearly shows that Φ_{CB}(solid) tends to increase with an increased electron-donating ability of the substituent R, while there are no such trends in Φ_{CB}(soln).

The photocyclization **1** → **2** in solution is believed to occur through n,π^*-triplet-induced intramolecular hydrogen abstraction, whose stereoelectronic factor requires that the molecule must undergo significant conformational changes (single-bond rotations around the carbonyl group) in the course of the reaction.[3] In the solid state, however, this mechanism will be topochemically very unfavorable. It is well established that solid-state reactions proceed with minimum motion of atoms and molecules.[5]

For ring-substituted aromatic ketones in their lowest excited triplet state (T_1), the quantity of π,π^* character relative to n,π^* character is known to be increased by increasing electron-donating ability of substituents, i.e., the π,π^* character increases in the order CF_3 < H < alkyl < OMe.[3b,6] Therefore, the observed Φ_{CB}(solid) values rising in the same order (Table I) seem to suggest that the π,π^* excited state of **1** is responsible for the solid-state photocyclization.[7] Indeed in rigid matrices, several hydrogen abstraction reactions by aromatic carbonyl compounds are thought to occur from excited states other than the $T_1(n,\pi^*)$ state.[9]

As seen from a stereoview and geometrical parameters (Figure 1 and Table II: θ_1 ∿ 85° and

$\alpha \sim 55°$), the molecule 1 is severely twisted.[12] Under this conformation, the intramolecular hydrogen abstraction by the π,π^* excited carbonyl oxygen will be stereoelectronically more favorable than that by the n,π^* excited carbonyl oxygen.[3a,b] Furthermore, from examination of the molecular models, the molecules 1 and 2 are similar in size and shape, i.e., the reaction proceeds with small distortion of the reaction cavity.[13] From these reasons, the π,π^* photocyclization 1 → 2 is expected to be topochemically feasible. In fact, in the case of 1a and 1c, Φ_{CB}(solid) is comparable to or even larger than Φ_{CB}(soln).

In summary, from the consideration of the solid-state quantum yield and the topochemistry, the photoreaction 1 → 2 in the solid state seems to occur from the π,π^* excited state rather than the n,π^* excited state (Scheme I).

The most attractive topic of recent progresses in synthetic solid-state photochemistry is obviously absolute asymmetric synthesis.[14] However, the present paper as well as Scheffer's work[1] will also serve synthetic organic photochemists as a reminder of usefulness of classical methods such as sensitization, quenching, and quantum yield measurement, when they want to carry out mechanistic studies of their solid-state photoreactions.

crystal data: monoclinic, $P2_1/c$, $a = 9.304(4)$, $b = 12.001(4)$, $c = 18.792(5)$ A, $\beta = 90°$, $V = 2098$ A^3, $Z = 4$, $D_c = 1.07$ g/cm^3
final $R = 0.065$

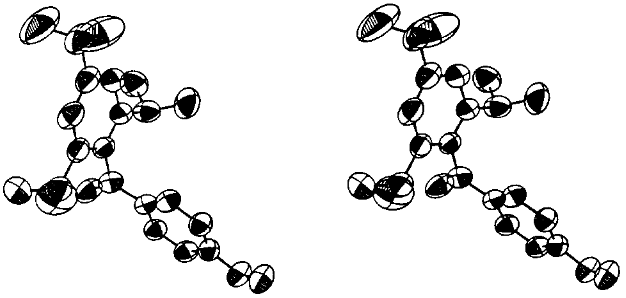


Figure 1. Stereoview of 1a

Table II. Distances and Angles Relevant to Solid-State Intramolecular Hydrogen Abstraction for 1a and 1d.[a]

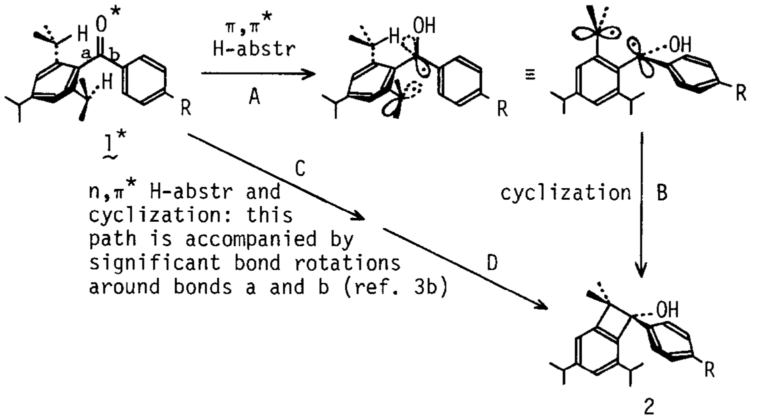
	d(A)	α(°)	β(°)	θ_1(°)	θ_2(°)
1a (R = OMe)[b]	2.88	55	55	82	15
	2.97	58	59		
1d (R = H)[c]	2.94	52	52	86	4
	2.90	55	57		

[a] d: the distance between the carbonyl oxygen (O_c) and the ortho isopropyl methine hydrogen being abstracted (H_o). α: the angle between the $O_c \cdots H_o$ vector and its projection on the plane of the carbonyl group. β: the angle C $O_c \cdots H_o$. θ_1: the torsion angle between the triisopropylphenyl ring and the carbonyl plane. θ_2: the torsion angle between the unsubstituted (or p-MeO-substituted) phenyl ring and the carbonyl plane. [b] Note 10. [c] Ref. 11.

References and Notes

(1) Garcia-Garibay, M.; Scheffer, J. R.; Trotter, J.; Wireko, F. Tetrahedron Lett. 1987, 28, 1741.

Scheme I



Path A → B, favorable in the solid phase.

Path C → D, favorable in the solution phase.

(2) (a) Lazare, S.; de Mayo, P.; Ware, W. R. Photochem. Photobiol. 1981, 34, 187. (b) Rennert, J.; Ruggiero, E. M.; Rapp, J. Ibid. 1967, 6, 29.

(3) (a) Ito, Y.; Umehara, Y.; Hijiya, T.; Yamada, Y.; Matsuura, T. J. Am. Chem. Soc. 1980, 102, 5917. (b) Ito, Y.; Nishimura, H.; Umehara, Y.; Yamada, Y.; Tone, M.; Matsuura, T. Ibid. 1983, 105, 1590. (c) Ito, Y.; Giri, B. P.; Nakasuji, M.; Hagiwara, T.; Matsuura, T. Ibid. 1983, 105, 1117. (d) Ito, Y.; Matsuura, T. Ibid. 1983, 105, 5237. (e) Ito, Y.; Kawatsuki, N.; Giri, B. P.; Yoshida, M.; Matsuura, T. J. Org. Chem. 1985, 50, 2893.

(4) The quantum yield for photodimerization of solid α-trans-cinnamic acid into α-truxillic acid was measured by the same method. The value (Φ = 0.59) was comparable to that previously reported (Φ = 0.7).[2b] In our case, however, formation of a small amount of cis-cinnamic acid was observed, indicating the presence of some defects in the crystal.

(5) Schmidt, G. M. J. Pure Appl. Chem. 1971, 27, 647.

(6) (a) Wagner, P. J.; Siebert, E. J. J. Am. Chem. Soc. 1981, 103, 7329. (b) Wagner, P. J.; Thomas, M. J.; Harris, E. Ibid. 1976, 98, 7675. (c) Wagner, P. J.; Kemppainen, A. E. Schott, H. N. Ibid. 1973, 95, 5604.

(7) This result and the wavelength-independence of Φ_{CB} for 1d[8] may implicate that the predominant nature of the lowest excited state for 1d is of π,π* in the solid state and of n,π* in the liquid state. The lifetime of the excited state is probably much longer in the solid state than in solution. Of course, further experiments are required to settle these issues.

(8) The values of Φ_{CB} for 1d are found to be essentially independent of the excitation wavelength in both the solid and solution phases: Φ_{CB}(solid), 0.13 at 313 nm and 0.15 at >355 nm; Φ_{CB}(soln), 0.52 at 313 nm and 0.52 at >355 nm.

(9) (a) Murai, H.; Obi, K. J. Phys. Chem. 1975, 79, 2446. (b) Brauchle, C.; Burland, D. M. ; Bjorklund, G. C. Ibid. 1981, 85, 123. (c) Suter, G. W.; Wild, U. P.; Schaffner, K. Ibid. 1986, 90, 2358. (d) Winkler, I. C.; Hanson, D. M. J. Am. Chem. Soc. 1984, 106, 923.

(10) The X-ray crystallography of 1a was done at Rigaku Denki.

(11) Takemoto, Y.; Fukuyama, K.; Tsukihara, T.; Katsube, Y.; Ito, Y.; Matsuura, T. Reports of the Faculty of Engineering Tottori University, 1983, 14, 148.

(12) The distance between the carbonyl oxygen and the ortho isopropyl methine hydrogen (d) is ca. 2.9 A (Table II), somewhat longer than the critical distance (2.72 A) which Scheffer has proposed for the n,π* hydrogen abstraction: Scheffer, J. R. Acc. Chem. Res. 1980, 13, 283.

(13) Cohen, M. D. Angew. Chem. Int. Ed. Engl. 1975, 14, 386.

(14) (a) Evans, S. V.; Garcia-Garibay, M.; Omkaram, N.; Scheffer, J. R.; Trotter, J.; Wireko, F. J. Am. Chem. Soc. 1986, 108, 5648. (b) Green, B. S.; Arad-Yellin, R.; Cohen, M. In "Topics in Stereochemistry", Eliel, E. L.; Wilen, S. H.; Allinger, N. L., Eds., Wiley, New York, Vol. 16, 1986, 131. (c) Green, B. S.; Lahav, M.; Rabinovich, D. Acc. Chem. Res. 1979, 12, 191.

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