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Solid-State Photocyclization of 2,4,6-Triisopropyl-4′-(methoxycarbonyl)benzophenone. Evidence for a Narrow Reaction Cavity and a Photoenol Diradical Intermediate[†]

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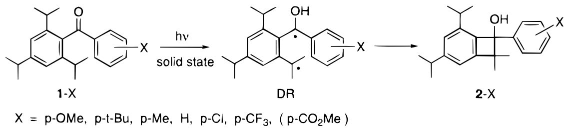
The origin of the previously observed unusual photostability of 2,4,6-triisopropyl-4′-(methoxycarbonyl)-benzophenone (**1**-*p*-CO_2Me) in the solid state was investigated. **1**-*p*-CO_2Me was found to photocyclize normally to produce the corresponding benzocyclobutenol **2**-*p*-CO_2Me when its solid-state photolysis was carried out either (a) after thorough grinding, (b) after solid−solid mixing with 2,4,6-triisopropyl-4′-(ethoxycarbonyl)-benzophenone (**1**-*p*-CO_2Et), or (c) at elevated temperatures (an estimated energy barrier of 20 kcal/mol). Furthermore, when the photolysis was performed under more carefully deoxygenated conditions (closed argon atmosphere), formation of blue species that are persistent in the absence of oxygen was observed. On the basis of oxygen trapping and ESR experiments, the blue species are regarded as a mixture of a diradical intermediate DR and monoradicals derived thereof. The X-ray study of **1**-*p*-CO_2Me had revealed that the distances between the carbonyl oxygen and the *o*-*i*-Pr methine hydrogens are within the critical limit for hydrogen abstraction to occur, but a small reaction cavity or the compact crystal packing around both of the *o*-*i*-Pr groups is interfering with the photocyclization. The present results are consistent with this X-ray crystal structure; i.e., the photochemical hydrogen abstraction of **1**-*p*-CO_2Me to DR can take place, but DR reketonizes back to **1**-*p*-CO_2Me under the usual photolysis conditions because there is a high topochemical barrier to cyclization leading to **2**-*p*-CO_2Me.

Introduction

In contrast with efficient solid-state photocyclizations of several 2,4,6-triisopropylbenzophenones **1**-X (*X* = *p*-OMe, *p*-*t*-Bu, *p*-Me, H, *p*-Cl, *p*-CF_3) into the corresponding benzocyclobutenols **2**-X (89−100% conversion, ∼100% yield), **1**-X → DR → **2**-X (Scheme 1), 2,4,6-triisopropyl-4′-(methoxycarbonyl)-benzophenone (**1**-*p*-CO_2Me) underwent virtually no photoreaction.[1] This has been curious for us because we found later that all the other carboxy derivatives **1**-X (X = *m*- and *p*-CO_2H, *m*-CO_2Me, *p*-CO_2Et, *p*-$CO_2Ca_{0.5}$·$0.5H_2O$, *p*-(R)-$CO_2CH^*(Me)$-Et, *m*- and *p*-(S)-$CONHCH^*(CH_2Ph)CO_2Me$, *m*-COCl), excluding **1**-*p*-COCl, photocyclized with fair to good efficiencies in the solid state (no. 1−10 in Table 1).[2] Therefore, the X-ray study for photoinert **1**-*p*-CO_2Me and **1**-*p*-COCl was carried out.[3] The result has revealed that the distances between the carbonyl oxygen and the *o*-*i*-Pr methine hydrogens (2.95 and 2.98 Å for **1**-*p*-CO_2Me, 2.94 and 2.98 Å for **1**-*p*-COCl) are within the critical limit (3 Å)[4] for hydrogen abstraction to occur, but a narrow reaction cavity or the compact crystal packing around both of the *o*-*i*-Pr groups is interfering with the photocyclization. We have now found that the photocyclization of **1**-*p*-CO_2Me occurs in the solid state when the photolysis was carried out either (a) at elevated temperatures, (b) after thorough grinding, or (c) after solid−solid mixing with **1**-*p*-CO_2Et. Furthermore, when the solid-state irradiation of **1**-*p*-CO_2Me was performed under more carefully deoxygenated conditions, formation of blue radical species were observed, indicative of the existence of the diradical intermediate DR. These findings are nicely consistent with the above-mentioned X-ray crystal structure for **1**-*p*-CO_2Me.

SCHEME 1



Results and Discussion

The results that we have obtained so far from photolyses of various carboxy derivatives of 2,4,6-triisopropylbenzophenone in the solid state or in benzene solution are summarized in Table 1. Solid samples were prepared by gently pulverizing the crystals with a mortar and pestle, and the powder was placed in the Pyrex made apparatus for solid-state photolysis.[5] Irradiations were carried out with a 400-W high-pressure mercury lamp for several hours under an argon stream. During the irradiation, samples were cooled from the outside of the reaction vessel either by circulation of cold water maintained at 4 °C (solid) or by running water from a faucet (solution). However, in the case of experiments 14 and 15, the vessel was mounted on a hot plate.

Experiments 1−11 in Table 1 show that in solution, all the carboxy derivatives **1**-X can photocyclize to yield quantitatively

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[†] This work is dedicated to Professor N. J. Turro on the occasion of his 60th birthday.

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TABLE 1: Photolyses of Carboxy Derivatives of 2,4,6-Triisopropylbenzophenone in the Solid State or in Benzene Solution (0.01 M)[a]

	1-X		solid		solution	
no.	X	mp, °C	h	conv, %	h	conv, %
1	*p*-CO_2H	221−223	4	28	5	100
2	*m*-CO_2H	185−186	2	100[#]	2	100
3	*p*-$CO_2Ca_{0.5}\cdot 0.5H_2O$	>271	4	100	4[b]	100
4	*p*-(*S*)-$CONHCH(CH_2Ph)CO_2Me$	213−214	5	96[c]	5	100[d]
5	*m*-(*S*)-$CONHCH(CH_2Ph)CO_2Me$	116−118	4	100[d]	4	100[d]
6	*p*-COCl	119−120	10	0	4	21
7	*m*-COCl	127−128	4	35	4	100
8	*p*-(*R*)-$CO_2CH(Me)Et$	77−78	5	85	4	100
9	*p*-CO_2Et	98−101	4	76	4	100
10	*m*-CO_2Me	118−120	2	100[#]	2	100
11	*p*-CO_2Me	142−143	10	0[e]	4	100
12	*p*-CO_2Me[f]		10	4		
13	*p*-CO_2Me[g]		8	30[h]		
14	*p*-CO_2Me[i]		10	54		
15	*p*-COCl[j]		10	5		

[a] Conversions were estimated by NMR and HPLC analyses. Yields of **2**-X were nearly 100% in all cases unless marked by #, where minor amounts of uncharacterized products were formed (<10% by NMR). [b] A suspension. [c] Diastereomer excess of **2**, 87%. [d] Diastereomer excess of **2**, ∼0%. [e] Reference 1. From closer examinations by HPLC, it became clear that a trace of **2**-*p*-CO_2Me (<1%) was always formed probably at crystal defects. [f] The crystals were ground thoroughly by using an agate mortar and pestle. [g] An equimolar mixture of crystals of **1**-*p*-CO_2Me and **1**-*p*-CO_2Et was ground together in an agate mortar and pestle. [h] Conversion for the **1**-*p*-CO_2Et component, 78%. [i] Irradiated at 84 °C. [j] Irradiated at 69 °C. Irradiation at 86 °C resulted in a higher conversion but side reactions occurred.

the corresponding **2**-X. These compounds also photocyclized in the solid state (28−100% conversions, >90% yields) except **1**-*p*-CO_2Me and **1**-*p*-COCl, which were virtually photoinert.[1,2]

It was suggested on the basis of the crystal structure of **1**-*p*-CO_2Me that a deficient free space around the *o*-*i*-Pr groups might be responsible for the observed lack of its solid-state photoreactivity.[3] If this is true, any treatment that can disturb the crystal lattice of this material may result in recovery of its photoreactivity owing to decrease in the topochemical restriction to the benzocyclobutenol formation. We carried out several kinds of experiments, (i)−(iv), in order to prove this prediction.

(i) First, since there are in general more defects on the crystal surface than in the bulk, pulverization of the crystal should increase its defects. Therefore, the effect of complete grinding was examined. The crystals of **1**-*p*-CO_2Me were ground into fine powders with a mortar and pestle for a long time (30 min) and then irradiated. As expected, **1**-*p*-CO_2Me was transformed to the benzocyclobutenol **2**-*p*-CO_2Me, although the conversion was low (4%) (Table 1, no. 12).

(ii) It is known that molecules of similar shape and size can be easily substituted for each other in molecular crystals to form mixed crystals (a solid solution).[6] Hence, unreactive **1**-*p*-CO_2Me and reactive **1**-*p*-CO_2Et may mix freely, giving the former a more vacant space. Thus, an equimolar mixture of crystals of **1**-*p*-CO_2Me and **1**-*p*-CO_2Et was ground together in a mortar and pestle, and this solid mixture was irradiated. Both compounds were competitively converted to the corresponding benzocyclobutenols **2**-*p*-CO_2Me and **2**-*p*-CO_2Et at 30% and 78% conversion, respectively (Table 1, no. 13). It seems that **1**-*p*-CO_2Me acquired the photoreactivity as a result of mixed crystal formation with **1**-*p*-CO_2Et.

(iii) Third, inclusion of **1**-*p*-CO_2Me in the cavities of suitable host crystals is expected to impart an increased free space to the guest molecule.[5] Therefore, cocrystallization of **1**-*p*-CO_2Me with (±)-1-phenyl-1,2-ethanediol, deoxycholic acid, or cholic acid was attempted. However, the resultant crystal mixtures were photoinert. Probably **1**-*p*-CO_2Me failed to form inclusion crystals with these hosts.

(iv) Fourth, a temperature effect was examined. It is remarkable that upon solid-state photolysis at 84 °C, 54% of **1**-*p*-CO_2Me was converted to the benzocyclobutenol **2**-*p*-CO_2Me (Table 1, no. 14). Another photoinert crystal **1**-*p*-COCl also reacted at elevated temperatures (Table 1, no. 15). Figure 1a shows that the conversion to **2**-*p*-CO_2Me dramatically increased at temperatures higher than 55 °C. An energy term obtained from the plot of ln(conversion) against 1/*T* (Figure 2) had as large a value as 20 kcal/mol. This energy barrier might reflect a high stiffness of the cavity wall as well as an unfavorable size/shape of the reaction cavity.[7] In contrast, a temperature effect on the solution-state photolysis of **1**-*p*-CO_2Me was small (Figure 1b). We have previously shown that the quantum yield for photocyclization of **1**-H to **2**-H in benzene increased only slightly with increasing temperatures: Φ = 0.50, 0.52, 0.58, and 0.58 at 11.0, 25.0, 56.0, and 68.0 °C, respectively.[8] A temperature effect on the solid-state photolysis of **1**-*p*-CO_2H was also examined and turned out to be relatively small (Figure 1c).

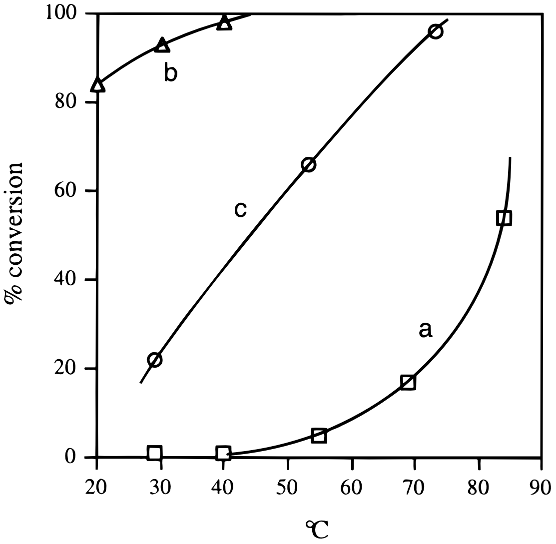


Figure 1. Temperature effects (a) on photolysis of **1**-*p*-CO_2Me in the solid state (irradiated for 10 h) or (b) in benzene solution (0.01 M, irradiated for 1 h) and (c) on photolysis of **1**-*p*-CO_2H in the solid state (irradiated for 5 h).

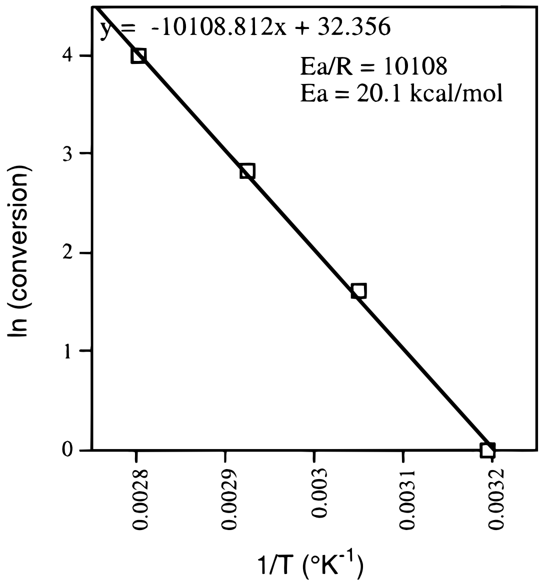


Figure 2. Plot of ln(conversion) vs 1/*T* for photolysis of **1**-*p*-CO_2Me in the solid state (the original data from Figure 1a).

The results described in (i), (ii), and (iv) led us to conclude that the unusual photostability of crystalline **1**-*p*-CO_2Me is simply due to its compact crystal packing, as was indicated by the X-ray study.[3] This conclusion is also consistent with the calculated high crystal density for **1**-*p*-CO_2Me (1.14 g/cm^3), which is somewhat larger than that for **1**-p-OMe (1.07), **1**-H (1.04), **1**-*p*-CO_2Et (1.10), **1**-*p*-CO_2H (1.11), or **1**-*m*-CO_2Me (1.10).[3] Since the reaction is sequential like **1**-*p*-CO_2Me → DR → **2**-*p*-CO_2Me, the observed stability may be ascribed to a topochemical hindrance to either of these steps. As we will show later, however, photolysis of nonpulverized crystals of **1**-*p*-CO_2Me generated oxygen-sensitive blue radical species that are likely to be a mixture of a diradical intermediate DR and other radicals derived thereof. Therefore, it is probably the process DR → **2**-*p*-CO_2Me that is hindered in the crystal lattice. This inference is reasonable, since the carbonyl oxygen and the *o*-*i*-Pr methine hydrogens are close enough for the hydrogen abstraction to occur but the vacant space around the *o*-*i*-Pr groups is too limited for the cyclization to take place.[3]

When the nonpulverized crystals of **1**-*p*-CO_2Me were irradiated in a closed apparatus filled with the argon gas rather than under an argon stream, their surfaces turned to deep blue, although the inside remained colorless. In the aforementioned photolysis of the powdered sample under an argon stream, such blueing was not obvious.[9] The photolysis of the nonpowdered crystals was followed by diffuse-reflectance spectroscopy (Figure 3A). The absorptions at $\lambda_{max} = 624$, 501, 480, 457, and ~360 nm continued to increase during irradiation for several hours. This blue color did not fade visibly under argon. In the air, however, the absorbance at 624 nm decayed rapidly at first, then gradually more slowly in the course of a few days, as displayed in Figure 3B. The absorbance at 624 nm decreased more than that at 501 nm, indicating that the photogenerated species are not a single substance. The decay rate became very slow after several days. For instance, the remaining absorbance at 624 nm relative to that immediately after irradiation was 38% even after 40 days. This result can be understood by assuming that more than one-third of the blue species are well protected from the attack by oxygen owing to their presence in the crystal bulk, which the oxygen molecule cannot easily penetrate into. The blue species in the crystal bulk had a high thermal stability; e.g., their decay rate at room temperature was increased only by 1.3 times at 83 °C.

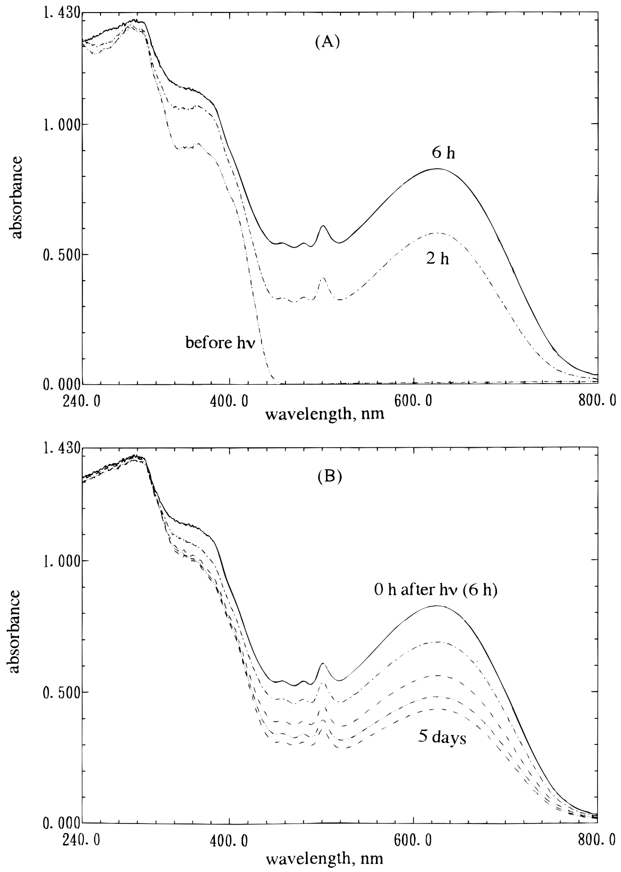


Figure 3. (A) Change in diffuse-reflectance spectra upon photolysis of nonpulverized crystals of **1**-*p*-CO_2Me irradiated for 0, 2, and 6 h. (B) Decay of photogenerated blue species in the air 0 h, 2 h, 1 day, 3 days, and 5 days after irradiation for 6 h.

When the blue crystals were dissolved in organic solvent, the color disappeared immediately and a number of very minor products were detected in the solution with virtually quantitative recovery of **1**-*p*-CO_2Me (NMR and HPLC). Among these minor products, two main products were identified as **2**-*p*-CO_2Me and a cyclic peroxide **3** by means of HPLC analyses (Figure 4). After repeated experiments, it was found that **3** was always formed in a higher yield when the blue crystals were dissoved in the presence of air (0.28−0.33% yield) than when dissoved under argon (0.09−0.19% yield) (Scheme 2). This result supports the existence of a small amount of DR in the blue crystals because the peroxide **3** must have been produced as a result of reaction between oxygen and the diradical DR.[10] The photoenol of 2,4,6-triisopropylbenzophenone (**1**-H) absorbs at 360 nm in hexane.[11] Diradicals derived from *o*-alkylbenzophenones exhibit a long-wavelength absorption band around 520−550 nm[12−15] and do not much differ from the blue species (λ_{max} 624 nm). This finding also seems to indicate the presence of some DR in the blue species.

Since the blue species were considerably quenched by contact with air, they must be radicals. ESR spectra measured for a single crystal showed one intense absorption with a *g* value of 2.002 87 and several paired lines on both sides of the central line (Figure 5). The former is assigned mainly to monoradicals produced in the crystals. However, there is a possibility of overlapping triplet species with small fine structures. Variation of its spectral intensity with irradiation time is shown in Figure 6. The time courses for the photolysis monitored by diffuse-

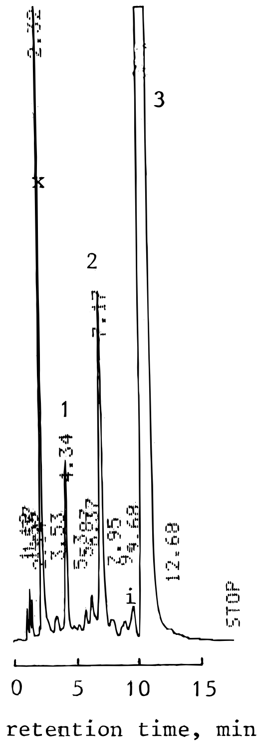
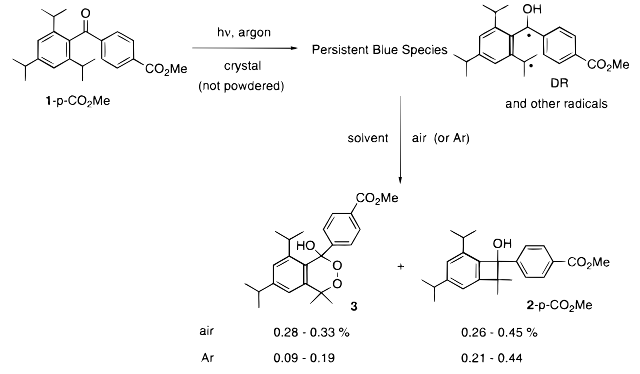


Figure 4. HPLC analysis of the blue crystals. In this experiment, only the blue surface was washed off with MeOH in the presence of air and was analyzed: (1) peroxide **3**; (2) **2**-*p*-CO_2Me; (3) **1**-*p*-CO_2Me; x, solvent; i, an impurity in **1**-*p*-CO_2Me.

SCHEME 2



reflectance spectroscopy (Figure 3A) and ESR spectroscopy (Figure 6) correlated with each other well, considering their different irradiation conditions. Spin counting of the central lines made after 13 h of irradiation showed the radical concentration of ca. 0.3% on the basis of 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl as standard.

Several paired lines seen in Figure 5 exhibited a strong angular dependence with respect to the magnetic field. Since the ESR fine structure of a triplet species in a single crystal comprises paired two lines and their separation changes depending on crystal orientation, these paired peaks indicate unambiguously the zero-field splitting tensor for the triplet radical species. Thus, we analyzed the angular dependence of the spectral separation for the most dominant triplet species (designated by arrows in Figure 5). The principal values of the zero-field splitting gave $|D| = 5.962$ and $|E| = 0.537$ mT. This triplet species ($S = 1$) comes either from the intramolecular or intermolecular radical ($S = {}^1/_2$) pairs. The zero-field splitting parameters obtained suggest the distance between the radicals to be in the range 7−8 Å. This value is too large for an intramolecular pair such as the diradical DR in Scheme 1. Moreover, a crystallographic inspection has revealed that the analyzed principal axes coincide not with the direction of the two radical centers of DR but with the intermolecular direction between the nearest-neighboring molecules, i.e., between molecule (x, y, z) and molecule ($1-x$, $-y$, $1 -z$) as is shown in Figure 7. Consequently, the most intense line pair in Figure 5 is assigned to an intermolecular radical pair, which was probably

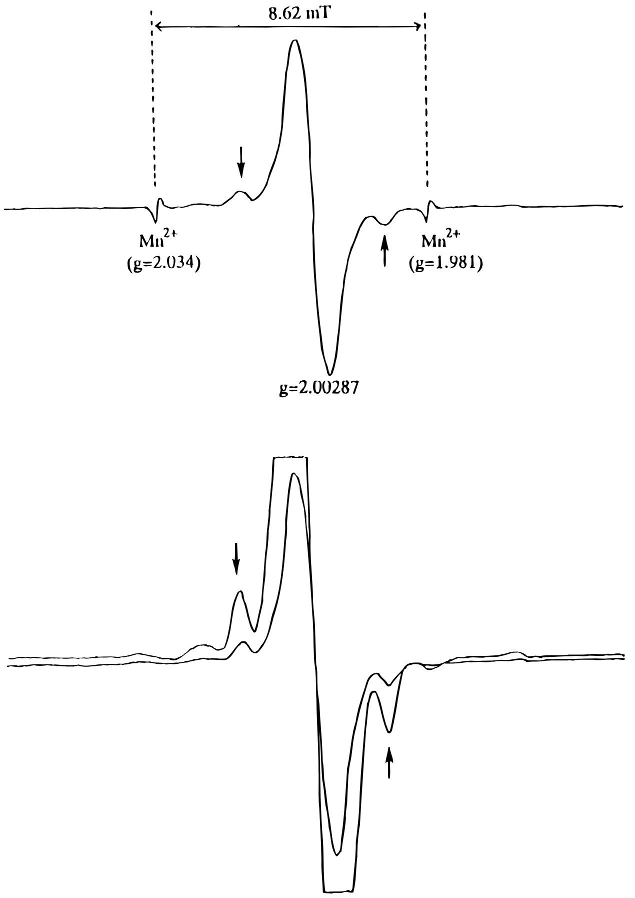


Figure 5. ESR spectra of the photoirradiated (3 h) **1**-*p*-CO_2Me single crystal in vacuo observed under amplitude of 320 with 0.2-mT field modulation. The upper spectrum consists of the central intense line, the paired two lines (designated by arrows), and the Mn^{2+} standard signals of the third and fourth hyperfine components. The lower spectra were taken under different amplitudes: 320 and 1000.

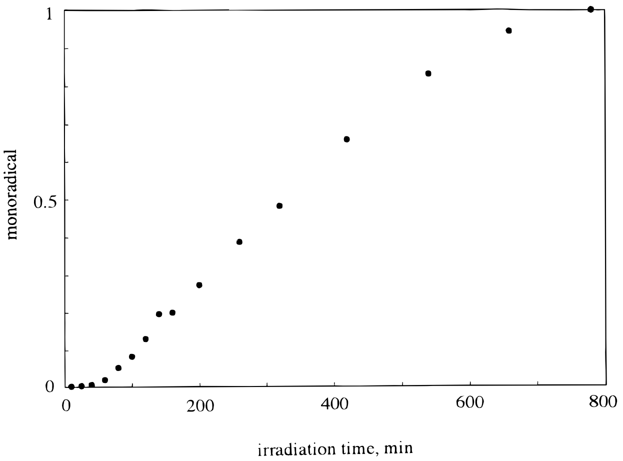


Figure 6. ESR spectral variation of the monoradical species depending on the irradiation time. Intensities were normalized at ca. 800 min irradiation.

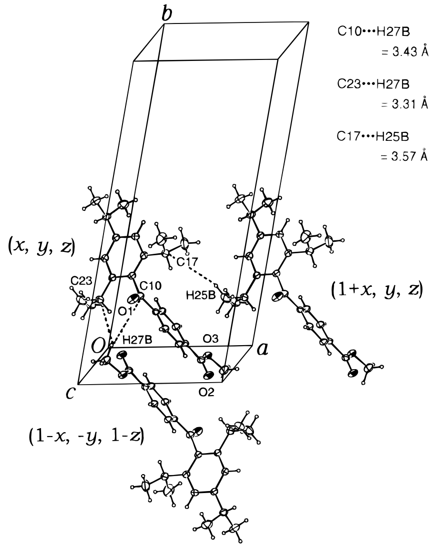


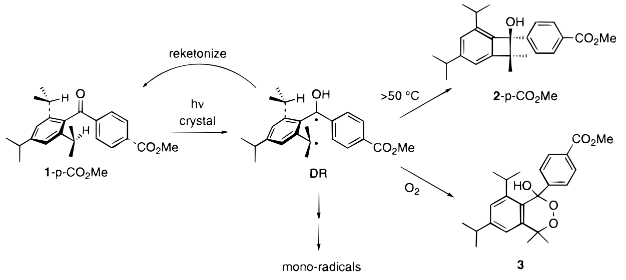
Figure 7. Crystal structure of **1**-*p*-CO_2Me.

formed via DR through H abstraction from the nearest-neighboring molecule. Judging from the yield of the O_2-trapped product **3** (0.28−0.33%), the DR species present in the crystal is very small in quantity and hence may elude detection under the present condition of ESR measurements.

Figure 7 displays the crystal structure of **1**-*p*-CO_2Me as well as the hydrogen atoms (H27B and H25B) that are nearest the ketone carbonyl carbon (C10) or nearest the *o*-*i*-Pr methine carbon (C23 or C17). Molecule (x, y, z) and molecule ($1 - x$, $-y$, $1 - z$), which are related by a center of symmetry, are close to each other, and this characteristic dimeric packing was considered to be a major driving force leading to its narrow reaction cavity.[3] The distances between the above carbon atoms and hydrogen atoms are 3.3−3.5 Å. Although these distances are considerably longer than the sum of van der Waals radii of C and H (2.9 Å), the intermolecular H abstraction, unlike the intramolecular one, may occur beyond this limit.[16] Of course, it is presumed here that the conformation of DR is not very different from that of the original ketone and that the radical centers are nearly localized. Indeed, the angular analysis of the most intense ESR triplet peaks demonstrated that the hydrogen-atom transfers occurred between DR and ketone in the dimeric structure (vide supra).

Photogeneration of similar blue species was observed for none of the other 2,4,6-triisopropylbenzophenones thus far studied. ESR signals observed from photolysis of the crystals of **1**-*p*-COCl or **1**-*p*-CO_2H were by far the weaker compared with those of **1**-*p*-CO_2Me. ESR signals were negligible in the case of **1**-H. The reason for this conspicuously high radical yield from **1**-*p*-CO_2Me is not clear at this moment. Possibly DR is longer-lived in the rigid crystal lattice of **1**-*p*-CO_2Me owing to inhibition of the cyclization process DR → **2**-*p*-CO_2Me. Hence, DR may have chances to be trapped by oxygen to yield **3** and to further abstract hydrogen atoms of neighboring **1**-*p*-CO_2Me molecules, giving a mixture of monoradical and diradical species (Scheme 3). Although DR has been assumed to exist in photocyclization of 2,4,6-triisopropylbenzophenones to benzocyclobutenols in solution,[8,10,17,18] they were unable to be detected by laser flash photolysis probably because of their short lifetimes ($\ll$100 ns).[11,12] The present results suggest that the lifetime of DR photogenerated from crystalline **1**-*p*-CO_2Me is lengthened as a consequence of its compact crystal packing around the *o*-*i*-Pr groups, and hence, DR may be directly detectable. Time-resolved ESR spectroscopy is in progress along this line.[20]

SCHEME 3



In summary, we have demonstrated by three simple means (thorough grinding, solid−solid mixing, and elevated temperatures) that a narrow reaction cavity is responsible for the previously found lack of solid-state photoreactivity for **1**-*p*-CO_2-Me. Blue radical species, which are very stable in the absence of oxygen, are regarded as a mixture of the photoenol-type diradical DR and monoradicals derived thereof.

Experimental Section

General Procedures. ^{1}H-NMR spectra (200 MHz) were measured on a Varian Gemini-200 spectrometer in $CDCl_3$. IR and mass spectra were recorded on JASCO FT/IR-5M and JEOL JMS-DX 300 spectrometers, respectively. Diffuse-reflectance spectra were measured with a Shimadzu UV-2400PC spectrometer equipped with a diffuse-reflectance attachment, and a $BaSO_4$ powder was used as a standard for reflectivity. HPLC analyses were performed with a Shimadzu LC-5A chromatograph and a UV detector (fixed at 217 nm) by using a Cosmosil 5C_{18}-AR column (4.6 mm i.d. × 150 mm) and a mixture of methanol and water (85:15 v/v) as eluent. ESR spectra were measured at the X band using JEOL-FE1XG with a 100-kHz field modulation.

Materials. 2,4,6-Triisopropyl-4′-(methoxycarbonyl)benzophenone (**1**-*p*-CO_2Me) and other derivatives (**1**-*p*-CO_2Et, **1**-*p*-CO_2H, **1**-*p*-COCl, **1**-H) employed in the present work were available from our previous work.[1,8,10,17−19] Preparations and photolyses of **1**-X ($X = p\text{-}CO_2Ca_{0.5}\cdot 0.5H_2O$, p-(R)-$CO_2CH^*(Me)$-Et, and *m*- and *p*-(S)-$CONHCH^*(CH_2Ph)CO_2Me$) will be reported elsewhere.[2]

Solid-State Photolysis. Crystals, which were ground into powders in an agate mortar and pestle, were placed in our solid-state photolysis vessel made of Pyrex glass.[5] Then irradiation was carried out with a 400-W high-pressure mercury lamp under a slow stream of argon. During the irradiation, the vessel was cooled from outside by circulation of cold water (4 °C) or heated on a hot plate (±2 °C). After the photolysis, the reaction mixture was dissolved in suitable solvents (usually MeOH and $CDCl_3$) and analyzed by NMR and HPLC.

Diffuse-Reflectance Spectra Measurements. Into a shallow hollow for the diffuse-reflectance spectrum measurement, 3 g of $BaSO_4$ powders and subsequently 150 mg of nonpulverized crystals of **1**-*p*-CO_2Me were pressed. This was placed in our solid-state photolysis vessel[5] and was degassed, then filled with argon. This degassing−argon-charge cycle was repeated three times and the vessel was closed. The sample was irradiated as described above. The diffuse-reflectance spectra were measured in the air at room temperature before and after irradiation.

ESR Measurements. An ESR tube containing a crystalline 2,4,6-triisopropylbenzophenone was sealed under high vacuum. This was irradiated with a 450-W high-pressure mercury lamp at ambient temperature, and the ESR spectra were measured. Mn^{2+} solid solution in MgO (1/2000) and 4-hydroxy-2,2,6,6-

tetramethylpiperidine-1-oxyl benzene solution were used for the calibration of the magnetic field and for spin-counting, respectively.

Preparation of Cyclic Peroxide 3. An authentic sample of a cyclic peroxide **3** was prepared by solution photolysis of **1**-*p*-CO_2Me in the presence of oxygen.[10] A 0.01 M solution of **1**-*p*-CO_2Me (226 mg) in benzene (60 mL) was irradiated through Pyrex with a 400-W high-pressure mercury lamp for 3 h under bubbling of oxygen. The reaction mixture was evaporated under reduced pressure to remove the solvent. The pale-yellow residue, which was a mixture consisting of **2**-*p*-CO_2Me and a small amount of **3** (NMR), was recrystallized from hexane (20 mL) to afford 108 mg of **2**-*p*-CO_2Me as colorless needles. The mother liquor was concentrated and then was subjected to preparative TLC on silica gel (Merck Kieselgel 60 F_{254}, benzene) followed by recrystallization with pentane (2 mL) to give 14 mg (6%) of **3** as white crystals, mp 143−147 °C. ^1H NMR ($CDCl_3$, 200 MHz): δ 0.47 (3H, d, $J = 7.0$ Hz, CH*Me*), 1.06 (3H, d, $J = 7.0$ Hz, CH*Me*), 1.27 (6H, d, $J = 7.0$ Hz, CHMe_2), 1.55 (3H, s, Me), 1.75 (3H, s, Me), 2.91 (2H, finely split septet, $J = 7$ Hz, 2-C*H*Me_2), 3.91 (3H, s, CO_2Me), 4.12 (1H, s, OH), 6.92 (1H, finely split s, aromatic), 7.04 (1H, finely split s, aromatic), 7.53 (2H, broad s, phenylene), 7.99 (2H, d, $J = 8.4$ Hz, phenylene). MS *m*/*z* (rel intensity): 398 (2, M^+), 367 (91), 366 (72), 365 (100), 351 (57), 307 (71), 231 (71). IR (KBr): 3467, 2962, 1721, 1711, 1611, 1282, 1188, 1114, 771 cm^{-1}.

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References and Notes

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(20) There is a dispute about which is an immediate precursor to benzocyclobutenol, diradical (=enol triplet) or enol.[18,21] This paper cannot answer this question. Certainly, however, the blue species are radical, not enol.[22]

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(22) We have recently reported a single-crystal-to-single-crystal diastereoselective photocyclization of *N*-(*p*-(2,4,6-triisopropylbenzoyl)benzoyl)-L-phenylalanine methyl ester (**1**-*p*-(*S*)-CONHCH*(CH_2Ph)CO_2Me).[23] The X-ray crystal-structure analysis of this transformation has revealed that the carbonyl carbon and the nearer *o*-*i*-Pr methine carbon approached each other with nearly no rotation around the single bonds linking these carbons to the triisopropylphenyl ring. This result seems to eliminate enol as an intermediate to benzocyclobutenol. More detailed discussion will be reported elsewhere.

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