

SOLID STATE PHOTOCHEMISTRY OF 2,5-CYCLOHEXADIENONES

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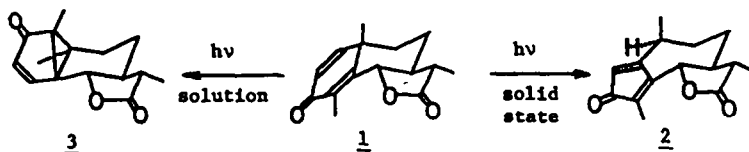
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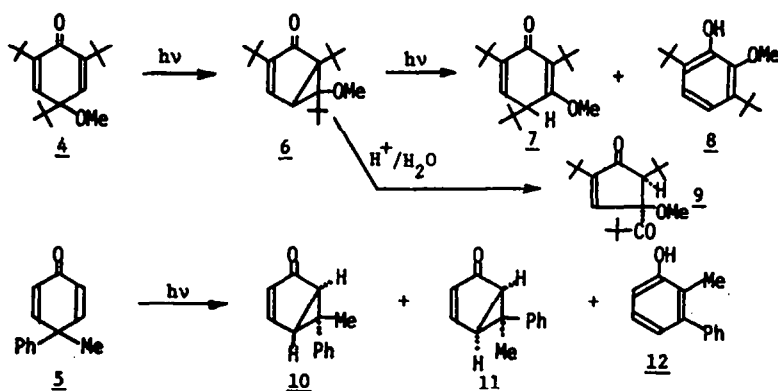
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Abstract — Santonin, a 2,5-cyclohexadienone, is known to undergo photo-rearrangement to lumisantonin in solution but to a cyclopentadienone in the solid state in accordance with the topochemical principle of a minimum of atomic movement in crystal lattice. In contrast to this fact, 2,5-cyclohexadienones 4 and 5 were found to undergo photoreactions similar to those in solution, possibly due to their loose crystal lattice structure. Irradiation of 4 gave 7 and 8 via lumiketone 6. The ratio 8/7 was found to decrease with decreasing temperature in the solid-state photoreaction of 4 and 6 and also to decrease with the addition of naphthalene to 6. The X-ray crystallographic analysis of 6 is reported.

In our laboratory α -santonin (1) was found to undergo a different type of photoisomerization reaction in the crystalline state yielding a cyclopentadienone 2 instead of lumisantonin (3) which had been known as the major photoproduct of α -santonin in solution.¹ The rearrangement to 3 requires a large spatial movement of the skeletal atoms, while the solid state photoreaction to 2 does no such a large movement of atoms. This interpretation appeared to fit to a topochemical principle proposed by Cohen and Schmidt² that a reaction in the solid state occurs with a minimum amount of atomic movement. In accordance with this interpretation, the X-ray structure analysis of α -santonin has shown that short intermolecular contacts permitting only restricted movement of atoms are seen between neighbouring α -santonin molecules in the crystalline state.³



In recent years much attention has been drawn to organic photochemistry of non-homogeneous systems including solid states.⁴ However, most of the solid state photoreactions so far reported involve mainly photodimerization of olefinic compounds but only several examples of photoisomerization^{4b,6} such as the solid state photoreaction of α -santonin. In order to explore a new field of organic photochemistry in solid state, we have revisited to examine the photochemical behaviors of other 2,5-cyclohexadienones 4 and 5 in the crystalline state. The solution photochemistry of these cyclohexadienones has been well studied. Compound 4 undergoes photorearrangement to a lumiketone 6 which is further transformed to photoketone 7 and photophenol 8.⁷ In an aqueous acidic medium, lumiketone 6 is hydrolyzed to a cyclopentenone 9 and its stereoisomer. Compound 5 gives



two isomeric photoketones (lumi-type photoproducts) A and B (10 and 11 respectively) and a photophenol.⁸ Although the structure of the photophenol was not given in the original paper, we have now given structure 12 for this photoproduct. (See below.)

Two reports have appeared on the solid state photochemistry of cyclohexadienones, 2,4,6,6-tetrachloro-3-methyl-5-isopropyl-2,4-cyclohexadienones⁹ and 4-trichloromethyl-4-methyl-2,5-cyclohexadienone¹⁰ giving an isomeric 2,4,4,6-tetrachloro-3-methyl-5-isopropyl-2,5-cyclohexadienone and a homopolymer, respectively.

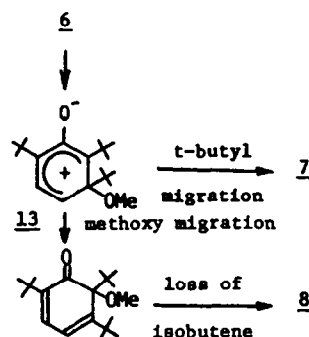
Results and Discussion

Irradiation of cyclohexadienone 4 in the solid state at various temperatures with Pyrex-filtered light ($>290\text{nm}$) gave lumiketone 6, photoketone 7 and photophenol 8 as products detectable by the NMR analysis of the irradiated mixture. On preparative TLC of the mixture of 6, 7 and 8, cyclopentenone 9 was obtained in a detectable amount which was formed from 6 by hydrolysis during TLC. The ratio of 8/7 decreased with decreasing temperature, while the ratio was not much altered by changing the irradiation temperature in hexane solution (Table 1). The results indicate that in the solid state, the phototransformation of lumiketone 6 to 8 is retarded at lower temperatures, probably because the formation of 8 may be more sensitive to environmental conditions than that of 7 from 6. A zwitterionic species 13 has been proposed as the intermediate for the formation of 7 and 8 from 6.^{7b}

Table 1. Yields of photoproducts on irradiation of 4 at various temperatures in the solid state and in solution.^a

	Irradn. time (h)	Temp. (°C)	% yield of				Ratio <u>8/7</u>
			<u>4</u>	<u>6</u>	<u>7</u>	<u>8</u>	
Solid state	10	0	0	0	71	29	0.41
	10	-40	13	20	51	16	0.31
	10	-80	29	22	41	7	0.17
Hexane solution	1.5	r.t.	0	0	55	45	0.83
	10	-40	0	0	53	47	0.88
	10	-80	0	0	58	42	0.73

^aYields were obtained from the NMR analysis of the irradiated mixture in CDCl_3 .



It should be noted that irradiation of 4 in hexane solution with longer wavelength light ($>410\text{ nm}$) gave a high yield (78 %) of lumiketone 6 compared with the previous result (maximum 18 % by irradiation with a tungsten lamp).^{7b} Similarly, irradiation of 4 with $>410\text{ nm}$ light in the

solid state gave lumiketone 6 exclusively. In both cases the transformation of 6 to 7 and 8 is negligibly small under the irradiation conditions.

One can conclude that, in contrast to the solid state photochemistry of α -santonin,¹ 2,5-cyclohexadienone 4 does not suffer topochemical restriction in its solid state photoreaction and gives lumiketone 6 which is the main photoproduct in solution. In order to testify this conclusion the crystal of 4 was submitted to X-ray crystallographic analysis. However, we failed to obtain crystals good enough to the X-ray analysis. This is possibly due to insufficient compactness of the crystal packing of 4 caused by relatively weak intermolecular forces between bulky *t*-butyl groups, compared with the short intermolecular contacts in the crystal of α -santonin.³

In order to get more insight to the temperature dependence of the product ratio (8/7) in the solid state photoreaction of 4, the photochemical behavior of 6, the intermediate for 7 and 8 formation, was examined in the solid state. Irradiation of the crystals of 6 with Pyrex-filtered light was made at various temperatures. The results are summarized in Table 2, indicating that 7 and 8 were the only photoproducts and that the ratio 8/7 decreased with decreasing temperature, similarly to the temperature dependence in the solid state photoreaction of 4.

The X-ray crystallographic analysis of lumiketone 6 was performed (Figure 1 and Figure 2). The crystal data were as follows: $C_{19}H_{32}O_2$, $M = 292.5$, monoclinic, space group $P2_1/n$, $a = 15.46$ (2), $b = 18.46$ (2), $c = 6.54$ (1) Å, $\beta = 99.7$ (1)°, $V = 1839$ Å³, $Z = 4$, $D_c = 1.06$ g/cm³. The final atomic coordinates for non-hydrogen atoms (Table 3) and the bond lengths and angles (Table 4) are tabulated. The final R value was somewhat large as 0.12 for 1324 reflections. This is because the accurate intensities could not be measured due to extremely broad diffraction profiles and anisotropy of diffraction profiles. The low density (1.06 g/cm³) of the crystals compared with that (1.265 g/cm³) of α -santonin³ indicates that the crystal packing has loose compactness similar to that considered for cyclohexadienone 4. One can conclude that the photoreaction of 4 and 6 in the solid state may not be affected by topochemical factors involving the restriction of a spatial movement of the skeletal atoms, but may occur in the similar manner to the solution phase.

Table 2. Yields of photoproducts on irradiation of 6 at various temperatures in the solid state.^a

Irradn. time (h)	Temp. (°C)	% Yield of			Ratio <u>8/7</u>
		<u>6</u>	<u>7</u>	<u>8</u>	
10	1	19	55	26	0.48
10	-40	39	44	17	0.40
10	-80	42	44	14	0.32

^a Yields were obtained from the NMR analysis of the irradiated mixture in $CDCl_3$.

Table 5. Effect of added naphthalene in the solid state photoreaction of 6.^a

w/w ratio of naphthalene to <u>6</u>	Ratio of <u>8/7</u>
0 : 1	0.48
1 : 50	0.19
1 : 2	0.13
1 : 1	0.09

^a A mixture was irradiated in the solid state with a high-pressure mercury lamp through Pyrex at 0°C for 8 hr. The product ratio was obtained by the NMR analysis of the irradiated mixture.

In the course of the photochemical study of lumiketone 6 in the solid state, we found an interesting phenomenon on the effect of naphthalene doping. As shown in the Table 5, the product ratio (8/7) decreased with increasing amount of added naphthalene. Similar irradiation of a 1 : 1 molar mixture of 6 and tetracyanoethylene at 0°C in the solid state resulted in the exclusive formation of 7 and 8 at the ratio 8/7 of 0.33, showing a little effect of added tetracyanoethylene. The role of added naphthalene in the decrease of the ratio 8/7 is not clear at present.

Next, we examined the photochemical behavior of cyclohexadienone 5 in the solid state. Irradiation of crystals of 5 at 0°C with light through Pyrex under nitrogen resulted in slow photo-conversion (85 % recovery after 30 h's irradiation) to give a mixture of at least four products, from which two phenolic products, photophenol A and photophenol B in 6.7 % and 4.4 % yields,

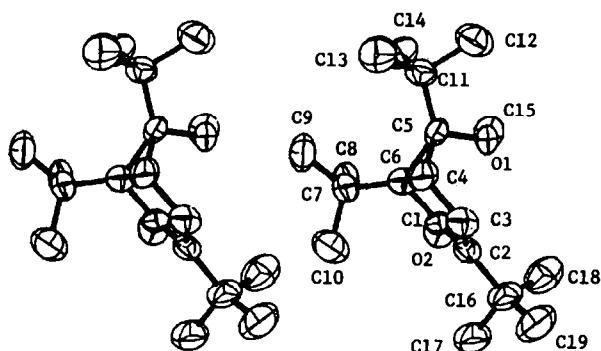


Figure 1. Stereoscopic view of lumiketone 6 drawn by DCMS-3.¹¹

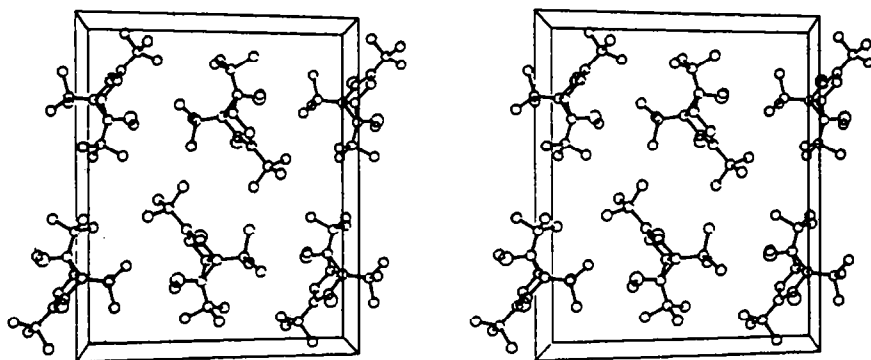


Figure 2. Stereodrawing of the molecular packing in the crystal viewed along the *c* axis.

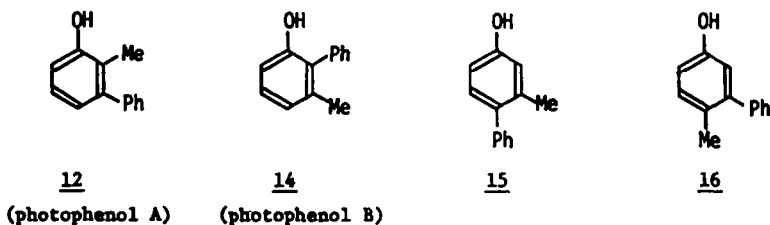
Table 3. Final atomic coordinates for non-hydrogen atoms.

	x	y	z
C(1)	0.5748(6)	0.6584(5)	0.1967(16)
C(2)	0.6234(6)	0.6257(5)	0.3916(14)
C(3)	0.6134(7)	0.6649(5)	0.5529(14)
C(4)	0.5514(7)	0.7250(5)	0.4982(16)
C(5)	0.5706(6)	0.7852(5)	0.3532(16)
C(6)	0.5136(6)	0.7184(5)	0.2683(15)
C(7)	0.4168(7)	0.7081(6)	0.1772(19)
C(8)	0.4008(7)	0.7210(7)	-0.0619(16)
C(9)	0.3512(7)	0.7552(7)	0.2726(20)
C(10)	0.3940(8)	0.6263(7)	0.2260(21)
C(11)	0.5451(7)	0.8638(5)	0.3881(17)
C(12)	0.6307(8)	0.9032(6)	0.4857(20)
C(13)	0.4839(8)	0.8745(7)	0.5545(19)
C(14)	0.5065(8)	0.9031(6)	0.1868(18)
C(15)	0.6643(7)	0.7945(6)	0.0885(17)
C(16)	0.6878(8)	0.5623(6)	0.3777(19)
C(17)	0.6348(10)	0.4994(7)	0.2667(23)
C(18)	0.7604(10)	0.5850(8)	0.2490(23)
C(19)	0.7288(9)	0.5383(7)	0.5967(22)
O(1)	0.5750(5)	0.6438(4)	0.0195(11)
O(2)	0.5750(5)	0.6438(4)	0.0195(11)

Table 4. Bond lengths (Å) and angles (°) of 6 with estimated standard deviations in parentheses.

C(1)-C(2)	1.49(1)	C(1)-C(6)	1.58(1)	C(1)-O(2)	1.19(1)
C(2)-C(3)	1.31(1)	C(2)-C(16)	1.55(2)	C(3)-C(4)	1.47(2)
C(4)-C(5)	1.52(2)	C(4)-C(6)	1.52(1)	C(5)-C(6)	1.56(2)
C(5)-C(11)	1.53(2)	C(5)-O(1)	1.43(1)	C(6)-C(7)	1.56(2)
C(7)-C(8)	1.56(2)	C(7)-C(9)	1.52(2)	C(7)-C(10)	1.59(2)
C(11)-C(12)	1.55(2)	C(11)-C(13)	1.57(2)	C(11)-C(14)	1.53(2)
C(15)-C(1)	1.45(1)	C(16)-C(17)	1.53(2)	C(16)-C(18)	1.57(2)
C(16)-C(19)	1.53(2)				
C(2)-C(1)-C(6)	106(1)	C(2)-C(1)-O(2)	131(1)		
C(6)-C(1)-O(2)	123(1)	C(1)-C(2)-C(3)	111(1)		
C(1)-C(2)-C(16)	119(1)	C(3)-C(2)-C(16)	129(1)		
C(2)-C(3)-C(4)	112(1)	C(3)-C(4)-C(5)	121(1)		
C(3)-C(4)-C(6)	108(1)	C(5)-C(4)-C(6)	62(1)		
C(4)-C(5)-C(6)	59(1)	C(4)-C(5)-C(11)	121(1)		
C(4)-C(5)-O(1)	111(1)	C(6)-C(5)-C(11)	131(1)		
C(6)-C(5)-O(1)	110(1)	C(11)-C(5)-O(1)	113(1)		
C(1)-C(6)-C(4)	102(1)	C(1)-C(6)-C(5)	109(1)		
C(1)-C(6)-C(7)	114(1)	C(4)-C(6)-C(5)	59(1)		
C(4)-C(6)-C(7)	125(1)	C(5)-C(6)-C(7)	134(1)		
C(6)-C(7)-C(8)	109(1)	C(6)-C(7)-C(9)	116(1)		
C(6)-C(7)-C(10)	105(1)	C(8)-C(7)-C(9)	110(1)		
C(8)-C(7)-C(10)	110(1)	C(9)-C(7)-C(10)	107(1)		
C(5)-C(11)-C(12)	106(1)	C(5)-C(11)-C(13)	115(1)		
C(5)-C(11)-C(14)	113(1)	C(12)-C(11)-C(13)	103(1)		
C(12)-C(11)-C(14)	108(1)	C(13)-C(11)-C(14)	110(1)		
C(2)-C(16)-C(17)	108(1)	C(2)-C(16)-C(18)	111(1)		
C(2)-C(16)-C(19)	109(1)	C(17)-C(16)-C(18)	109(1)		
C(17)-C(16)-C(19)	109(1)	C(18)-C(16)-C(19)	111(1)		
C(5)-O(1)-C(15)	116(1)				

respectively. Attempts to isolate other two products were not successful because of their instability to transform into a mixture of photophenol A and photophenol B on standing at room temperature. Irradiation of 5 in an acetone solution gave two lumi-products, 10 (11 %) and 11 (24 %), and photophenol A (25 %) as previously reported.⁸ Provided that the lumi-type photoproducts 10 and 11 are the precursors of all photophenols, four possible structures, 12, 14, 15 and 16 can be written for the photophenols. Photophenol 14 is a known compound¹² whose IR spectrum was identical with that of photophenol B. Among three other structures 12, 15 and 16 for photophenol A, the spectral data of the newly synthesized 15 (see Experimental) and the known 16¹³ did not coincide with those of photophenol A, showing that photophenol A is formulated as 12.



Conclusion

In the solid state photoreaction of both cyclohexadienones, 4 and 5, we did not find any evidence for the formation of a cyclopentadienone product of type 2 which was the major photoproduct of α -santonin (1) in the solid state. In these cases, most of the photoproducts identified were essentially same as those in solution. The results suggest that the topochemical principle of a minimum amount of atomic movement in the solid state photochemistry is not necessarily valid for certain kinds of crystalline compounds. Such compounds may have empty spaces in their crystal lattice sufficient enough to permit easier atomic movement during photoreaction. There have been several reports on the deviation from the topochemical principle in the solid state photodimerization of olefins.¹⁴

EXPERIMENTAL

Melting points were determined on a Yanagimoto micro-melting-point apparatus and are uncorrected. ¹H-NMR, IR, UV and mass spectra were taken on Varian T-60, JASCO IRA-1, Shimadzu UV-200 and JEOL JMS-DX 300 spectrometers, respectively.

Irradiation in the solid state. Crystals of the substrates were ground to a fine powder in a mortar. The powder was placed between two Pyrex disks (8cm dia., 2mm thickness) and irradiated under a nitrogen atmosphere at given temperature by using a 400-W high-pressure mercury lamp as a light source. The separation between the lamp and the sample was approximately 5 cm.

Irradiation of 2,4,6-tri-*t*-butyl-4-methoxy-2,5-cyclohexadienone (4).

In the solid state. Compound 4⁷ (0.50 g) was irradiated as above at 0°C (ice-water cooling) for 8 h. The pale yellow colored solid was recrystallized from methanol to give photoketone 7 (230 mg, 46 %), which was identical with an authentic sample.^{7b} Preparative TLC of the mother liquor (silica gel, 1 : 2 hexane-benzene) gave photophenol 8 (80 mg, 17 %) and cyclopentenone 9 (15 mg, 3.4 %) which were identified by a comparison with authentic samples.^{7b,c} In a preparative scale experiment at -40°C, 7, 8 and 9 were obtained in 31.4, 6.6 and 4.0 % yields, respectively. The temperature dependence of this photoreaction has been examined at 0°, -40° and -80°C. The result is shown in Table 1. In these experiments, cyclopentenone 9 was detected only by TLC but the yield was so low that it could not be determined by NMR analysis.

In solution. Irradiations were made by Pyrex-filtered light as reported previously.^{7b} The results are shown in Table 1. When compound 4 (1.00 g) in hexane (200 ml) was irradiated with a 400-W high-pressure mercury lamp through an NaNO₂ filter solution (>410 nm) at 0°C, the formation of 7 and 8 was not observed by NMR analysis of the irradiated mixture and lumiketone 6 (0.78 g, 78 %) was isolated by recrystallization. In the previous report^{7b} the highest yield of 6 was 18 %.

Irradiation of lumiketone 6.

In the solid state. Irradiations were made in a similar manner to that described above. The temperature was controlled by a circulating cooling bath (Cryocool CC-100 (NESLAB)). See Table 2.

The effect of added naphthalene and tetracyanoethylene. A mixture of 6 and the added compound of a given ratio was ground to a fine powder in a mortar. The mixture was heated to a melt which solidified on cooling. The solid was powdered and irradiated under similar conditions (Table 5).

Irradiation of 4-methyl-4-phenyl-2,5-cyclohexadienone (5).

In the solid state. Compound 5 (0.50 g) was irradiated at 0°C under nitrogen for 30 h. The photoreaction proceeded very slowly, especially after several hour's irradiation. The NMR spectrum

of the reaction mixture revealed that about 85 % of the starting material remained unreacted. The pale yellow colored mixture was submitted to preparative TLC (silica gel, 95 : 5 hexane-benzene) gave 3-methyl-2-phenylphenol (**13**) (5.0 mg, 7 % based on the reacted **5**), 2-methyl-3-phenylphenol (**12**) (3.3 mg, 4 %) and two unidentified products (total 11.6 mg). Both of the unidentified products were unstable to give a mixture of **12** and **14** on standing at room temperature and their purification was unsuccessful.

In acetone solution. Irradiation of **5** in acetone at room temperature gave **10** (11 %), **11** (24 %) and **12** (25 %).

2-Methyl-3-phenylphenol (**12**): m.p. 57-58°C; $^1\text{H-NMR}$ (CDCl_3) δ 2.15 (s, 3H), 5.10 (s, 1H), 6.75-7.42 (m, 8H); MS m/e 184 (M^+ , rel.int. 100); λ_{max} (EtOH) 245 nm (log ϵ 4.6), 280 (4.3); ν_{max} (neat) 3420, 785, 760, 695 cm^{-1} . Anal. Calcd. for $\text{C}_{13}\text{H}_{12}\text{O}$: C, 84.75; H, 6.57. Found: C, 84.11; H, 6.61.

3-Methyl-2-phenylphenol (**14**): m.p. 54-56°C; $^1\text{H-NMR}$ (CDCl_3) δ 2.01 (s, 3H), 4.75 (s, 1H), 6.65-7.40 (m, 8H); MS m/e 184 (M^+ , rel.int. 100); λ_{max} (EtOH) 235 nm (log ϵ 4.6), 279 (4.4); ν_{max} (neat) 3600, 785, 750, 708 cm^{-1} . Anal. Calcd. for $\text{C}_{13}\text{H}_{12}\text{O}$: C, 84.75; H, 6.57. Found: C, 84.53; H, 6.45. This compound was identified with the known compound by a comparison of IR spectra.¹²

4-Methyl-3-phenylphenol (**16**) was prepared by the method of Marx, *et al.*:¹³ a liquid; $^1\text{H-NMR}$ (CDCl_3) δ 2.15 (s, 3H), 5.00 (s, 1H), 6.60-7.40 (m, 8H); MS m/e 184 (M^+); λ_{max} (EtOH) 225 nm (log ϵ 4.0), 287 (3.4); ν_{max} (neat) 3350, 775, 750, 695 cm^{-1} .

3-Methyl-4-phenylphenol (**15**).

A solution of 3-methyl-4-bromophenol¹⁵ (1.89 g, 0.01 mol) in benzene (100 ml) was irradiated with a 10-W low-pressure mercury lamp (quartz made) for 50 h under nitrogen according to the known procedure.¹⁶ The solvent was removed in vacuo and the residual oil was chromatographed on a silica gel column with benzene to give 18 mg (1 %) of **15**: a liquid; $^1\text{H-NMR}$ (CDCl_3) δ 2.30 (s, 3H), 5.10 (s, 1H), 6.80-7.50 (m, 8H); MS m/e 184 (M^+ , rel.int. 100); λ_{max} (EtOH) 223 nm (log ϵ 4.0), 245 (3.8), 295 (2.5); ν_{max} (neat) 3530, 800, 760, 695 cm^{-1} . Anal. Calcd. for $\text{C}_{13}\text{H}_{12}\text{O}$: C, 84.75; H, 6.57. Found: C, 84.99; H, 6.59.

X-Ray crystallography.

The unit-cell constants and intensities were measured at room temperature using Ni-filtered $\text{CuK}\alpha$ radiation on a Rigaku four-circle diffractometer.¹⁷ Crystal data are given in the text. Due to broad diffraction profiles ω -scan technique was applied with scan width of $20^\circ + 0.2^\circ \tan\theta$. The backgrounds were counted for 5 s at start and end points of the scan. Of the 2236 independent reflections measured up to $2\theta = 110^\circ$, 1324 reflections with $F > 2\sigma$ were used for the structure analysis. The intensities of monitored reflection decreased as the measurement proceeded. The decay was estimated as a function of $(\sin \theta/\lambda)^2$ from the intensities of 98 reflections at the start and end of the measurement. The intensities were corrected for the decay as function of elapsed time and $(\sin \theta/\lambda)^2$ as well as for Lorentz and polarization factors.

The structure was solved by the program MULTAN.¹⁸ The positional and anisotropic thermal parameters of non-hydrogen atoms were refined by the block-diagonal least-squares method.¹⁹ Most of hydrogen atoms were located in the difference Fourier synthesis, and included in the successive refinement with isotropic thermal parameters. The unit weight was applied for all reflections. The final R value was 0.12 for 1324 reflections. The atomic scattering factors were taken from the International Tables for X-ray Crystallography.²⁰

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