Tetrahedron Vol. 43, No. 7, pp. 1307 to 1312, 1987
Printed in Great Britain.

0040-4020/87 \$3.00+.00
Pergamon Journals Ltd.

SOLID STATE PHOTOCHEMISTRY OF METHYL-SUBSTITUTED BENZOPHENONES

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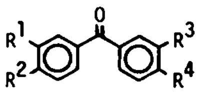
(*Received in UK* 16 *February* 1987)

Abstract - Upon UV irradiation in the solid-state 4,4'-dimethylbenzophenone (1a) underwent intermolecular hydrogen abstraction, followed by radical coupling, to give solely a dimeric product, 4-(2-hydroxy-2,2-di-p-tolylethyl)-4'-methylbenzophenone (2). By contrast, 3,3'-dimethylbenzophenone (1b), 3,4'-dimethylbenzophenone (1c), and 4-methylbenzophenone (1d) were photostable under the same conditions. From X-ray crystallographic analysis of 1a and 1d, the distances between the C=O group and the nearby methyl C-H bond are 3.32 Å for O··H and 3.87 Å for C··C for reactive 1a and 2.77 (or 2.72) Å for O··H and 4.39 (or 4.53) Å for C··C for unreactive 1d. The angle C=O··H is 92° for 1a and 121 or 137° for 1d. The long C··C distance or/and the large C=O··H angle is probably responsible for the photoinertness of 1d.

It is generally accepted that reactions in solid states tend to occur with a minimum amount of atomic and molecular motion (topochemical principle). Since this concept was first stated by Schmidt,[1a] it has been refined with several other concepts. For example, the course of solid state reactions has been interpreted in terms of reaction cavity,[2] molecular volume and free space,[3] local stress,[4] and steric compression.[5]

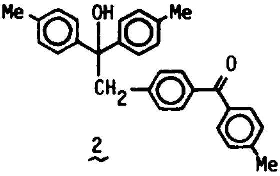
Investigation about the solid-state photochemical cycloaddition of olefins has been extensively done and this led to the formulation of Schmidt's criterion: the double bonds should be approximately parallel and no further than ca. 4.1 Å apart for dimerization to occur.[1] This rule, however, has several exceptions.[6]

Photochemical hydrogen abstraction by ketones in the solid state has also attracted considerable attention. The detailed study of the tetrahydronaphthoquinone system has revealed the steric compression control of the reaction.[5,7] Other carbonyl compounds studied so far include α-cyclohexylacetophenones,[8] α-adamantylacetophenones,[9] N,N-dialkyl-α-oxoamides,[10] cyclopentane-1,2-diones,[11] 2-tert-butylbenzophenones,[12] and 2,4,6-triisopropylbenzophenones.[13] We note that the hydrogen abstraction reactions occurring in these compounds are of intramolecular type. Photochemical intermolecular hydrogen abstraction in pure ketone crystals appears still unreported. We will now describe that crystalline 4,4'-dimethylbenzophenone (1a) undergoes dimerization through intermolecular hydrogen abstraction, whereas 3,3'-dimethylbenzophenone (1b), 3,4'-dimethylbenzophenone (1c), and 4-methylbenzophenone (1d) are photostable in the solid state.



1

a, $R^1=R^3=H$, $R^2=R^4=Me$
b, $R^1=R^3=Me$, $R^2=R^4=H$
c, $R^1=R^4=Me$, $R^2=R^3=H$
d, $R^1=R^3=R^4=H$, $R^2=Me$



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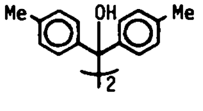

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RESULTS AND DISCUSSION

Each sample of crystalline methyl-substituted benzophenones **1a** - **1d** (recrystallized from ethanol) was ground to a fine powder in a mortar. The powder was spread between two Pyrex plates and irradiated with a high-pressure mercury lamp under a nitrogen atmosphere at 0 °C for 10 - 20 h (Table 1, runs 1 and 5 - 7). As shown in the table, **1a** reacted to give a dimer **2** as a sole product (run 1). In sharp contrast, no reaction was observed for **1b** - **d** (runs 5 - 7). HPLC monitoring of the photolysis of solid **1a** indicated that the conversion of **1a** levelled off at ca. 15 % after irradiation for ca. 1 h. The selective dimerization of **1a** into **2** implies that the photoreaction (intermolecular hydrogen abstraction and radical coupling) proceeded under topochemical control (cf. Scheme Ia).

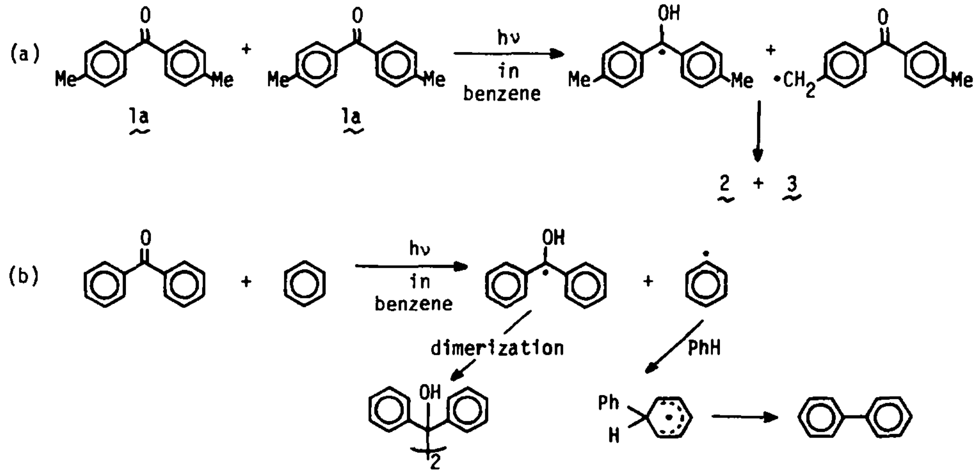
Table 1. Photolyses of methyl-substituted benzophenones **1a** - **d** in the solid and solution phases.

run	reactant	mp, °C	phase	irradn time, h	product (%)^a	recovered (%)^a
1	**1a**	95	solid	10	**2** (∿100)	85
2	**1a**		soln; 0.10 M in PhH	12	**2** (22), **3** (35)	46
3	**1a**		soln; 1.15 M in PhH	12	**2** (11), **3** (14)	72
4	**1a**		soln; 0.095 M in i-PrOH/PhH (1 : 10 v/v)	0.7	**3** (∿100)^b	0
5	**1b**	49 - 50	solid	12	none	∿100^b
6	**1c**	71 - 73	solid	20	none	∿100^b
7	**1d**	59 - 60	solid	12	none	∿100^b

^{a}Isolation yield by preparative TLC. ^{b}Yield estimated from NMR and TLC.

In order to compare between solid-phase and solution-phase photoreactions, photolysis of **1a** in benzene was carried out. While the photolysate obtained in a benzene solution was a complex mixture, the dimer **2** and a benzopinacol **3** could be isolated from it in low yields (Table 1, runs 2 and 3). In the presence of isopropyl alcohol, a good hydrogen donor, **3** was furnished quantitatively (run 4). Irradiations of **1b** - **d** in solution gave similar results.

Scheme I



Production of **2** and **3** from **1a** in benzene will need some comments. The triplet state of benzophenone itself can abstract a hydrogen atom from benzene with a low efficiency, resulting in slow production of benzopinacol and biphenyl as main products (Scheme Ib).[14] In the present case, however, the hydrogen source should be a methyl group of the reactant **1** (Scheme Ia), since even a trace amount of biphenyl was unable to be detected upon photolyses of **1** in benzene.

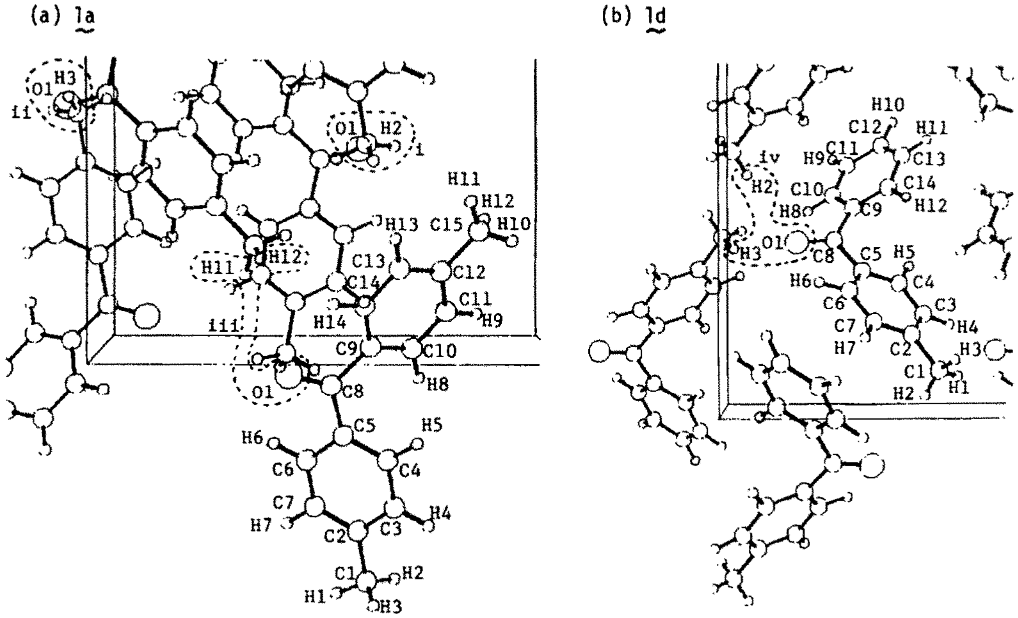


Figure 1. The numbering schemes used for **1a** and **1d**. The carbonyl oxygen and the nearby hydrogen atom are indicated by enclosing them with a dotted line. Symmetry operation: (i) -1/2 + x, 3/2 - y, -z, (ii) -1/2 + x, 1/2 - y, -z, (iii) 1/2 - x, 1 - y, -1/2 + z, (iv) 1/2 - x, 1/2 + y, 1 - z and -1/2 + x, 1/2 - y, -1 + z.

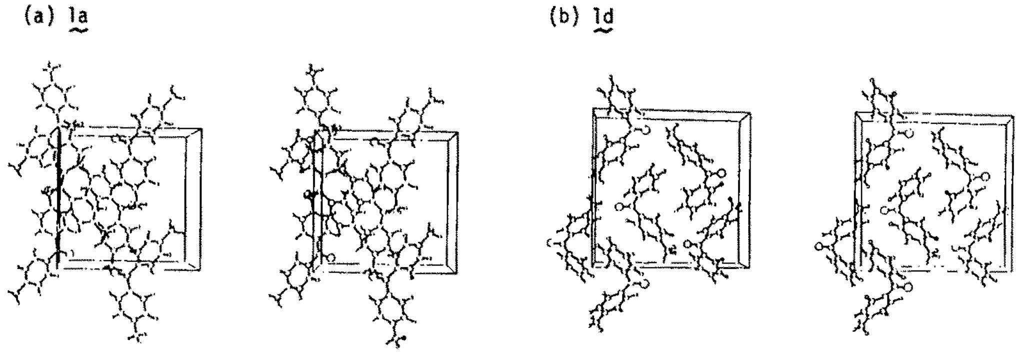


Figure 2. The molecular crystal packing for **1a** and **1d**. (a) **1a**, view along b axis; (b) **1d**, view along c axis.

The selective dimerization of **1a** into **2** in the solid state contrasts with the complete lack of reactivity of crystalline **1b** - **d**. Thus X-ray crystallography of 4,4'-dimethylbenzophenone (**1a**) and 4-methylbenzophenone (**1d**) was performed. The crystal data are summarized in the experimental section. Figures 1 and 2 display the numbering schemes and the stereoviews of the crystal packing, respectively. Figure 1 also indicates the sites where the carbonyl oxygen and the methyl hydrogen stand close to each other (sites i - iv). The distance between the carbonyl oxygen and the nearby hydrogen H_n (d), the degree to which H_n lies outside the mean plane of the carbonyl group (α), the angle C_8-O1-H_n (β), and the distance between the carbonyl carbon and the methyl carbon to which H_n is bonded (d') are summarized in Table 2.

Scheffer has suggested that, for (intramolecular) hydrogen abstraction by the carbonyl group to occur in the solid state, the upper limit of the distance d should be the sum of the van der Waals radii of the hydrogen and oxygen atoms (2.72 Å).[7] The angles α and β can deviate considerably from their optimum values (0° and 90°, respectively), e.g., a successful hydrogen abstraction

Table 2. Distances and angles relevant to solid-state intermolecular hydrogen abstraction and radical coupling.

reactant	site of close contact[a]	d (Å)	α (°)	β (°)	d' (Å)
1a	i	O1···H2, 3.32	80	92	C8···C1, 3.87
	ii	O1···H3, 3.13	72	108	C8···C1, 4.53
	iii	O1···H11, 3.29	43	116	C8···C15, 4.38
		O1···H12, 3.25	16	117	
1d	iv	O1···H2, 2.77	42	121	C8···C1, 4.39
		O1···H3, 2.72	29	137	C8···C1, 4.53

[a] See Figure 1.

reaction with α = 60°[9a] or with β = 80°[5b] is known. The van der Waals radii sum limit is not an appropriate measure in the present case, since reactive 1a has an unsuitable hydrogen abstraction distance (the shortest d = 3.13 Å) while unreactive 1d has a suitable one (the shortest d = 2.72 Å) (Table 2).

The differing solid-state reactivity of 1a and 1d appears to be consistent with the criterion proposed by Lahav.[15] He studied photoaddition in crystalline channel inclusion complexes formed between deoxycholic acid and several ketones and proposes that the maximal distances for the photoaddition reaction (intermolecular hydrogen abstraction followed by radical coupling) to occur are that d = 3.5 Å and d' = 4.2 Å. The requirement for the angle α is found to be unimportant. Inspection of Table 2 readily shows that only the site i of crystalline 1a (d = 3.32 Å and d' = 3.87 Å) satisfies the conditions for d and d'. It is noticeable that the angle β of this site (= 92°) is close to the ideal value. Probably 1d is unreactive as a result of either one or both of two unfavorable crystallographic arrangements: (1) the separation d' (= 4.39 or 4.53 Å) is too long for the radical coupling to occur and (2) the value of β (= 121 or 137°) is too large for the hydrogen abstraction to occur.[21]

EXPERIMENTAL

Starting Materials. 4,4'-Dimethylbenzophenone (1a) and 4-methylbenzophenone (1d) are commercially available. 3,3'-Dimethylbenzophenone (1b) and 3,4'-dimethylbenzophenone (1c) were prepared by the Grignard reaction.[16] All these benzophenones were purified by repeated recrystallization from ethanol.

Solid-State Photolysis of 1a. Crystals of 1a were ground to a fine powder in a mortar. The powder (210 mg) was placed between two Pyrex disks (8 cm diameter) and irradiated under a nitrogen atmosphere for 10 h at 0 °C (ice - water) 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. The reaction mixture was separated by preparative TLC (silica gel, benzene as eluent) to give 178 mg of the recovered 1a and 31 mg (∿100 % yield) of a dimeric product, 4-(2-hydroxy-2,2-di-p-tolylethyl)-4'-methylbenzophenone (2). This was recrystallized from hexane - ethyl acetate (10 : 1 v/v) to give colorless crystals: mp 53 - 55 °C; ^{1}H NMR (60 MHz, $CDCl_3$) δ 2.22 (broad, 1 H, OH, disappeared on deuteration), 2.28 (s, 6 H, CH_3), 2.39 (s, 3 H, CH_3), 3.61 (s, 2 H, CH_2), 6.84 - 7.32 (m, 12 H, aromatic), 7.39 - 7.67 (q, 4 H, aromatic); ^{13}C NMR (100.4 MHz, $CDCl_3$) 196.3 (C=O), 143.6, 142.9, 141.5, 136.5, 136.0, 135.1, 130.8, 130.2, 129.5, 128.9, 128.8, 126.1, 78.0 (COH), 48.0 (CH_2), 21.6 (CH_3), 21.0 (CH_3); IR (nujol) 3460 (OH), 1635 (C=O), 1605, 1280, 1175, 780, 760, 730 cm^{-1}; MS m/e 420 (M^+, relative intensity 0.3), 210 (100). Anal. Calcd for $C_{30}H_{28}O_2$: C, 85.68; H, 6.71. Found: C, 85.56; H, 6.73.

Solid-state photolyses of 1b - d were similarly carried out. The starting materials were quantitatively recovered (NMR and TLC).

Solution-Phase Photolysis of 1a. A solution of 1a (210 mg, 1 mmol) in 10 mL of benzene was irradiated with a 400-W high-pressure mercury lamp (Pyrex) for 12 h under bubbling of nitrogen. The reaction mixture was evaporated and the residue was separated by preparative TLC (silica gel; benzene as solvent). The dimer 2 (26 mg, 22 % yield), 1,1,2,2-tetrakis(4-methylphenyl)-1,2-ethanediol (3) (41 mg, 35 % yield), and the recovered 1a (96 mg) were obtained. Pinacol 3 was characterized by comparison with the authentic sample (NMR, IR, and TLC); mp 169 - 172 °C (lit.[17] mp 175 - 177 °C).

Photolysis of a solution of 1a (726 mg, 3.5 mmol) in 3 mL of benzene or of a solution of 1a (216 mg, 1 mmol) in a mixture of isopropyl alcohol (1 mL) and benzene (10 mL) was similarly carried out.

X-ray Analyses of 1a and 1d. The unit-cell constants and intensities were measured at room temperature using Ni-filtered CuKα radiation on a Rigaku four-circle diffractometer. The intensities of independent reflections were measured up to 2θ = 120° with θ-2θ scan technique. The width and speed of the scan were 0.9° + 0.15°tanθ and 4°/min, respectively. The backgrounds were counted for 4 s on both sides of the scan range. The crystal data and number of reflections obtained for each crystal are given in Table 3. The intensities of periodically monitored reflections showed no significant change for 1a, but gradual decrease for 1d (about 7 % in F at the end of the measurement). The correction for the decay was applied for 1d. The usual Lorentz and polarization corrections were made for both crystals. 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] The hydrogen atoms were located in the difference Fourier synthesis, and included in the successive refinement with isotropic temperature factors. Extinction correction was made for the six strongest reflections for 1a and for the eight strongest ones for 1d. The unit weight was applied for all reflections. The final R values were 0.044 and 0.082 for 1a and 1d respectively. The atomic scattering factors were taken from the International Tables for X-ray Crystallography.[20] The atomic parameters are given in Tables 4 and 5.

Table 3. Crystal data and number of reflections measured.

	1a	1d
molecular formula	$C_{15}H_{14}O$	$C_{14}H_{12}O$
molecular weight	210.3	196.2
crystal system	orthorhombic	monoclinic
space group	$P2_12_12_1$	$P2_1/a$
a	12.164(3) Å	14.071(3) Å
b	7.950(2)	13.884(4)
c	12.263(3)	5.694(2)
β	-	95.15(2)°
unit-cell volume	1185.9 $Å^3$	1107.9 $Å^3$
Z	4	4
D_c	1.18 g/cm^3	1.18 g/cm^3
no of measured reflections	1026	1653
no of significant reflections	971 (F>3σ)	1288 (F>2σ)

Acknowledgment. We thank all the staffs of the Crystallographic Research Center of Osaka University for permitting us to use the four-circle diffractometer.

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Table 4. Final atomic coordinates of **1a**.

	x	y	z		x	y	z
C(1)	1.0362(3)	0.5980(7)	0.0920(4)	O(1)	0.5511(2)	0.4086(5)	-0.0821(2)
C(2)	0.9160(3)	0.5596(5)	0.0718(3)	H(1)	1.070(4)	0.656(6)	0.026(3)
C(3)	0.8546(3)	0.4790(5)	0.1521(3)	H(2)	1.043(4)	0.691(6)	0.158(4)
C(4)	0.7439(3)	0.4431(5)	0.1346(3)	H(3)	1.075(4)	0.482(6)	0.106(4)
C(5)	0.6938(3)	0.4876(5)	0.0370(3)	H(4)	0.890(3)	0.440(5)	0.227(3)
C(6)	0.7562(3)	0.5662(5)	-0.0435(3)	H(5)	0.702(3)	0.379(5)	0.198(3)
C(7)	0.8656(3)	0.6026(5)	-0.0256(3)	H(6)	0.720(3)	0.592(5)	-0.119(3)
C(8)	0.5768(3)	0.4457(5)	0.0112(3)	H(7)	0.911(3)	0.671(5)	-0.089(3)
C(9)	0.4913(3)	0.4490(5)	0.0985(3)	H(8)	0.572(3)	0.614(5)	0.209(3)
C(10)	0.5021(3)	0.5445(5)	0.1929(3)	H(9)	0.427(3)	0.616(5)	0.341(3)
C(11)	0.4183(3)	0.5451(5)	0.2698(3)	H(10)	0.253(3)	0.400(6)	0.409(3)
C(12)	0.3227(3)	0.4537(5)	0.2544(3)	H(11)	0.164(3)	0.394(6)	0.318(3)
C(13)	0.3125(3)	0.3574(5)	0.1593(3)	H(12)	0.208(3)	0.571(6)	0.356(3)
C(14)	0.3952(3)	0.3562(5)	0.0824(3)	H(13)	0.246(3)	0.283(5)	0.149(3)
C(15)	0.2323(3)	0.4563(6)	0.3388(3)	H(14)	0.388(3)	0.275(5)	0.013(3)

Table 5. Final atomic coordinates of **1d**.

	x	y	z		x	y	z
C(1)	0.4831(4)	0.1008(4)	0.7800(10)	O(1)	0.1660(2)	0.3869(3)	0.2767(8)
C(2)	0.4246(3)	0.1787(3)	0.6480(8)	H(1)	0.528(4)	0.085(4)	0.673(10)
C(3)	0.4554(3)	0.2215(3)	0.4496(8)	H(2)	0.450(4)	0.046(5)	0.813(11)
C(4)	0.4017(3)	0.2933(3)	0.3321(7)	H(3)	0.514(5)	0.129(5)	0.947(11)
C(5)	0.3154(3)	0.3217(3)	0.4102(7)	H(4)	0.518(3)	0.196(3)	0.380(8)
C(6)	0.2840(3)	0.2779(3)	0.6073(8)	H(5)	0.427(3)	0.331(3)	0.184(7)
C(7)	0.3383(3)	0.2076(3)	0.7270(8)	H(6)	0.218(3)	0.296(4)	0.656(8)
C(8)	0.2524(3)	0.3927(3)	0.2779(8)	H(7)	0.318(3)	0.177(3)	0.881(8)
C(9)	0.2961(3)	0.4720(3)	0.1434(7)	H(8)	0.190(3)	0.464(4)	-0.128(8)
C(10)	0.2492(3)	0.5020(3)	-0.0675(8)	H(9)	0.250(4)	0.593(4)	-0.354(9)
C(11)	0.2840(4)	0.5771(4)	-0.1891(9)	H(10)	0.393(4)	0.685(4)	-0.191(9)
C(12)	0.3646(4)	0.6249(4)	-0.0996(10)	H(11)	0.468(4)	0.632(4)	0.176(9)
C(13)	0.4116(4)	0.5965(4)	0.1106(10)	H(12)	0.417(3)	0.492(3)	0.399(8)
C(14)	0.3781(3)	0.5187(3)	0.2352(8)				

(21) A relative twist of the two benzene rings is 51° for **1a** and 62° for **1d**. A possible correlation between the twist angle and the reactivity cannot be judged at present.