

PHOTOREACTION OF 2-BENZOYLCYCLOHEXANONES ON A SILICA GEL SURFACE: DEVIATION FROM THEIR SOLUTION PHOTOCHEMISTRY

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On irradiation on a dry silica gel surface, 2-benzoylcyclohexanones which have the lowest n, π^* state and are devoid of methyl substituents on their cyclohexanone rings, undergo an oxidative cleavage to give adipic acid and substituted benzoic acid along with the Norrish Type II product. Irradiation of 2-chlorocyclohexanone and cyclohexane-1,2-dione on silica gel also gives adipic acid. The cyclohexanonyl radical on the surface, which is produced from the α -cleavage of the 2-benzoyl group of the 2-benzoylcyclohexanones or the cleavage of the C—Cl bond of 2-chlorocyclohexanone, is suggested as the precursor of adipic acid; the radical is probably converted into cyclohexane-1,2-dione, which undergoes a secondary photoreaction to give adipic acid on the surface.

INTRODUCTION

The photochemistry and spectroscopy of organic molecules adsorbed on a silica gel or alumina surface have been investigated extensively because of their potential use as diagnostic probes of surface-adsorbate interactions.¹ However, the types of photoreaction observed on the surface are fundamentally the same as those seen in solution,² although large differences in the product distributions have been observed in some cases.³ We have recently reported that the photoreactivity of 2-benzoylcycloalkanones in solution is conformationally sensitive;⁴ 2-benzoylcyclohexanone undergoes an exclusive Norrish Type II cleavage⁵ while 2-benzoylcyclooctanone undergoes a Type II cyclization and α -cleavage in competition with the Type II cleavage. This was attributed to the stereoelectronic requirements of the reactants.⁴ We report here that 2-benzoylcyclohexanones show a different photochemical behaviour on a silica gel surface to that observed in solution.

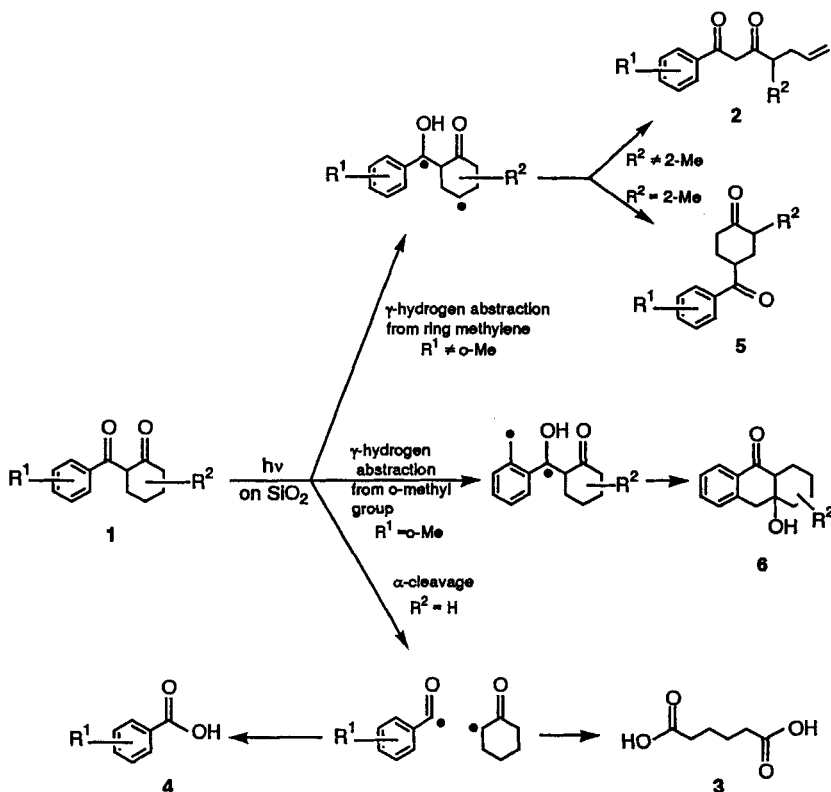
RESULTS AND DISCUSSION

Irradiation of 2-benzoylcyclohexanone (**1a**) on dry

silica gel with a 100 W high-pressure mercury lamp gave 1-phenylhept-6-ene-1,3-dione (**2a**), adipic acid (**3**) and benzoic acid (**4a**) (Scheme 1) in 19, 16, and 11% yields, respectively. A trace of cyclohexanone was also detected. Formation of **2a** can be explained in terms of a Type II cleavage of **1a**;⁵ however, the other photoproducts cannot be derived from a Type II cleavage. It is improbable that **3** and **4a** are produced by a secondary photoreaction of **2a** because **2a** was stable under these irradiation conditions.

The formation of **3** and **4a** might be explained in terms of a photooxidation of the enol form of **1a** on a silica gel surface. However, this possibility is excluded by the following. Benzoic acid, albeit in low yield, was detected in the heterogeneous photoreaction of 2-benzoyl-2-methylcyclohexanone (**1b**), which has no enol form. The main photoproduct from **1b** was 4-benzoyl-2-methylcyclohexanone (**5b**), as found in solution, which is formed through ring opening of the Type II cyclization product.⁶ Formation of **4a** can be explained in terms of the oxidation of benzaldehyde formed by the α -cleavage of **1a**. Indeed, irradiation of benzaldehyde on a silica gel surface gave benzoic acid. Adipic acid may be derived from the other α -cleavage fragment, the cyclohexanonyl radical. The following results support this interpretation.

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It is known that α -halo ketones undergo a cleavage of their carbon-halogen bond on irradiation.⁷ The photoreaction of 2-chlorocyclohexanone (7), expected to produce the cyclohexanoyl radical both on the silica gel surface and in solution, was carried out in order to determine the behaviour of the cyclohexanoyl radical on the silica gel surface. Irradiation of a benzene solution of 7 with a 450 W high-pressure mercury lamp gave cyclohexanone in 38% yield. This suggested the intervention of the cyclohexanoyl radical and its intermolecular hydrogen abstraction. On the other hand, irradiation of 7 on dry silica gel gave adipic acid in 25% yield. A trace of cyclohexanone was also detected. Cyclohexanone irradiated on the silica gel surface could, in principle, be a precursor of adipic acid. However, irradiation of cyclohexanone on the surface gave no adipic acid and 98% of cyclohexanone was recovered, supporting the view that adipic acid is derived from the cyclohexanoyl radical itself produced from the α -cleavage of 1a. Irradiation of 1a on a silica gel surface under degassed conditions also gave adipic acid. Therefore, it is probable that the cyclohexanoyl radical is trapped by silanol oxygen rather than by an oxygen molecule. However, the participation of an

oxygen molecule could not be completely eliminated because perfect degassing of the adsorbed oxygen on the surface may not be achieved by usual freeze-pump-thaw cycle. The cyclohexanoyl radical may be converted into cyclohexane-1,2-dione (9) and adipic acid may be formed via a secondary photoreaction of 9. Then, photoreaction of 9 was carried out in order to explore this possibility. When cyclohexane-1,2-dione was irradiated on a silica gel surface, adipic acid could be obtained in 47% yield. This supports the above interpretation although 9 could not be detected in the photoreaction of 1a. The formation of adipic acid can be explained in terms of an α -cleavage of 9.

There may be active sites acting as a hydrogen donor and a hydroxyl or oxygen donor on a silica gel surface and radicals on the surface may receive a hydrogen atom or a hydroxyl radical. Stable radicals such as 1,1-diphenyl-2-picrylhydrazyl (DPPH) are known to act as a hydrogen acceptor from a solid surface.⁸ When silica gel was kept standing in a benzene solution of the radical for 48 h, the presence of a hydrogenated product, 1,1-diphenyl-2-picrylhydrazine (DPPH₂), was observed by ultraviolet spectroscopy⁸ and thin-layer chromatograph and could be isolated by thick-layer

chromatography. Under the experimental conditions of the isolation the radical was stable and no conversion from the radical to the hydrazine was observed. We can safely conclude that there is a hydrogen donor centre on the silica gel surface and the benzoyl radical acquires hydrogen from the centre to form benzaldehyde. If there is a hydroxyl donor centre on the surface, hydrogen of DPPH₂ may be abstracted by the radical to form DPPH. However, no evidence for the presence of the donor centre was obtained by the experiment using DPPH₂.

Since molecules of benzoylcyclohexanone in a greater than monomolecular layer would be expected to act as a filter for the benzoylcyclohexanone molecules in the adsorbed layer,^{2a,5a} the coverage could be an important factor in the photoreaction. The surface area per gram of the silica gel used (Merck Kieselgel 60, Art. 7734) was 494 m². Using Dreiding molecular models the area per molecule of **1a** can be estimated to be $ca\ 1.2 \times 10^{-18}\ m^2$, whence monolayer coverage may be estimated as $ca\ 0.7\ mmol\ g^{-1}$, ($A = 1$). When the ratio of **1a** to silica gel is over $0.7\ mmol\ g^{-1}$, multiple layers must be formed and, indeed, may be formed at lower coverages in 'pools.' In the region $A > 1$ the yield of the Type II product should increase with increase in the coverage, and the conversion yield should reach a limiting value which may approximate that in the solution photoreaction of **1a** when the surface reaction becomes negligible because of the internal filter effect by molecules that exist in a layer that is more than a monomolecular layer. Indeed, the expected effect of the variation in coverage on the production of the Type II product **2a** was observed (Figure 1). The conversion

yield of **2a** in the reaction on the surface at coverages exceeding $A = 2$ was constant and was consistent with that observed in solution (82%).^{5a} Adipic acid and benzoic acid were not detected at these coverages.

Irradiation of 2-(*m*-methyl)- and 2-(*p*-methyl)benzoylcyclohexanone (**1e** and **1f**) on the silica gel surface also gave the Type II cleavage products **2e** and **2f**, adipic acid and substituted benzoic acids **3e** and **3f**, respectively. The irradiation of 2-(*o*-methyl)benzoylcyclohexanone (**1d**) proceeded differently. Irradiation of **1d** on the silica gel surface gave adipic acid and *o*-toluic acid in 11 and 10% yields, respectively, along with **6** (17%). In homogeneous solution intramolecular hydrogen abstraction from an *o*-methyl group is known to occur *ca.* 100 times faster than that from an alkyl methylene.⁹ Indeed, irradiation of **1d** in methanol has been reported to give **6**, through γ -hydrogen abstraction from the *o*-methyl group, but no photoproducts derived from hydrogen abstraction from the cycloalkane ring.¹⁰ The process to form adipic acid and *o*-toluic acid apparently competes with the hydrogen abstraction from the *o*-methyl group; the latter may be relatively lower on the surface than in solution.

In the irradiation of *p*-methoxybenzoylcyclohexanone (**1g**), the lowest excited state of which is expected to be the π, π^* state, no photoproduct was obtained. Therefore, the photoreaction of **1** on the surface seems to proceed from the n, π^* state.

Methyl substitution on the benzene ring did not affect the yields of **3** and **4**, but that on the cyclohexanone ring did. Thus 2-methylcyclohexanone (**1b**) gave only a trace of benzoic acid, as mentioned above. Irradiation of 2-benzoyl-4-methylcyclohexanone (**1c**) gave **2c** in 13%

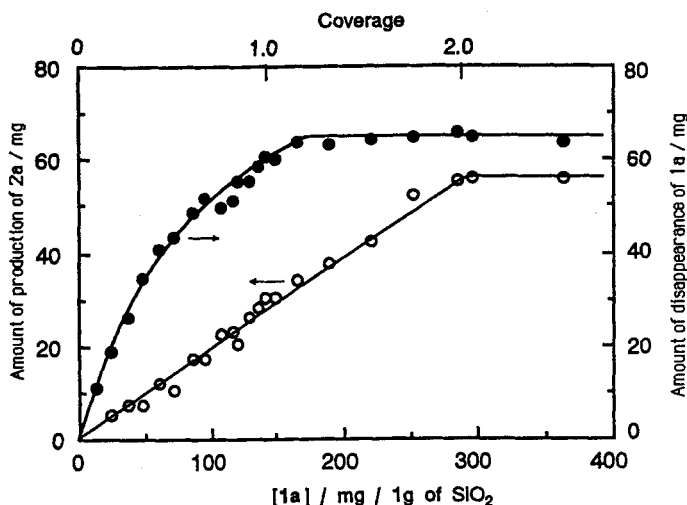
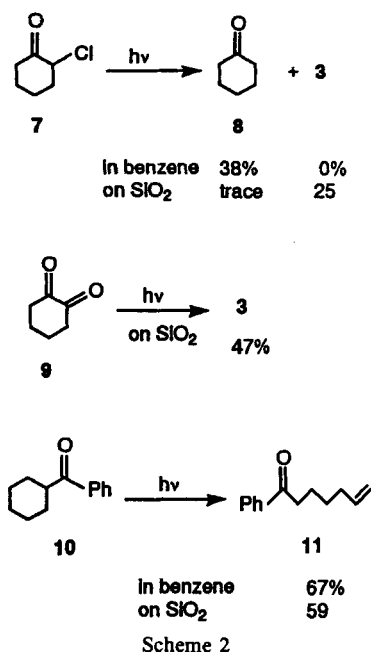


Figure 1. Dependence of the coverage on the extent of disappearance of **1a** and production of **2a** in the surface photoreaction of **1a**. A 1 g amount of silica gel was used for all runs. (○) Production of **2a**; (●) disappearance of **1a**

yield. In this case neither benzoic acid nor 3-methyladipic acid could be detected. These results indicate that the manner of adsorption of **1b** and **1c** on a silica gel surface is probably different from that of the 2-aryl-cyclohexanones lacking alkanone substituents; the difference may be conformational in origin. Conformational flexibility has been shown to be an important factor in the photoreactivity of **1** in solution.⁴ The conformational change of 2-aryl-cyclohexanones lacking an alkanone substituent seems to be more restricted than 2-aryl-cycloalkanones having an alkyl substituent and the restriction decreases the population of conformers suitable for the Type II reaction and increases the relative rate of α -cleavage. The alkanone substituent may reduce surface-adsorbate interactions because of a steric effect.

Since irradiation of benzoylcyclohexane (**10**) both in benzene¹¹ and on a silica gel surface gave the Type II cleavage product (**11**), in 67 and 59% yields, respectively, it can be concluded that the presence of the secondary carbonyl group on the cyclohexanone ring is important for the reaction observed on the silica gel surface. The binding may involve chelation by the 1,3-dicarbonyl group.



CONCLUSIONS

When 2-benzoylcyclohexanones which have no methyl substituents on their cyclohexanone rings were irradiated on a silica gel surface, a new type of photo-

reaction to give adipic and benzoic acid occurred along with the Type II reaction. The cyclohexanoyl radical formed on the surface is proposed as the precursor of the acids.

EXPERIMENTAL

Silica gel (Merck Kieselgel 60, Art. 7734) was used as received. Benzoylcyclohexanones **1**,^{5,6,12} 2-chlorocyclohexanone (**7**),¹³ cyclohexanone-1,2-dione (**9**)¹⁴ and benzoylcyclohexane (**10**)¹⁵ were prepared according to literature methods. A Taika 100 W or Ushio 450 W high-pressure mercury lamp was used as an irradiation source.

General procedure for preparative photolyses of 1, 7, 9 and 10 on a dry silica gel surface. The compound, **1**, **7**, **9** or **10** (ca 1.5 mmol) in 5 cm³ of dichloromethane (acetone was used for dissolving **9** because of the insolubility in dichloromethane) was added to 5 g of silica gel in a 100 cm³ round-bottomed flask. The mixture was sonicated for 5 min and the solvent was evaporated under reduced pressure.

The coated silica gel was divided into six nearly equal portions which were placed in Pyrex tubes (18 × 180 mm). In the experiments under oxygen-free conditions the tubes were degassed by three freeze-pump-thaw cycles and sealed. The tubes were rotated and irradiated for 48 h with a 100 W high-pressure mercury lamp. The irradiated silica gel was collected. Acetonitrile (20 cm³) was added to the silica gel for extraction of organic components and the mixture was sonicated for 10 min. The silica gel was separated by filtration and washed with 10 cm³ of acetonitrile. The filtrate and washings were collected and then the solvent was removed under reduced pressure. Most of organic material was recovered by this method (more than 95% based on the weight of starting material used). To the residue was added 20 cm³ of benzene and the mixture was sonicated for 10 min. Undissolved material was collected and recrystallized from acetone-hexane to give adipic acid. The mother liquid and washings were combined with the benzene solution, concentrated under reduced pressure and the residue was chromatographed on silica gel. Elution with a mixture of acetone-hexane (6:1, v/v) gave unreacted starting ketone and photoproducts. The yields are summarized in Table 1 and shown in Scheme 2. The structures of the photoproducts **2**,^{5,12} **5**⁶ and **6**¹⁰ were determined by direct comparison with authentic samples and those of **3** and **4** by comparison with commercial samples.

Photolysis of 2-chlorocyclohexanone (7) in benzene. A solution of **7** (40 mg, 0.31 mmol) in 5 cm³ of benzene containing a known amount of *n*-pentadecane as a calibrant for GLC analysis was irradiated with a 450 W

Table 1. Product yields of photoreaction of 1 on a silica gel surface

Compound	R ¹	R ²	Yield (%) ^a					Conversion of 1 (%)
			2	3	4	5	6	
1a	H	H	19	16	11	—	—	73
			(16) ^b	(15) ^b	(10) ^b	—	—	70
1b	H	2-Me	0	0	Trace	68	—	71
1c	H	4-Me	13	0	0	—	—	68
1d	<i>o</i> -Me	H	0	11	10	—	17	38
1e	<i>m</i> -Me	H	16	15	15	—	—	70
1f	<i>p</i> -Me	H	12	12	15	—	—	71
1g	<i>p</i> -MeO	H	0	0	0	—	—	3

^a Based on converted starting diketone 1.^b Degassed conditions.

high-pressure mercury lamp under nitrogen through a Pyrex filter for 40 h. The mixture was analysed with a Shimadzu GC-PA gas chromatograph equipped with a flame ionization detector using a 2 m column containing 5% DCQF-1 and 1% EGS on Chromosorb P.

Photolysis of 1a on a silica gel surface at different coverages. An appropriate amount of 1a was dissolved in 5 cm³ of dichloromethane and the solution was added to 1 g of silica gel in a Pyrex tube (18 × 180 mm). The mixture was sonicated for 5 min, then the solvent was evaporated under reduced pressure. The tubes were rotated and irradiated for 48 h with a 100 W high-pressure mercury lamp. The adsorbed material was sonicated and extracted with acetonitrile. To the acetonitrile solution was added 1 cm³ of an acetonitrile solution containing a known amount of phenanthrene (ca 0.001 mmol) as a calibrant for HPLC analysis. The analyses were performed using a Gasukuro Kogyo 570B high-performance liquid chromatograph with a Model 511 fixed-wavelength UV detector (254 nm). An Inertsil ODS-2 column was used with acetonitrile–water (1:1, v/v) as the mobile phase at a flow-rate of 0.9 cm³ min⁻¹.

Formation of DPPH₂ from DPPH. A solution of DPPH (10 mg, 0.025 mmol) in 30 cm³ of benzene was added to 3 g of silica gel in a 50 cm³ round-bottomed flask. The mixture was sonicated for 10 min and then kept standing for 48 h in the dark. The silica gel was filtered off and washed with 10 cm³ of benzene. The filtrate and washings were combined. The mixture was concentrated under reduced pressure. The unreacted starting material (4 mg) and DPPH₂ (8 mg) were isolated by alumina thick-layer chromatography using hexane–acetone (10:1, v/v) as developing solvent.

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