

Photochemical Reaction of Phenyl-substituted 1,3-Diketones

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Irradiation of 2,2-dimethyl-1-phenyl-1,3-diketones with 3-ethyl or 3-isopropyl substituents gave type II cyclization product, 3-hydroxy-2,2,4-trimethyl-3-phenylcyclobutanone or 3-hydroxy-2,2,4,4-tetramethyl-3-phenylcyclobutanone, along with type I cleavage products. The type II cyclization/type I cleavage ratio is greater with a 3-isopropyl group than with a 3-ethyl group. A similar irradiation of 2,2-dimethyl-1-phenyl-1,3-butanedione gave type I cleavage products and no type II cyclization product. Irradiation of 2,4-dimethyl-1-phenyl-1,3-pentanedione gave 3-hydroxy-2,2,4-trimethyl-3-phenylcyclobutanone and propiophenone. The geometry of 3-hydroxy-2,2,4-trimethyl-3-phenylcyclobutanone which arose from 2,2-dimethyl-1-phenyl-1,3-pentanedione was *cis* with respect to phenyl and 4-methyl groups and that which arose from 2,4-dimethyl-1-phenyl-1,3-pentanedione was *trans*.

Two major photochemical processes, Norrish type I and Norrish type II, have been widely studied.¹⁾ The type II process is the most common photoreaction of monoketones with γ -hydrogens in the alkyl chain. However, in the case of 1,3-diketones, no example of type II photoreaction where an α -hydrogen to one carbonyl group undergoes 1,5-shift to another carbonyl oxygen has been found. Non- or difficultly-enolizable aliphatic 1,3-diketones have been found to undergo type I cleavage.²⁾ The photochemistry of aromatic 1,3-diketones has been studied for 3-arylchromones³⁾ and 2-diaza-1-aryl-1,3-diketone compounds.⁴⁾ Little attention has been given to aromatic 1,3-diketones with an sp^3 carbon α to both carbonyl groups.⁵⁾ Since, for the same electronic and spin configuration, aryl alkyl ketones undergo type I cleavage more slowly than the analogous dialkyl ketones,⁶⁾ 1-aryl-3-alkyl-1,3-diketone compounds may undergo type II photoreaction where the aromatic carbonyl oxygen abstracts a hydrogen from the α -carbon on the 3-alkyl substituent, in competition with type I cleavage. In this paper, we report the photochemistry of 1-phenyl-3-alkyl-1,3-diketone compounds.

Results and Discussion

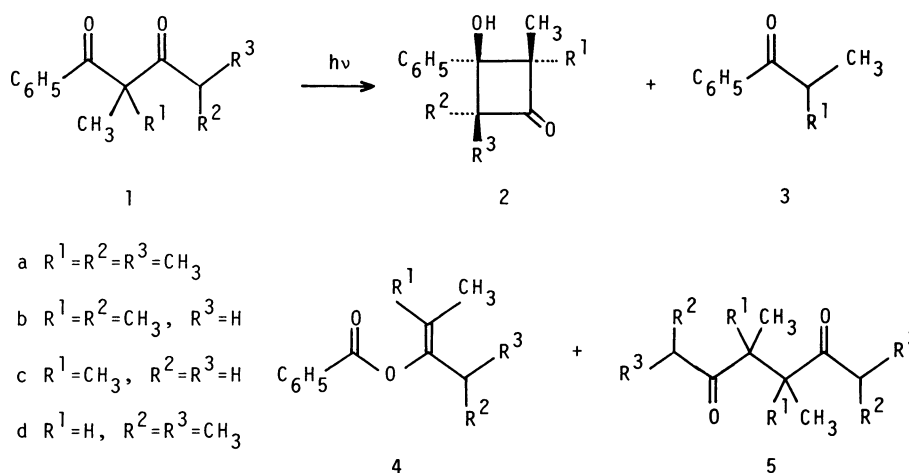
An acetonitrile solution of 2,2,4-trimethyl-1-phenyl-1,3-pentanedione (**1a**) was irradiated under nitrogen with a Pyrex filter. After removal of the solvent, 3-

hydroxy-2,2,4,4-tetramethyl-3-phenylcyclobutanone (**2a**), isobutyrophenone (**3**), enol ester (**4a**), and 1,4-diketone (**5a**) were isolated by silica gel chromatography. A similar reaction was found to occur with 2,2-dimethyl-1-phenyl-1,3-pentanedione (**1b**). As shown in Table 1, the yield of **2** was higher with **1a** than with **1b**, and the yields of **4** and **5** were lower with **1a** than with **1b**. Irradiation of 2,2-dimethyl-1-phenyl-1,3-butanedione (**1c**) gave isobutyrophenone (**3**), enol ester (**4c**), and 1,4-diketone (**5c**), along with benzaldehyde and benzoic acid. In this case, no hydroxycyclobutanone was detected. Similar irradiation of 2,4-dimethyl-1-phenyl-1,3-pentanedione (**1d**) gave propiophenone (**3d**) and 3-hydroxy-2,2,4-trimethyl-3-phenylcyclobutanone (**2d**) which was a geometrical isomer of **2b**, along with several

TABLE 1. PHOTOREACTION OF **1** IN ACETONITRILE^{a)}

1	Irradiation time h	Conversion %	Yield/%			
			2 ^{b)}	3 ^{c)}	4 ^{c)}	5 ^{c)}
1a	3.5	78	47	2	6	8
1b	4	68	11	3	9	14
1c	11	45	—	11	7	27
1d	26	88	16	12	—	—

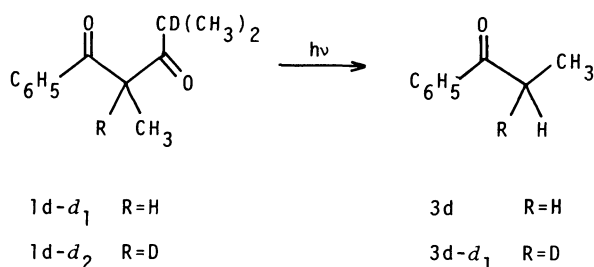
a) Irradiation of 20 mmol of **1** in 400 cm³ of acetonitrile with a 450 W high-pressure mercury lamp through a Pyrex filter. b) Isolated yield. c) Determined by GLC.



Scheme 1.

unidentified products. The structures of **2a**, **2b**, and **2d** were based on their spectroscopic and analytical properties and further supported by chemical evidence. The IR spectra showed a four-membered carbonyl band at $1770\text{--}1775\text{ cm}^{-1}$ and a hydroxyl band at 3600 cm^{-1} . The ^1H NMR spectrum of **2a** showed singlets at δ 1.38 and 1.40 due to four methyl groups, a singlet at δ 1.91 due to a hydroxyl group, and a singlet at δ 7.32 due to aromatic protons. This simple pattern is caused by the symmetry of the molecule. Compound **2a** underwent cycloreversion reaction to **1a** on heating at 150°C or by treatment with aqueous sodium hydroxide. This chemical behavior strongly supports the proposed structure for **2a**. The ^1H NMR spectra of **2b** and **2d** resemble each other in their splitting patterns except for the aromatic protons, suggesting that they are geometrical isomers with respect to the phenyl and 4-methyl groups. In the spectrum of **2b**, the signal due to the aromatic protons appeared as a multiplet between δ 7.1–7.4, being consistent with the proposed structure in which the phenyl group was restricted to rotate by virtue of its *cis*-relationship to two methyl groups on C₂ and C₄. Whereas, in the spectrum of **2d**, the aromatic protons appeared as a singlet at δ 7.36. Compound **2b** underwent cycloreversion reaction to **1b** and **1d** in a ratio of 1:2 by heating at 150°C , but **2d** converted mostly to **1d** under the same reaction conditions. The IR spectra of **4a–c** showed a strong band at $1730\text{--}1735\text{ cm}^{-1}$ due to ester carbonyl. The ^1H NMR spectra of **4a** and **4b** showed two singlets at the region between δ 1.5–1.8 due to two methyl groups attached to olefinic carbon atoms. The ^1H NMR spectrum of **4c** showed three singlets at δ 1.55, 1.75, and 1.95 due to three methyl groups attached to olefinic carbon atoms. These spectroscopic properties are consistent with the proposed structures for **4a–c**. The structures of **5a–c** were unambiguously assigned by their IR and NMR spectra.

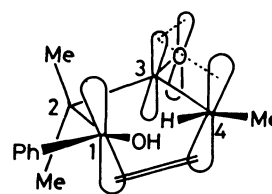
The formation of **2** can best be explained by type II cyclization which involves 1,5-hydrogen shift from C₄ to the carbonyl oxygen on C₁. The product **3** may be formed by a type II elimination process or by a type I cleavage of the C₂–C₃ bond. It is known that α -diketones⁷⁾ and β,γ -unsaturated ketones⁸⁾ with $\gamma\text{C–H}$ bonds undergo type II cyclization and no type II elimination. The lack of elimination has been attributed to the perpendicular orientation of the p orbital on one radical site relative to the C₂–C₃ σ bond in the 1,4-biradical intermediate. In the 1,4-biradical formed from 1,3-diketone **1**, the C₄ radical site is allylic such that its π -system is completely perpendicular to the C₂–C₃ bond. This suggests that the 1,4-biradical will result in the formation of the cyclization product.



Scheme 2.

Thus, **3** probably arises from a type I cleavage. In order to provide experimental information for the formation of **3**, photolysis of 2,4-dimethyl-1-phenyl-1,3-pentanedione-4-*d*₁ (**1d-d**₁) and 2,4-dimethyl-1-phenyl-1,3-pentanedione-2,4-*d*₂ (**1d-d**₂) was investigated. Photolysis of **1d-d**₁ in benzene gave propiophenone (**3d**) and not its deuterio derivative. Similar irradiation of **1d-d**₂ gave propiophenone- α -*d*₁ (**3d-d**₁) and no α,α -dideuterio derivative. These results suggest that **3** may arise from a type I cleavage.

It is noteworthy that **2b** and **2d** are geometrical isomers with respect to the phenyl and the 4-methyl groups. The ^1H NMR spectra of the irradiation mixtures showed no evidence for the formation of **2d** from **1b** and **2b** from **1d**. Lewis and Hilliard studied⁹⁾ the photochemistry of methyl-substituted 1-phenyl-1-butanones. They reported that both 2-methyl-1-phenyl-1-butanone and 1-phenyl-1-pentanone form 2-methyl-1-phenylcyclobutanol; however, only the *trans* isomer with respect to the phenyl and methyl groups is observed for 2-methyl-1-phenyl-1-butanone, whereas a 3.1:1 *trans*:*cis* ratio is observed for 1-phenyl-1-pentanone. They explained the specificity of 2-methyl-1-phenyl-1-butanone by a repulsive interaction of the phenyl and α -methyl groups in the 1,4-biradical. The interaction between the phenyl and γ -methyl groups in the 1,4-biradical was regarded as being small until the 1,4-bond is almost completely formed. The formation of *r*-3-hydroxy-2,2,4-trimethyl-3-phenylcyclobutanone **2d** from **1d** is consistent with their results. However, the preferential formation of *r*-3-hydroxy-2,2,4-trimethyl-3-phenylcyclobutanone **2b** rather than the corresponding 2,2,4-trimethyl isomer **2d** from **1b** is not expected. In the 1,4-biradical from **1b**, the methyl group on the C₄ radical site is probably *trans* to the C₂–C₃ bond owing to the steric effect, and the rotation of the C₁–C₂ bond is probably hindered by the interactions between the phenyl and α,α -dimethyl groups. Therefore, the transition state for cyclization of the 1,4-biradical from **1b** is pertinently depicted as **6** and results in the formation of **2b**.



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Scheme 3.

The formation of **4** and **5** is explained by combination of radicals resulting from type I cleavage. Diketones **1a**, **1b**, and **1c** vary only at C₄. The photochemical results of **1a–c** indicate that as the C₄–H bond strength increases the type II cyclization decreases with increasing type I cleavage. Thus, as expected, appropriate 1-phenyl-1,3-diketones with 3-alkyl substituent undergo type II cyclization *via* 1,5-hydrogen shift from carbon atom α to aliphatic carbonyl group to the aromatic carbonyl oxygen, in competition with type I cleavage. Finally, both cyclization and α -

cleavage were completely quenched by 1,3-pentadiene suggesting a triplet state reaction.

Experimental

All melting points were uncorrected. ^1H NMR spectra were recorded on a Varian A-60D or a JEOL FX-90Q spectrometer with tetramethylsilane as an internal standard. ^{13}C NMR spectra were recorded on a JEOL FX-90Q spectrometer. IR spectra were recorded on a JASCO IRA-2 spectrometer. GLC analyses and preparative purification were performed on a Hitachi K-53 instrument using Silicone SE-30 as the stationary phase. Irradiations were carried out with an Ushio UM-452 high-pressure mercury lamp (450 W) or a Rikoh Kagaku UVL-100 high-pressure mercury lamp (100 W) with a water-cooled Pyrex jacket. For column chromatography, Wakogel C-300 or Merck Silica Gel 60 Art. 7734 was used.

Materials. Phenyl 1,3-diketones **1a–c** were prepared by condensation of isobutyrophenone with the corresponding aliphatic aldehydes using methylanilinumagnesium bromide as the condensing agent,¹⁰ followed by chromium(VI) oxide oxidation. Similarly, **1d** was prepared from propiophenone and isobutyraldehyde. Compound **1a** was also prepared by a similar procedure from 2,4-dimethyl-3-pentanone and benzaldehyde. The deuterio derivatives (**1d₁** and **1d₂**) of **1d** were prepared as follows. A mixture of 400 mg of **1d**, 100 mg of TsOH, 4 cm³ of D₂O, and 4 cm³ of dioxane was heated under reflux for 70 h. The solvent was evaporated, and the residue was extracted with ether. A usual work-up and purification by GLC gave 2,4-dimethyl-1-phenyl-1,3-pentanedione-2,4-*d₂* (**1d₂**). A mixture of 100 mg of **1d₂**, a trace amount of TsOH, 2 cm³ of H₂O, and 2 cm³ of dioxane was heated at 80 °C for 40 h. The same procedures as described above gave 2,4-dimethyl-1-phenyl-1,3-pentanedione-4-*d₁* (**1d₁**).

Photolysis of 1. A typical procedure is described. A solution of 20 mmol of **1** in 400 cm³ of acetonitrile was irradiated. The progress of the reaction was monitored by TLC and GLC. After removal of the solvent, the residue was chromatographed on silica gel eluted with a hexane-ethyl acetate mixture as eluent to give **2–5**. Compounds **2a**, **2b**, and **2d** were recrystallized from a mixture of hexane and a small amount of benzene. Compounds **3–5** were purified by preparative GLC. Yields are given in Table 1 on the basis of **1** consumed. Physical properties of the isolated products are shown below.

3-Hydroxy-2,2,4,4-tetramethyl-3-phenylcyclobutanone (2a). Mp 135 °C. IR (CHCl₃) 1775 (C=O), 3600 (OH) cm⁻¹. ^1H NMR (CDCl₃) δ =1.38 (s, 6H, Me), 1.40 (s, 6H, Me), 1.91 (s, 1H, OH), and 7.32 (s, 5H, Ph). ^{13}C NMR (CDCl₃) δ =18.643 (2q), 24.452 (2q), 63.538 (2s), 79.808 (s), 127.591 (d), 128.045 (2d), 128.374 (2d), 141.362 (s), and 221.386 (s). MS *m/z* (rel intensity) 218 (M⁺, 3), 148 (M⁺–Me₂C=C=O, 55), 105 (PhCO, 100), 77 (Ph, 96). Found: C, 77.07; H, 8.34%. Calcd for C₁₄H₁₈O₂: C, 77.03; H, 8.31%.

r-3-Hydroxy-2,2,4,4-trimethyl-3-phenylcyclobutanone (2b). Mp 126–127 °C. IR (CHCl₃) 1770 (C=O), 3600 (OH) cm⁻¹. ^1H NMR (CDCl₃) δ =0.80 (s, 3H, Me), 1.04 (d, *J*=7.2 Hz, 3H, Me), 1.48 (s, 3H, Me), 2.46 (s, 1H, OH), 3.96 (q, *J*=7.2 Hz, 1H, CH), and 7.1–7.4 (m, 5H, Ph). ^{13}C NMR (CDCl₃) δ =8.200 (q), 18.667 (q), 22.243 (q), 63.018 (d), 64.839 (s), 76.739 (s), 126.553 (2d), 126.943 (d), 127.854 (2d), 140.275 (s), and 215.191 (s). MS *m/z* (rel intensity) 204 (M⁺, 10), 148 (M⁺–MeCH=C=O, 32), 134 (M⁺–Me₂C=C=O, 99), 105 (PhCO, 100), 77 (Ph, 39). Found: C, 76.42; H, 7.85%. Calcd for C₁₃H₁₆O₂: C, 76.43; H, 7.89%.

r-3-Hydroxy-2,2,4,4-trimethyl-3-phenylcyclobutanone (2d). Mp 106–107 °C. IR (CHCl₃) 1775 (C=O), 3600 (OH) cm⁻¹.

^1H NMR (CDCl₃) δ =0.92 (s, 3H, Me), 1.22 (d, *J*=7.2 Hz, 3H, Me), 1.26 (s, 3H, Me), 1.94 (s, 1H, OH), 4.10 (q, *J*=7.2 Hz, 1H, CH), and 7.36 (s, 5H, Ph). MS *m/z* (rel intensity) 204 (M⁺, 16), 148 (M⁺–MeCH=C=O, 46), 134 (M⁺–Me₂C=C=O, 67), 105 (PhCO, 100), 77 (Ph, 100). Found: C, 76.32; H, 7.89%. Calcd for C₁₃H₁₆O₂: C, 76.43; H, 7.89%.

1-Isopropyl-2-methyl-1-propenyl Benzoate (4a). IR (CCl₄) 1735 (C=O) cm⁻¹. ^1H NMR (CDCl₃) δ =1.08 (d, *J*=7.0 Hz, 6H, Me), 1.56 (s, 3H, Me), 1.81 (s, 3H, Me), 3.03 (hep, *J*=7.0 Hz, 1H, CH), 7.3–7.7 (m, 3H, aromatic), and 8.1–8.3 (m, 2H, aromatic). Found: C, 77.12; H, 8.33%. Calcd for C₁₄H₁₈O₂: C, 77.03; H, 8.31%.

1-Ethyl-2-methyl-1-propenyl Benzoate (4b). IR (CCl₄) 1730 (C=O) cm⁻¹. ^1H NMR (CDCl₃) δ =1.02 (t, *J*=7.0 Hz, 3H, Me), 1.56 (s, 3H, Me), 1.74 (s, 3H, Me), 2.36 (q, *J*=7.0 Hz, 2H, CH₂), 7.3–7.7 (m, 3H, aromatic), and 8.0–8.2 (m, 2H, aromatic). ^{13}C NMR (CDCl₃) δ =11.581 (q), 17.626 (q), 18.406 (q), 23.350 (t), 117.969 (s), 128.374 (2d), 129.870 (2d), 130.455 (s), 132.926 (d), 144.372 (s), and 164.791 (s). Found: C, 76.34; H, 8.01%. Calcd for C₁₃H₁₆O₂: C, 76.43; H, 7.89%.

1,2-Dimethyl-1-propenyl benzoate (4c).¹¹ IR (CCl₄) 1730 (C=O) cm⁻¹. ^1H NMR (CCl₄) δ =1.55 (s, 3H, Me), 1.75 (s, 3H, Me), 1.95 (s, 3H, Me), 7.2–7.6 (m, 3H, aromatic), and 8.0–8.2 (m, 2H, aromatic). Found: C, 75.55; H, 7.40%. Calcd for C₁₂H₁₄O₂: C, 75.76; H, 7.42%.

2,4,4,5,5,7-Hexamethyl-3,6-octanedione (5a).¹² IR (CCl₄) 1700 (C=O) cm⁻¹. ^1H NMR (CCl₄) δ =1.01 (d, *J*=7.0 Hz, 12H, Me), 1.21 (s, 12H, Me), and 3.03 (hep, *J*=7.0 Hz, 2H, CH). Found: C, 73.98; H, 11.59%. Calcd for C₁₄H₂₆O₂: C, 74.28, H, 11.57%.

4,4,5,5-Tetramethyl-3,6-octanedione (5b). IR (CCl₄) 1700 (C=O) cm⁻¹. ^1H NMR (CDCl₃) δ =1.00 (t, *J*=7.0 Hz, 6H, Me), 1.16 (s, 12H, Me), and 2.50 (q, *J*=7.0 Hz, 4H, CH₂). ^{13}C NMR (CDCl₃) δ =8.135 (2q), 22.438 (4q), 32.165 (2t), 52.679 (2s), and 215.841 (2s).

3,3,4,4-Tetramethyl-2,5-hexanedione (5c).¹² IR (CCl₄) 1700 (C=O) cm⁻¹. ^1H NMR (CCl₄) δ =1.14 (s, 12H, Me) and 2.05 (s, 6H, Me).

Pyrolysis of 2. Pyrolysis was done at 150 °C in a sealed Pyrex tube for 3 h. The ^1H NMR analysis revealed that **2a** was quantitatively converted to **1a**, **2b** was converted to a 1:2 mixture of **1b** and **1d**, while **2d** was converted to **1d** along with a trace of **1b**.

Treatment of 2a with Aqueous Sodium Hydroxide. To a solution of 50 mg of **2a** in 6 cm³ of acetone was added one drop of 2 M (1 M=1 mol dm⁻³) sodium hydroxide. The mixture was stirred at room temperature for 4 h, acidified with 3 M hydrochloric acid, and extracted with ether. A usual work-up gave **1a** in quantitative yield.

Irradiation of 1d₁ and 1d₂. A solution of 40 mg of **1d₁** in 4 cm³ of benzene was placed in a Pyrex tube, and irradiated with a 100 W high-pressure mercury lamp for 5 h. From the irradiation mixture, unlabelled propiophenone was isolated by preparative GLC. A similar irradiation of **1d₂** gave propiophenone- α -*d₁*.

Irradiation of 1a,d in the Presence of 1,3-Pentadiene. a): A solution of 10 mg of **1a,d** in 1 cm³ of acetonitrile was placed in a Pyrex tube. b): A solution of 10 mg of **1a,d** in 1 cm³ of a 1:1 mixture of acetonitrile and 1,3-pentadiene was placed in a Pyrex tube. Both solutions were irradiated under the same conditions with a 100 W high-pressure mercury lamp for 5 h. The ^1H NMR analysis showed that no reaction occurred in the case of b), while complete disappearance of **1a,d** was observed in the case of a).

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