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Photochemical Cyclization of *o*-Methylphenyl 1,3-Diketones

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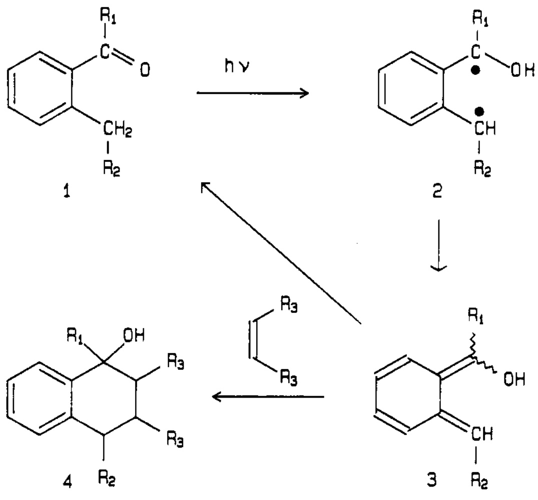
The photochemistry of five 1,3-dicarbonyl compounds, substituted at the 1-position with an *o*-methylphenyl group, has been investigated. Compounds **5a–c** cyclize upon irradiation to give tetralones **6a** and **6c** and octahydroanthracene derivative **6b**, respectively. Compounds **5d** and **5e** do not form similar photoproducts. Diketone **5c** is the most efficient in this reaction, indicating that the reaction probably occurs via the keto tautomer. A mechanism involving initial γ-hydrogen abstraction followed by interception of the resulting 1,4-biradical by the second carbonyl group is proposed.

The photochemistry of *o*-alkylphenyl ketones has been the subject of numerous studies.[1,2] Scheme I shows a greatly simplified mechanism for the photoreactions of these compounds. Irradiation of **1** results in intramolecular hydrogen abstraction by the oxygen of the triplet excited state[3] of the carbonyl group, producing triplet biradical **2**. Intersystem crossing results in the formation of photoenol **3**, an *o*-xylylene. The photoenol is a short-lived species because of the strong driving force for rearomatization. Commonly, **3** reverts to **1**. In some cases, however, cyclization of **3** to a benzocyclobutenol is observed.[2c,4] The presence of **3** has been detected by deuterium incorporation into **1** and by the trapping of **3** with dienophiles to give Diels–Alder adduct **4**.[1a,5] Irradiation of **1** containing dienophiles as part of R_1 or R_2 results in an intramolecular Diels–Alder reaction of the photoenol, a reaction of considerable synthetic utility.[6] The importance of conformational effects in the ground state and in the excited state has been reported.[1b,2e] Biradical **2** has been trapped by electron acceptors[1d] and by intramolecular addition to a triple bond[2a,7] in the case of a derivative of **1** with R_1 = C$\equiv$C^{t}Bu. The biradical, or a related intermediate, has also been trapped by an α-carbonyl group,[8-12] in the case where R_1 = O=CR, and by sulfur dioxide.[12]

Scheme I



In this paper we report the results of our study of the photochemistry of derivatives of **1** containing β-carbonyl

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(1) For recent reviews, see: (a) Sammes, P. G. *Tetrahedron* **1976**, *32*, 405. (b) Wagner, P. J. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic: New York, 1981; Vol. 3, p 381.

(2) For some leading references, see: (a) Agosta, W. C.; Caldwell, R. A.; Jay, J.; Johnston, L. J.; Venepalli, B. R.; Scaiano, J. C.; Singh, M.; Wolff, S. *J. Am. Chem. Soc.* **1987**, *109*, 3050. (b) Gebicki, J.; Krantz, A. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1623. (c) Ito, Y.; Nishimura, H.; Umehara, Y.; Yamada, Y.; Tone, M.; Matsaura, T. *J. Am. Chem. Soc.* **1983**, *105*, 1590. (d) Das, P. K.; Encinas, M. V.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 6965. (e) Wagner, P. J.; Chen, C.-P. *J. Am. Chem. Soc.* **1976**, *98*, 239.

(3) In some instances, some of the photoenol has been shown to arise from the singlet excited state.[2e]

(4) Matsuura, T.; Kitaura, Y. *Tetrahedron* **1969**, *25*, 4487.

(5) Yang, N. C.; Rivas, C. *J. Am. Chem. Soc.* **1961**, *83*, 2051.

(6) Oppolzer, W. *Synthesis* **1978**, 793. Funk, R. L.; Vollhardt, K. P. C. *Chem. Soc. Rev.* **1980**, *9*, 44. Kametani, T.; Nemoto, H. *Tetrahedron* **1981**, *37*, 3.

(7) Rao, V. B.; Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1985**, *107*, 521.

(8) Burkoth, T. L.; Ullman, E. F. *Tetrahedron Lett.* **1970**, 145.

(9) Bishop, R.; Hamer, N. K. *J. Chem. Soc. C* **1970**, 1193.

(10) Ogata, Y.; Takagi, K. *J. Org. Chem.* **1974**, *39*, 1385.

(11) Hamer, N. K. *J. Chem. Soc., Chem. Commun.* **1975**, 557.

(12) Hamer, N. K. *J. Chem. Soc., Perkin Trans 1* **1979**, 508.

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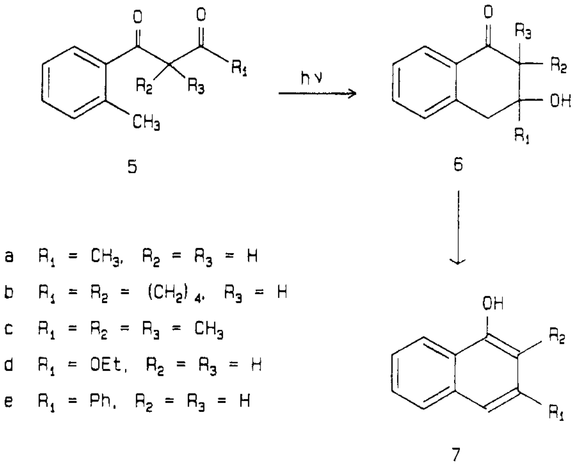
Scheme II



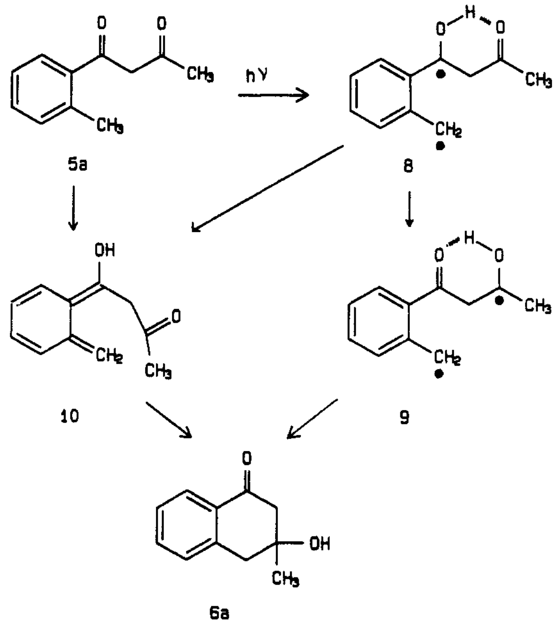
groups. In these cases, the biradical is trapped by the β-carbonyl group to produce tetralone derivatives in a reaction that may have some utility for the preparation of 3-substituted 1-tetralones and 1-naphthols.

Results and Discussion

Diketone **5a** (Scheme II) was prepared by acylation of the enolate anion derived from *o*-methylacetophenone with ethyl acetate. Irradiation of **5a** in methanol resulted in the slow disappearance of the starting material and the formation of a photoproduct, **6a**, which was isolated in 35% yield. The GC yield of **6a** was 48% at 74% conversion of **5a**. The structure of the photoproduct was assigned on the basis of its IR spectrum, which showed the presence of both a hydroxyl group and a conjugated carbonyl group, and its ^{1}H and ^{13}C NMR spectra. This assignment was confirmed by distillation of **6a** from a trace of acid, which resulted in dehydration to give naphthol **7a**.[13]

Similarly, irradiation of **5b**[14] in methanol resulted in the formation of two photoproducts, which were isolated in 13 and 44% yields. The structure of the major photoproduct was assigned as **6b** on the basis of its IR and ^{1}H and ^{13}C NMR spectra. Again, the structure assignment was confirmed by dehydration of **6b**, by distillation from acid, which resulted in the formation of 1,2,3,4-tetrahydro-9-anthranol, **7b**.[15] The IR and NMR spectra of the minor photoproduct, **6b′**, were very smiliar to those of the major photoproduct. Therefore, its structure was assigned as the diastereomer of **6b** with the opposite stereochemistry at the ring junction. On the basis of their ^{1}H NMR spectra, the major photoproduct, **6b**, has been tentatively assigned as having cis stereochemistry at the ring junction while the minor photoproduct, **6b′**, has been assigned as the trans diastereomer. In the spectrum of the minor photoproduct, the hydrogen at the ring junction adjacent to the carbonyl appears as a doublet of doublets with $J = 3.5$ and 11.7 Hz. These values are typical for the coupling constants for an axial hydrogen coupled to a vicinal equatorial hydrogen and a vicinal axial hydrogen, respectively,[16] consistent with this hydrogen being held in the axial position in the rigid trans diastereomer. In contrast, this hydrogen of the major photoproduct has $J = 4.4$ and 9.9 Hz, consistent with averaged coupling constants for the more conformationally mobile cis diastereomer.

Scheme III



Diketone **5c** was prepared by dialkylation of **5a** with excess methyl iodide and potassium carbonate. Irradiation of **5c** in methanol resulted in the formation of **6c** in 60% yield. The structure of **6c** was assigned by comparison of its spectral properties with those of **6a** and **6b**.

The photochemistry of two additional compounds was also investigated. Keto ester **5d**[17] was prepared by acylation of the enolate anion of ethyl acetate with *o*-methylbenzoyl chloride. Irradiation of **5d** for extended periods in various solvents resulted in no detectable reaction. A similar lack of photochemical reactivity was noted for the phenyl-substituted diketone **5e**. Irradiation of **5e**[18] in methanol for times comparable to those of **5a** and **5b** did not result in any observable reaction. At longer irradiation times, a small amount of an unidentified photoproduct, which as not **6e**, was formed.

β-Dicarbonyl compounds **5** (except, of course, **5c**) exist as an equilibrium mixture of keto and enol tautomers. It was of interest to determine if the position of this equilibrium affected the photoreactivity of the diketones. From their NMR spectra, the amount of keto tautomer present for each compound is 7% for **5a**, 5% for **5b**, 85% for **5d**, and less than 5% for **5e**. The observation that **5c**, which is incapable of enolization, reacted 20 to 30 times more rapidly than **5a** and **5b**, which were of comparable reactivity, suggests that it is the keto tautomer that is the reactive one.[19] This is consistent with a report[21] that nonenolizable β-diketones give more rapid Norrish type

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[13] Christen, M.; Funderbunk, L.; Halevia, E. A.; Lewis, G. E.; Zollinger, H. *Helv. Chim. Acta* **1966**, *49*, 1376.

[14] House, H. O.; Carlson, R. G.; Muller, H.; Noltes, A. W.; Slater, C. D. *J. Am. Chem. Soc.* **1962**, *84*, 2614.

[15] Loewenthal, H. J. E.; Pappo, R. *J. Chem. Soc.* **1952**, 4799.

[16] Bothner-By, A. A. In *Advances in Magnetic Resonance*; Waugh, J. S., Ed.; Academic: New York, 1965; Vol. 1, p 195.

[17] Harris, R. N. L.; Huppatz, J. L.; Teitei, T. *Aust. J. Chem.* **1979**, *32*, 699.

[18] Harris, R. N. L.; Huppatz, J. L. *Aust. J. Chem.* **1977**, *30*, 2225.

[19] A referee has suggested that the fact that **5c** is more reactive than **5a** and **5b** might be due to some factor other than the inability of **5c** to enolize, such as an enhanced rate of cyclization of the biradical derived from **5c** due to the Thorpe–Ingold effect.[20] We cannot rule out such explanations on the basis of our data. However, if **5a** and **5b** were producing biradicals that were not cyclizing, these biradicals would be expected to produce photoenols related to **3**. Aromatization of these enols in MeOD is expected to result in deuterium incorporation into the starting diketones. No such deuterium incorporation was observed (vide infra).

[20] Eliel, E. L.; Allinger, N. L.; Augyal, S. J.; Morrison, G. A. *Conformational Analysis*; Interscience: New York, 1965; pp 190–192.

[21] Yoshioka, M.; Suzuki, T.; Oka, M. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1604.

I and type II reactions than do similar β-diketones that can enolize. Another factor that might contribute to the lower reactivity of **5a** and **5b** is quenching of the excited state of the keto tautomer by the enol tautomer. However, such self-quenching was not observed in the case of **5a** (see Experimental Section).

The reactivity of these compounds is not controlled solely by the amount of the keto tautomer. In the case of keto ester **5d**, which is completely unreactive, the keto tautomer is the major species present at equilibrium. The low amount of keto tautomer present in **5e** may contribute to its photostability. However, enols of β-diketones are known to rearrange to the keto tautomer upon irradiation.[22] Thus, the amount of keto tautomer is expected to increase during the photolysis of **5e**. Other factors must be responsible for the lack of reactivity of this compound.

A number of mechanisms, as outlined in Scheme III, can be postulated to explain the conversion of **5** to **6**. These mechanisms are analogous to those proposed to explain the photochemistry of similar α-diketones.[8–12,23] Direct formation of **9** from **5a**, via an eight-membered transition state, seems improbable. While such processes are known,[24] they occur only when the more common hydrogen abstraction processes are blocked. Furthermore, to the extent that the two carbonyl groups of **5** can be considered to be separate chromophores, the excited-state energy would be localized in the wrong carbonyl group for this process to occur.

To check for the formation of photoenols, such as **10**, in these reactions, we irradiated **5a**, **c–e** in CD_3OD and monitored the progress of the reactions by NMR. Irradiation of diketone **5a** for 29 h resulted in the formation of ca. 10% of photoproduct **6a**. At this point no incorporation of deuterium into the aromatic methyl group could be detected. Similar irradiation of dimethyl diketone **5c** resulted in the formation of 20% of **6c** after 2 h of irradiation and 70% after 8 h. Again, no deuterium incorporation into the aromatic methyl group of **5c** could be detected. In contrast, irradiation of keto ester **5d** for 29 h did not result in the formation of any photoproduct. However, the integral for the aromatic methyl group had decreased to two-thirds of its original value. Finally, irradiation of phenyl diketone **5e** for 29 h did not result in the formation of any photoproduct, nor was any deuterium incorporation into the *o*-methyl group detected.

These results demonstrate that **5d** does produce a photoenol related to **10** upon irradiation[25] and that this photoenol does incorporate deuterium upon conversion back to **5d**. The lack of deuterium incorporation in the cases of **5a** and **5c** suggests that these compounds do not form photoenols.[26] Rather, it would appear that some intermediate on the way to the photoenol is intercepted to ultimately produce **6a** and **6c**.

The most reasonable mechanism remaining is initial hydrogen abstraction via a six-membered transition state to produce biradical **8**, which is probably hydrogen bonded.[27] This biradical, probably a triplet, can then rearrange to **9** in a process that is similar to that proposed for biradicals derived from α-diketones.[8,10,28] Other mechanisms where biradicals formed by irradiation of *o*-methylphenyl ketones have been diverted from their usual path to form photoenols by reaction with intramolecular triple bonds[2a] or with sulfur dioxide[12] have been proposed. Intersystem crossing in **9**, followed by coupling of the radical centers, would result in the formation of **6a**. The reasons why **5d** and **5e** do not produce photoproducts related to **6** are not known. The observation of deuterium incorporation into keto ester **5d** indicates that it does form a photoenol, presumably by way of a biradical intermediate related to **8**. In this case, the ester group must be unable to intercept the biradical before intersystem crossing to the photoenol occurs. In the case of **5e**, it appears that the initial hydrogen abstraction does not occur since no evidence for the formation of intermediates related to **8** or **9** is observed.

Experimental Section

General Methods. Boiling points are uncorrected; melting points are corrected. ^1H NMR spectra were obtained on a Varian EM-360 or a Magnachem A-200 spectrometer; ^{13}C NMR spectra were obtained on a Magnachem A-200 spectrometer. IR spectra were obtained on a Perkin-Elmer 283-B spectrometer. UV spectra were obtained on a Beckman Acta V spectrophotometer. Elemental analyses were obtained from Atlantic Microlab, Inc., Atlanta, GA. GC analyses employed a Hewlett-Packard 5750 chromatograph with a 1.8 m × 3.2 mm 10% silicon gum rubber UCW-982 on 60/80 Chromosorb W column.

1-(2-Methylphenyl)-1,3-butanedione (5a). The diketone was prepared according to the general procedure of Ainsworth.[29] A stirred slurry of 5.99 g (0.137 mol) of NaH (55% dispersion in mineral oil) in 100 mL of anhydrous ether was cooled in an icebath. To this mixture, under a N_2 atmosphere, was slowly added a solution of 3.62 g (0.027 mol) of *o*-methylacetophenone, 16.14 g (0.183 mol) of ethyl acetate, and 0.4 mL of anhydrous ethanol. The solution was stirred at room temperature for 46 h. To the reaction mixture was added 10 mL of water. The solution was extracted with three 100-mL portions of 10% aqueous NaOH solution. The combined aqueous phases were acidified with HCl and extracted with three 100-mL portions of ether. The combined ether solutions were washed twice with water and dried over anhydrous $MgSO_4$. Distillation gave 3.42 g (72%) of **5a**:[30] bp 122–124 °C at 2 mm; ^1H NMR ($CDCl_3$) δ 6.9–7.5 (m, 4 H, aromatics), 5.70 (s, 1 H, =CH), 2.40 (s, 3 H, CH_3), 2.04 (s, 3 H, CH_3) (in addition there were small s at 3.87 and 2.12 due to the CH_2 and CH_3 of ca. 7% of the keto tautomer); IR (neat) 1600 cm^{-1}; UV (CH_3OH) λ_{max} = 303 nm (ϵ = 21 500); λ_{sh} = 248 nm (ϵ = 9150).

Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.96; H, 6.87.

2,2-Dimethyl-1-(2-methylphenyl)-1,3-butanedione (5c). The reaction was patterned after the procedure of Johnson et al.[31] A solution of 3.00 g (0.0171 mol) of 1-(2-methylphenyl)-1,3-butanedione (**5a**), 9.68 g (0.0682 mol) of methyl iodide, and 9.43 g (0.0682 mol) of K_2CO_3 in 50 mL of acetone was heated to reflux for 60 h under a nitrogen atmosphere. The solution was cooled and diluted with 100 mL of pentane. The solids were removed by filtration and washed with 100 mL of acetone–pentane (1:1). Distillation of the filtrate gave 3.23 g (93%) of **5c**: bp 94–99 °C at 0.1 mm; IR (neat) 3065, 2980, 2935, 2875, 1716, 1683, 1619, 1603 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.0–7.5 (m, 4 H, Ar), 2.34 (s, 3 H, CH_3), 2.14 (s, 3 H, CH_3), 1.38 (s, 6 H, CH_3's); ^{13}C NMR ($CDCl_3$) δ 20.61, 22.85, 26.25, 62.66, 125.21, 126.03, 130.44, 131.79, 137.02, 137.78,

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[22] Markov, P. *Chem. Soc. Rev.* **1984**, *13*, 69. Veierov, D.; Bercovici, T.; Mazur, Y.; Fischer, E. *J. Org. Chem.* **1978**, *43*, 2006.

[23] For a review, see: Rubin, M. B. *Top. Curr. Chem.* **1985**, *129*, 1.

[24] Meador, M. A.; Wagner, P. J. *J. Org. Chem.* **1985**, *50*, 419. Carless, H. A. J.; Fekarurhobo, G. K. *Tetrahedron Lett.* **1984**, *25*, 5943.

[25] β-Keto esters have been demonstrated to undergo the Norrish type II reaction. Hasegawa, T.; Arata, Y.; Endoh, M.; Yoshioka, M. *Tetrahedron* **1985**, *41*, 1667.

[26] The absence of deuterium incorporation does not necessarily rule out the presence of enols in similar reactions. For example, Agosta and co-workers[2a] have observed an enol spectroscopically although no deuterium was incorporated into the starting material. These authors ruled out the presence of the enol on the *reaction pathway* on the basis of other evidence.

[27] Hydroxy biradicals are very susceptible to hydrogen bonding. See: Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168. Wagner, P. J.; Zepp, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 4958.

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[30] Eiglemeier, K. German Patent 2 337 396; *Chem. Abstr.* **1975**, *82*, P78865v.

[31] Johnson, A. W.; Markham, E.; Price, R. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. V, p 785.

204.79, 207.20; UV (CH_3OH) λ_{max} = 312 nm (ϵ = 10000), λ_{max} = 285 nm (ϵ = 9000), λ_{sh} = 237 nm (ϵ = 16300).

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.05; H, 7.80.

Ethyl 3-(2-Methylphenyl)-3-oxopropanoate (5d). A solution of 10.2 g (0.101 mol) of diisopropylamine in 200 mL of anhydrous ether, under a nitrogen atmosphere, was cooled in a dry ice–acetone bath. To this was added, via syringe, 41.6 mL of 2.4 M (0.10 mol) *n*-butyllithium solution, followed by the addition of 4.4 g (0.050 mol) of ethyl acetate in 25 mL of ether and 8.2 g (0.053 mol) of 2-methylbenzoyl chloride in 25 mL of ether. The solution was allowed to warm to room temperature and stirred overnight. The reaction mixture was added to a mixture of 28 mL of concentrated H_2SO_4 and 380 g of ice. The aqueous solution was extracted with three 300-mL portions of ether, and the combined extracts were washed three times with water and dried over anhydrous $MgSO_4$. Distillation gave 5.88 g (57%) of **5d**: bp 108–110 °C at 0.8 mm (lit.[17] bp 103–105 °C at 0.4 mm); IR (neat) 3070, 3025, 2980, 2935, 2910, 2875, 1740, 1690, 1625, 1602, 1570 cm^{-1}; proton NMR showed the presence of ca. 85% of the keto tautomer and 15% of the enol tautomer; ^1H NMR ($CDCl_3$) δ 1.20 (2 overlapping t, J = 6 Hz, 3 H, CH_3's of ethyls of both keto and enol tautomers), 2.51 and 2.42 (larger s and smaller s, respectively, 3 H, *o*-CH_3's of both tautomers), 3.90 and 4.14 (s and 2 overlapping q, respectively, 3.7 H, CH_2's of ethyls of both tautomers and CH_2 of keto tautomer), 5.24 (s, 0.15 H, =CH of enol tautomer), 7.0–7.8 (m, 4 H, Ar), 12.60 (s, 0.15 H, OH of enol tautomer); UV (CH_3OH) λ_{sh} = 312 nm (ϵ = 17100), λ_{max} = 287 nm (ϵ = 20100).

Photochemical Apparatus. Preparative irradiations employed a quartz immersion well and a Hanovia 450-W medium-pressure mercury-vapor lamp. Water-jacketed vessels of ca. 250 or 500 mL were used, and the solutions were purged continuously with a stream of oxygen-free nitrogen.[32] Small-scale photolyses employed the same light source and a merry-go-round apparatus.

Irradiation of 1-(2-Methylphenyl)-1,3-butanedione (5a). A solution of 1.009 g (5.73 mmol) of **5a** in 265 mL of methanol was irradiated for 17 h. The solvent was removed in vacuo, and the residue was chromatographed on silica gel, with 3% to 50% ether in hexane as eluent, to give 0.307 g of recovered starting material and 0.244 g (35%) of **6a**. A pure sample of **6a**, mp 84–85 °C, was obtained by recrystallization from ether–hexane: IR (CCl_4) 3620 (sh), 3450 (br), 3080, 2995, 1690, 1610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.40 (s, 3 H, CH_3), 2.37 (s, 1 H, OH), 2.71 (AB q, J = 17 Hz, 2 H, CH_2), 3.11 (s, 2 H, CH_2), 7.27 (m, 2 H, Ar), 7.50 (m, 1 H, Ar), 8.01 (br d, J = 8 Hz, 1 H, Ar); ^{13}C NMR ($CDCl_3$) δ 29.19, 43.47, 52.47, 71.82, 127.10, 129.72, 131.76, 134.24, 141.27, 197.75.

Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.99; H, 6.86.

A small-scale photolysis of **5a**, monitored by GC, showed a 48% yield of **6a** at a 74% conversion of **5a**. Another small-scale photolysis was done to determine if any self-quenching was occurring in the reaction. Four photolysis tubes, containing 0.211 M, 0.106 M, 0.0422 M, and 0.0211 M **5a** in CH_3OH, respectively, were irradiated for 45 min. This brief irradiation resulted in a very low conversion of the starting material. No significant differences in the amount of photoproduct could be detected by GC in any of the tubes.

3-Methyl-1-naphthol (7a). A mixture of 0.245 g (1.39 mmol) of **6a** and 0.001 g of *p*-toluenesulfonic acid was distilled at 0.25 mm to give 0.178 g (81%) of **7a**: mp 92–93 °C (lit.[13] mp 90–91 °C); IR (CCl_4) 3610, 3060, 2920, 1642, 1602 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.2–7.1 (m, 5 H, Ar), 6.46 (br s, 1 H, Ar), 5.20 (s, 1 H, OH), 2.33 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 21.61, 110.82, 119.69, 121.22, 122.57, 124.27, 126.39, 127.03, 134.84, 135.84, 150.99.

Irradiation of 2-(2-Methylbenzoyl)cyclohexanone (5b). A solution of 3.04 g of **5b**[14] (UV (CH_3OH) λ_{max} = 303 nm (ϵ = 21600), λ_{sh} = 247 nm (ϵ = 8200); ca. 95% enol in $CDCl_3$ by NMR) in 600 mL of HPLC grade methanol was irradiated for 24 h. After the solvent had been removed, the residue was chromatographed on silica gel, with 15–60% ether in hexane as the eluent, to give 2.11 g of recovered starting material, 0.117 g (13%) of a minor photoproduct, **6b′**, and 0.405 g (44%) of a major photoproduct, **6b**.

The major photoproduct, **6b**, gave the following spectral data: IR (neat) 3430, 3075, 3030, 2935, 2860, 1675, 1605 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.01 (d of d, J = 2, 8 Hz, 1 H, Ar), 7.47 (t of d, J = 2, 8 Hz, 1 H, Ar), 7.26 (4 lines, overlapping t and d, J = 8 Hz, 2 H, Ar), 3.32 and 2.82 (AB q, J = 16 Hz, 2 H, benzylic CH_2), 2.78 (br s, 1 H, OH), 2.49 (d of d, J = 4.4, 9.9 Hz, 1 H, CH), 1.1–2.0 (m, 8 H, CH_2's); ^{13}C NMR ($CDCl_3$) δ 23.14 (t), 23.73 (t), 26.37 (t), 37.82 (t), 56.26 (d), 73.00 (s), 126.50, 127.09, 129.50, 130.67, 133.73, 140.66, 200.68 (s). In C_6D_6 the signal at 37.82 ppm was resolved into two signals at 38.47 and 38.00 ppm. An analytical sample was obtained by short-path distillation, bp ca. 156 °C at 0.025 mm.

Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.83; H, 7.48.

The minor photoproduct, **6b′**, mp 155–156 °C after recrystallization from benzene–hexane, gave the following spectral data: IR (CCl_4) 3620, 3080, 3020, 2940, 2860, 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.03 (d, 1 H, Ar), 7.1–7.6 (m, 3 H, Ar), 3.20 and 3.00 (AB q, J = 16 Hz, 2 H, benzylic CH_2), 2.48 (d of d, J = 3.5 and 11.7 Hz, 1 H, CH), 2.25–1.0 (m, 9 H, OH and remaining CH_2's); ^{13}C NMR ($CDCl_3$) δ 21.04, 21.55, 25.31, 39.51, 44.38, 54.13, 73.46, 127.08, 129.73, 132.47, 133.84, 139.91, 198.32.

Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.70; H, 7.51.

1,2,3,4-Tetrahydro-9-anthranol (7b). A mixture of 0.378 g of **6b** and 0.014 g of *p*-toluenesulfonic acid monohydrate was heated in vacuo. The material darkened considerably. A red liquid slowly distilled at ca. 135–150 °C and 0.05 mm to give 0.183 g (53%) of solid product. Two recrystallizations from hexane gave a light yellow solid: mp 106–108 °C (lit.[15] mp 110–111 °C); IR (CCl_4) 3615, 3055, 3015, 2935, 2880, 2860, 2840, 1645, 1385 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.07–8.02 (m, 1 H, Ar), 7.69–7.64 (m, 1 H, Ar), 7.39–7.34 (m, 2 H, Ar), 7.18 (s, 1 H, Ar), 4.60 (s, 1 H, OH), 2.92 (distorted t, J = 6 Hz, 2 H, benzylic CH_2), 2.76 (distorted t, J = 6 Hz, 2 H, benzylic CH_2), 1.85 (m, 4 H, other CH_2's); ^{13}C NMR ($CDCl_3$) δ 23.00, 30.36, 117.16, 119.30, 120.84, 122.46, 125.54, 126.91, 132.64, 136.49, 148.20. In C_6D_6, there were three signals in the aliphatic region of the ^{13}C NMR spectrum, at 22.80, 23.20, and 30.52 ppm. The signal at 23.20 ppm was twice the size of the other two signals, suggesting that it resulted from two overlapping signals.

Irradiation of 2,2-Dimethyl-1-(2-methylphenyl)-1,3-butanedione (5c). A soltuion of 2.00 g of **5c** in 500 mL of methanol was irradiated for 4 h, at which time GC analysis showed that all the starting material had reacted and a single photoproduct had formed. The photoproduct was isolated by chromatography on silica gel, with 40% ether in hexane as eluent. Distillation of the appropriate fraction yielded 1.20 g (60%) of **6c**: bp 131 °C at 0.75 mm; IR (neat) 3480, 3070, 3015, 2975, 2940, 1680, 1610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.97 (d of m, J = 8 Hz, 1 H, Ar), 7.43 (t of m, J = 8 Hz, 1 H, Ar), 7.21 (5 lines, br t and br d, J = 8 Hz, 2 H, Ar), 3.09 and 3.06 (AB q, positions of larger peaks are listed, J = 18 Hz, 2 H, CH_2), 2.65 (s, 1 H, OH), 1.25 (s, 3 H, CH_3), 1.23 (s, 3 H, CH_3), 1.12 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 17.97, 20.38, 24.08, 40.52, 50.80, 75.11, 126.27, 127.38, 128.85, 130.33, 133.02, 139.36, 202.79.

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.23; H, 7.97.

Irradiation of Ethyl 3-(2-Methylphenyl)-3-oxopropanoate (5d). Solutions that were 0.02 M in **5d** in various solvents (methanol, benzene, acetonitrile, benzene with benzophenone photosensitizer) were irradiated. No photoproducts could be detected by TLC under any of the conditions tested.

Irradiation of 1-(2-Methylphenyl)-3-phenyl-1,3-propanedione (5e). A solution of 2.00 g of **5e**[18] (UV (CH_3OH) λ_{max} = 327 nm (ϵ = 17700), λ_{max} = 252 nm (ϵ = 7300); >95% enol in $CDCl_3$ by NMR) in 540 mL of methanol was irradiated for 44 h while the progress of the reaction was followed by TLC. The photolysis well was cleaned several times during the course of the reaction to remove a polymeric film which slowed the reaction. A very minor product, which was not identified, was isolated by column chromatography. No other product was detected.

Irradiations in CD_3OD. Solutions of compounds **5a** (0.361 M), **5c** (0.333 M), **5d** (0.342 M), and **5e** (0.496 M) in CD_3OD were placed in Pyrex NMR tubes and irradiated in a merry-go-round apparatus. The following results were found by NMR analysis: after 2 h of irradiation, **5c** had formed 20% of **6c**, no change in the other samples; after 8 h of irradiation, **5c** had formed 70%

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of **6c**, **5a** had formed a small amount of **6a**, the integral for the *o*-methyl of **5d** was somewhat smaller, and no change for **5e**; after 29 h of irradiation, **5a** had formed 10% of **6a** with no decrease in the integral for the *o*-methyl group of **5a**, the integral for the *o*-methyl group of **5d** had decreased to 67% of the value of the integral of the methyl of the ethyl group, and no change for **5e**.

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Registry No. **5a**, 56290-54-1; **5b**, 7402-38-2; **5c**, 116971-61-0; **5d**, 51725-82-7; **5e**, 61001-54-5; **6a**, 116971-62-1; **6b**, 116971-63-2; **6b′**, 116971-64-3; **6c**, 116971-65-4; **7a**, 13615-40-2; **7b**, 50703-94-1; *o*-methylacetophenone, 577-16-2; ethyl acetate, 141-78-6; 2-methylbenzoyl chloride, 933-88-0.

Photochemical Reaction between Naphthalenecarbonitriles and Dienes

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The photochemical reactions between 1- and 2-naphthalenecarbonitrile as well as 1,4-naphthalenedicarbonitrile with dienes (2,3-dimethyl-1,3-butadiene, 1,3-cyclohexadiene, 2,5-dimethyl-2,4-hexadiene, and 2,5-dimethylfuran) were examined. Different photoprocesses were observed, viz. 2 + 2 cycloaddition both across positions 1 and 2 and (formally) across positions 1 and 8a (in the latter case a secondary electrocyclic reaction leads to benzocyclooctenes as the isolated products); 2 + 2 cycloaddition at the cyano group to yield azetines, easily hydrolized to amino ketones; and 4 + 4 cycloaddition both at the substituted and the unsubstituted ring. A rationalization is offered on the basis of the charge-transfer contribution to the interaction between the partners, which favors 2 + 2 vs 4 + 4 addition.

The photochemistry of naphthalene derivatives with alkenes has been extensively investigated in the last two decades;[1] a large number of the reports involve the reactions of naphthalenecarbonitriles.[2] On the other hand, investigations of the reaction with dienes appear to be limited to the textbook case of the 4 + 4 concerted addition of naphthalene with cyclohexadiene and two hexadienes,[3] and the only report concerning naphthalenenitriles is the addition to furan.[2d,e,l] Our interest in charge-transfer and exciplex pathways in the photochemistry of aromatics[4] and the interesting results obtained in other laboratories about the photochemical reaction with dienes of other cyano- or chloro-substituted aromatics, e.g. antracene or phenanthrene derivatives,[5] prompted the present research, in which the interaction between photoexcited cyanated naphthalenes, viz. 1- and 2-naphthalenecarbonitriles (1-NN and 2-NN) and 1,4-naphthalenedicarbonitrile (NDN), with representative dienes was considered. The dienes we chose are 2,3-dimethyl-1,3-butadiene (DMB), 1,3-cyclohexadiene (CH), 2,5-dimethyl-2,4-hexadiene (DMH), and 2,5-dimethylfuran (DMFU), and the reactions were carried out in benzene or cyclohexane and, in some cases, also in a polar solvent (acetonitrile).

Table I. Photoproducts from the Irradiation of Naphthalenecarbonitriles in the Presence of Dienes

naphthalene	diene	solvent	products (% yield)
1-NN	DMB	C_6H_{12}	**1** (21), **2** (9), **3** (13), **4** (8), **5** (10), **7** + **8** (6)
	CH	C_6H_{12}	**9** (53), **10** (6), **11** (7)
	DMH	C_6H_{12}	**12** (23), **13** (20)
	DMFU	C_6H_{12}	*a*
	DMB	MeCN	**1** (23), **2** (12), **3** (b), **4** (10), **5** (b)
2-NN	DMB	C_6H_{12}	**15** (62), **16** (8)
	CH	C_6H_{12}	**17** (53), **18** (12)
	DMH	C_6H_{12}	**19** (75), **20** (5)
	DMFU	C_6H_{12}	*a*
	DMB	MeCN	**15** (60), **16** (3)
NDN	DMB	C_6H_{12}/C_6H_6	**22** (26), **24** (8)
	CH	C_6H_{12}/C_6H_6	*a*
	DMH	C_6H_{12}/C_6H_6	*a*
	DMFU	C_6H_{12}/C_6H_6	*a*

[a] The nitrile is recovered unchanged after 15 h of irradiation. [b] Present by TLC.

Results

Isolated yields of the adducts after chromatography and recrystallization are reported in Table I. GC and NMR analyses of the crude photolysates show that, while small amounts of other photoproducts are present, the identified compounds in every case account for more than 75% of converted nitriles.

Reactions of 1-NN (Scheme I). Irradiation of 1-NN in the presence of 0.1 M DMB in cyclohexane or benzene

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