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Photolysis of 1,1,4,4-Tetraphenyl-3-buten-2-one: Ketene Formation from an Acyclic α,β-Unsaturated Ketone

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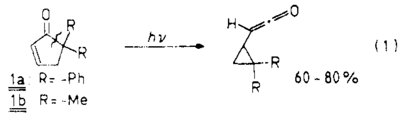
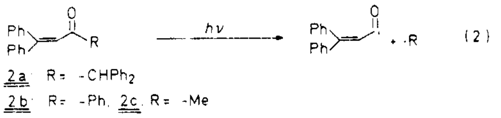
1,1,4,4-Tetraphenyl-3-buten-2-one (**2a**) was prepared by addition of the dianion of 1,1-diphenylacetone to benzophenone. Upon direct irradiation at 300 nm, the enone **2a** rearranged mainly to (1,1,2,2-tetraphenylethyl)ketene (**3**). Intramolecular acylation of the latter afforded 3-(diphenylmethyl)-3-phenylindanone (**5**) and trapping with methanol gave methyl 3,3,4,4-tetraphenylbutanoate (**4**). 1,1,2,2-Tetraphenylethane, methyl 3,3-diphenylacrylate, and traces of diphenylmethane were also formed as side products. These products are rationalized mechanistically in terms of a $D_{\sigma,\pi}$ 3,3-diphenylacrylyl–benzhydryl radical pair, which results from Norrish type I cleavage of the n,π* excited enone **2a**.

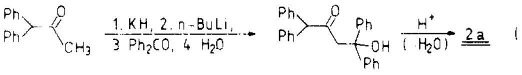
The photochemistry of α,β-unsaturated ketones has attracted much attention and is still a field of current interest.[1] Numerous examples of such photochemical transformations are well documented for *cyclic* enones and dienones, including both cycloaddition reactions and rearrangements. For example, cyclopentenones **1a,b** readily rearrange to cyclopropyl ketenes upon irradiation. A Norrish type I cleavage of the starting ketones **1a,b** serves as the initial step (eq 1).[2] Recently, the related cyclohexadienone–butadienyl ketene rearrangement has been shown to be a highly useful tool in the synthesis of natural products and macrocyclic lactones.[3] Whereas cis–trans isomerization, photodimerization, and [2 + 2] cycloadditions of *acyclic* α,β-unsaturated ketones are well investigated photochemical transformations,[1,4] comparatively little is documented concerning the photochemistry of such enones involving photodissociation and/or rearrangement.[5] Clearly, the absence of ring strain lowers the reactivity toward bond cleavage and renders an initial Norrish type I reaction unlikely. Introduction of radical stabilizing groups in the α-position of the enone may, however, be expected to change the reactivity of the enone in favor of the photochemical α-cleavage and subsequent reactions derived from the resulting radical pairs. With this in mind, the title ketone **2a** appeared to be a worthwhile substrate to probe this hypothesis, especially since it is known that the enones **2b,c** do *not* undergo photochemical α-cleavage[6] (eq 2).





Results

Syntheses. 1,1,4,4-Tetraphenyl-3-buten-2-one (**2a**)[7] was obtained in high yield by reacting the dianion of 1,1-diphenylacetone with benzophenone (eq 3). Dehydration of the resulting carbinol afforded **2a**.



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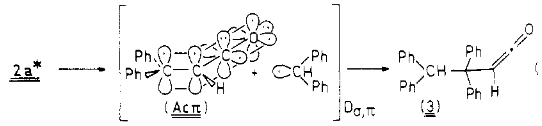
Product Studies. Irradiation of solutions of the ketone **2a** in benzene at 300 nm (Rayonet Photochemical Reactor) led to slow decomposition of the starting material. IR analysis of the photolysate revealed the formation of a ketene (strong band at 2140 cm^{-1}). Photolysis of the enone **2a** on a preparative scale in a 1:1 mixture of methyl *tert*-butyl ether and methanol (containing 0.4% acetic acid) afforded methyl 3,3,4,4-tetraphenylbutanoate (**4**) as the main product (30%), besides minor quantities of 1,1,2,2-tetraphenylethane, methyl 3,3-diphenylacrylate, and 3-(diphenylmethyl)-3-phenylindanone (**5**), isolated by silica gel flash chromatography. An orange-brown, immobile material accounted for the rest of the starting material. The hitherto unknown compounds **4** and **5** were identified by their spectral and analytical data. Unambiguous structure proof of the indanone **5** was achieved by means of X-ray crystallography. The identity of the tetraphenylethane and acrylate was established by comparison of their ^{1}H NMR, IR, and physical data with those of authentic samples.

HPLC monitoring of the concentration–time profiles showed that all products were primary photoproducts. No effects of the solvent polarity on the decay rate of the ketone **2a** could be observed on changing from benzene to 2-propanol. Methyl 3,3-diphenylacrylate and indanone **5** were found to be photolabile under the irradation conditions used, whereas the main product **4** and 1,1,2,2-tetraphenylethane were inert. Consequently, a quantitative determination of the yields of the latter ones could be carried out by means of ^{1}H NMR employing an internal standard. In the 1:1 methyl *tert*-butyl ether–methanol mixture, 39 ± 2% of the ester **4** was formed, while in 2-propanol 35 ± 2% of the corresponding 2-propyl ester was formed. In both cases 5–10% of 1,1,2,2-tetraphenylethane was detected. Traces of diphenylmethane could be found in the photolysates of the enone **2a** by means of capillary GC and HPLC coinjections in methyl *tert*-butyl ether–methanol, but no additional quantities were found in 2-propanol or diisopropyl ether. Since diphenylmethane is photostable in the photolysate of the ketone **2a**, secondary photolysis cannot account for its low yield.

3,3-Diphenyl-2-propenal as a potential photoproduct could not be detected (HPLC) under any of the irradiation conditions used. Control experiments showed, however, that the irradiation of this aldehyde in the presence of ketone **2a** leads to fast decomposition of the propenal. Thus, its formation but destruction by secondary photolysis cannot be excluded.

Discussion

The pronounced photoreactivity of ketone **2a** and its rearrangement to ketene **3** (eq 4) can readily be explained assuming an initial α-cleavage of excited enone **2a**. In contrast to the enones **2b,c** mentioned earlier, the Norrish type I reaction of the ketone **2a** generates a diphenylmethyl radical, which is resonance stabilized by about 30 kcal/mol,[8] thus making the initial α-cleavage energetically feasible. The acyl radical formed can be expected to be generated as a π-radical (Acπ), since this electronic configuration allows for interaction of the odd electron with the extended π-system of the diphenylvinyl moiety. On the basis of calculations for the unsubstituted acrylyl radical,[9a] it is reasonable to assume that the Acπ-radical constitutes the energetically lower lying acyl radical. Thus, the photochemical primary reaction of ketone **2a** closely resembles that of the cyclic 2,4-dienones, where α-cleavage of the ketone n,π* state leads to a $D_{\sigma,\pi}$ diradical (eq 5).[9] Alignment of the radical σ–orbital with the π-system by appropriate rotation affords the dienylketene. In competition, π,π* excitation leads to the bicyclic enone (eq 5). In some cases, the n,π* vs. π,π* reactivity of the dienone can be influenced by solvent polarity.[3a]



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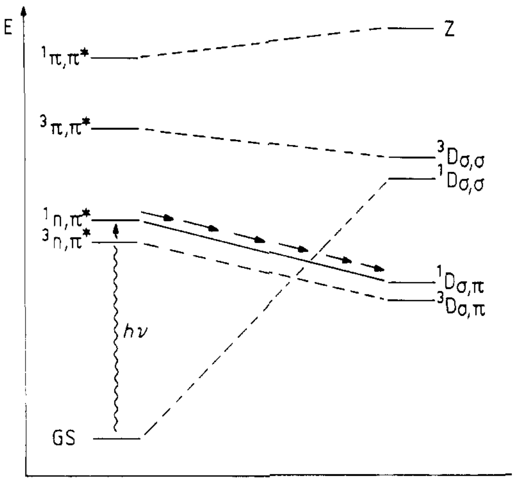
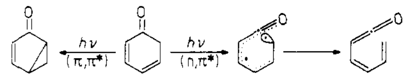
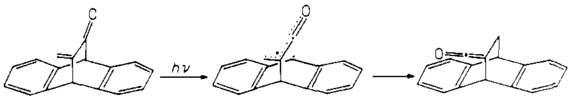


Figure 1. Salem diagram for the α-cleavage of 2,4-cyclohexadienones. Arrows indicate the reaction pathway followed by enone **2a**.



(5)

We assume that the Salem diagram for cyclic dienones also applies to the acyclic enones (Figure 1). However, as the solvent polarity does not affect the relative quantum yields of ketone **2a** consumption, the involvement of π,π* excitation appears unlikely. Thus, n,π* excitation of the enone **2a** followed by α-cleavage leads to a $D_{\sigma,\pi}$ radical pair, which serves as precursor to the observed products. For example, ketene formation (eq 4) is achieved by collapse of the $D_{\sigma,\pi}$ radical pair at the β-acrylic position. A related enone-ketene photorearrangement was reported[10a] for the anthracene derivative depicted in eq 6. Here the ketene formation occurs after 180° rotation of the acyl moiety.



(6)

The intermediary ketene **3** has several options of being transformed into final products. In the presence of methanol it is trapped in the form of the tetraphenylbutanoate **4** (eq 7). Alternatively, intramolecular acylation with the vicinal phenyl groups yields the indanone **5** (eq 7). While it is known that the acylation of aromatic hydrocarbons by ketenes requires Friedel–Craft catalysts[10b,c], in this case the acetic acid in the solvent mixture may serve as catalyst.

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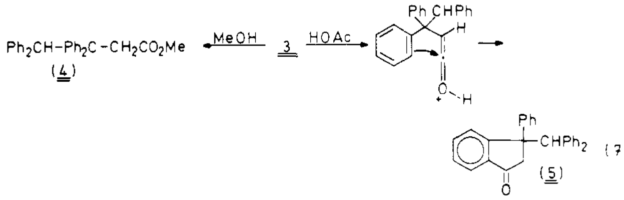
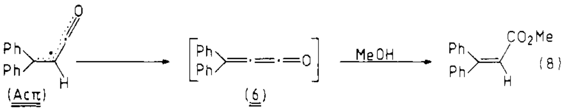


The formation of the other photoproducts of enone **2a** can also be explained in terms of initial α-cleavage (eq 4) and subsequent reactions of the radical pair. Thus, the statistically free diphenylmethyl radicals, which have escaped the solvent cage, dimerize to give 1,1,2,2-tetraphenylethane as one of the minor products. The fact that diphenylmethane is formed only in trace amounts even in 2-propanol or diisopropyl ether as solvents, can readily be explained by the literature data[11] that hydrogen abstraction from 2-propanol by the diphenylmethyl radical is endothermic by about 14 kcal/mol.

The fate of the statistically free acyl radical Acπ is quite interesting. Hydrogen abstraction to give 3,3-diphenyl-2-propenal appears also to be too endothermic since this product is not observed. However control experiments on authentic material revealed that this aldehyde is labile under the photolysis conditions. Thus, if small amounts of 3,3-diphenyl-2-propenal were formed, subsequent destruction would preclude detection. Instead, the acyl radical Acπ could account for the formation of the methyl 3,3-diphenylacrylate via the heterocumulene **6** (eq 8). The latter compound is known to react with methanol affording methyl 3,3-diphenylacrylate.[12] Since no methyl 3,3-diphenylpropanoate was detected in the photolysate of the enone **2a**, disproportionation of two acyl radicals Acπ to give the cumulene **6** and benzhydrylketene is unlikely. Disproportionation between benzhydryl and the acyl radical Acπ can only in part account for acrylate, since merely traces of diphenylmethane were detected in the photolysate of the enone **2a**. Possibly excited enone **2a** could serve as hydrogen acceptor.



Experimental Section

Melting points are uncorrected. Infrared spectra were taken on a Beckman Acculab 4 spectrometer, and ^1H NMR spectra at 90 MHz on a Varian EM-390 spectrometer. ^{13}C NMR spectra were measured at 22.6 MHz on a Bruker WH 90 spectrometer or at 100.61 MHz on a Bruker WM 400 spectrometer. Mass spectra were run on a Varian MAT CH7 spectrometer, UV spectra on a Cary 17 instrument. The elemental analyses were kindly run for us by Professor G. Maier's staff at the Universität Gießen. X-ray crystallography was carried out at the Max-Planck-Institut für Festkörperforschung, Stuttgart. Known compounds in this research were either purchased from standard suppliers or prepared according to literature procedures and purified to match the reported physical and spectral data. Only the experimental details of hitherto unknown compounds or procedures are provided. Photolyses were carried out in a Rayonet Model RP-100 (Southern New England Ultraviolet co.) photochemical reactor at 300 nm (quartz vessel) or at 333.6 nm with a Coherent CR 18 supergraphite argon ion laser (quartz vessel). Analytical HPLC was carried out on a Waters instrument (6000A, U6K, M440) by employing UV detection at 254 nm. Capillary GC was done on a Fractovap 2000 (Carlo Erba Co.).

Syntheses. 1,1,4,4-Tetraphenyl-4-hydroxy-2-butanone. A 500-mL three-necked, round-bottomed flask, equipped with a magnetic spin bar nitrogen inlet and outlet, and rubber septum, was charged with 6.57 g (57.2 mmol) 35% potassium hydride (mineral oil suspension). The hydride was briefly washed with dry THF and then suspended in 100 mL of dry THF. A solution of 10.0 g (47.7 mmol) of 1,1-dphenylacetone in 100 mL of dry THF was syringed into the stirred suspension at ca. 20 °C. After complete addition the evolution of hydrogen had ceased (ca. 30 min), the yellow solution was filtered under nitrogen into a dry 500-mL three-necked, round-bottomed flask, equipped with a magnetic stirrer, nitrogen inlet and outlet, and a rubber septum. At ca. 20 °C, 28.9 mL (53.7 mmol) of a 1.86 M solution of *n*-butyllithium in hexane was syringed into the stirred solution. The deep-red reaction mixture was stirred at ca. 20 °C for 15 min and cooled to 0 °C and 8.70 g (47.7 mmol) of benzophenone in 50 mL of dry THF was syringed into the mixture. The brownish solution was stirred at 0 °C for 15 min and for an additional 30 min at ca. 20 °C. It was then poured into 100 mL of ice water and acidified with concentrated hydrochloric acid to pH 2–3. The mixture was then extracted with ether (3 × 100 mL). The combined extracts were washed with water (150 mL), saturated aqueous sodium bicarbonate (100 mL), and water (100 mL) and dried over anhydrous sodium sulfate. After rotoevaporation of the solvent at 20 °C and 15 torr, a pale yellow solid remained. Washing with 100 mL of cold *n*-pentane and drying at 40 °C and 15 torr afforded 15.0 g (80%) of almost colorless prisms, mp 125–128 °C. An analytically pure sample was obtained by repeated recrystallization from ethanol: mp 134 °C; IR (KBr) 3445, 3055, 3028, 2900, 1697, 1498, 1453, 1416, 1398, 1074, 1016, 751, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 3.50 (s, 2 H, 3-H), 5.02 (s, 1 H, 1-H), 5.11 (s, 1 H, OH), 7.0–7.5 (m, 20 H, C_6H_5); ^{13}C NMR ($CDCl_3$, 22.6 MHz) δ 52.4 (t, C-3), 65.4 (d, C-1), 77.1 (s, C-4), 125.6, 126.9, 127.4, 128.1, 128.7, 129.0, 136.9, 145.8 (C_6H_5), 209.8 (s, C-2). MS (70 eV), *m/e* 374 (0.2, $M^+ - H_2O$), 207 (54, $M^+ - H_2O$, $C_{13}H_{11}$), 167 (100, $C_{13}H_{11}^+$), 105 (95, $C_7H_5O^+$). Anal. $C_{28}H_{24}O_2$ (392.5) Calcd: C, 85.68; H, 6.16. Found: C, 85.84; H, 6.12.

1,1,4,4-Tetraphenyl-3-buten-2-one (2a). A sample of 5.00 g (12.7 mmol) of 1,1,4,4-tetraphenyl-4-hydroxy-2-butanone, ca. 100 mg of *p*-toluenesulfonic acid, and 100 mL of dry toluene were placed into a 250-mL, round-bottomed flask, equipped with a magnetic spin bar and a reflux condenser. The mixture was refluxed for 10 min, allowed to cool to ca. 20 °C, washed with saturated aqueous sodium bicarbonate (70 mL) and water (70 mL), dried over anhydrous sodium sulfate, and rotoevaporated at 40 °C and 15 torr. Crystallization of the remaining yellow oil from ethanol afforded 4.00 g (84%) of yellow needles: mp 99 °C (lit. mp 98 °C[7]); IR (KBr) 3050, 3022, 1688, 1604, 1589, 1522, 1493, 1448, 1083, 1070, 719, 697 cm^{-1}; UV (methyl *tert*-butyl ether) λ_{max} (log ϵ) 292 (4.09); ^1H NMR ($CDCl_3$, 90 MHz) δ 5.10 (s, 1 H, 1-H), 6.68 (s, 1 H, 3-H), 7.1–7.6 (m, 20 H, C_6H_5); ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ 64.09 (d, C-1), 125.82 (d, C-3), 126.94, 128.18, 128.24, 128.45, 129.15, 129.30, 129.48, 138.63, 138.85, 141.03 (C_6H_5), 154.10 (s, C-4), 198.21 (s, C-2); MS (70 eV); *m/e* 374 (0.3, M^+), 207 (100, $M^+ - C_{13}H_{11}$), 179 (23, $C_{14}H_{11}^+$), 167 (34, $C_{13}H_{11}^+$).

Photolyses. Preparative Photolysis of Enone 2a. A sample of 1.50 g (4.01 mmol) of enone **2a** was dissolved in a mixture of 250 mL of absolute methanol, 250 mL of absolute methyl *tert*-butyl ether, and 2 mL of acetic acid. The soluton was flushed with nitrogen for 30 min and then irradiated at 300 nm under nitrogen for 9 h. The solvent was rotoevaporated at 30 °C and 15 torr and the remaining yellow oil was taken up in 100 mL of ether. The ether solution was washed with aqueous sodium carbonate (2 × 50 mL) and water (50 mL), dried over anhydrous sodium sulfate, and rotoevaporated at 20 °C and 15 torr, affording 1.54 g of a yellow solid. The solid was subjected to flash chromatography on silica gel (32–63 μm, adsorbant-substrate ratio 80:1) by eluting with a hexane and methylene chloride solvent gradient, starting with a 3:1 mixture, respectively, and finishing with pure CH_2Cl_2. The products eluted in the following order: 100 mg of 1,1,2,2-tetraphenylethane, 480 mg of methyl 3,3,4,4-tetraphenylbutanoate (**4**), 150 mg of methyl 3,3-diphenylacrylate, and 150 mg of 3-(diphenylmethyl)-3-phenylindanone (**5**).

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[12] Brown, R. F. C.; Eastwood, F. W.; Harrington, K. J. *Aust. J. Chem.* **1974**, *27*, 2373.

Methyl 3,3,4,4-Tetraphenylbutanoate (4). The crude product was taken up in ethanol and allowed to crystallize by cooling to 4 °C. An additional recrystallization from ethanol afforded analytically pure ester **4** as colorless plates: mp 106–107 °C; IR (KBr) 3060, 3025, 2940, 1735, 1600, 1498, 1449, 1204, 1178, 1155, 1033, 763, 747, 704 cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 3.07 (s, 2 H, 2-H), 3.23 (s, 3 H, OCH_3), 5.70 (s, 1 H, 4-H), 7.0–7.4 (m, 20 H, C_6H_5); ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ 47.15 (t, C-2), 51.03 (q, OCH_3), 54.52 (s, C-3), 56.98 (d, C-4), 126.26, 126.48, 126.81, 127.59, 130.59, 131.17, 141.97, 143.67 (C_6H_5), 171.57 (s, C-1); MS (70 eV), *m/e* 375 (1, $M^+ - CH_3O$), 239 (100, $M^+ - C_{13}H_{11}$), 197 (54), 167 (53, $C_{13}H_{11}^+$). Anal. $C_{29}H_{26}O_2$ (406.5) Calcd: C, 85.68; H, 6.45. Found: C, 85.69; H, 6.40.

3-(Diphenylmethyl)-3-phenyl-1-indanone (5). The crude product was recrystallized from hexane followed by recrystallization from 5:1 hexane–ethyl acetate affording colorless plates: mp 189 °C; IR (KBr) 3085, 3060, 3022, 1712, 1600, 1499, 1462, 1450, 1289, 1232, 1216, 1059, 955, 760, 700 cm^{-1}; UV (methyl *tert*-butyl ether) λ_{max} (log ϵ) 293 (3.23); ^{1}H NMR ($CDCl_3$, 90 MHz) δ AB-system ($\delta_A = 3.39$, $\delta_B = 3.61$, $J = 13$ Hz, 2-H), 5.39 (s, 1 H, C*H*Ph_2), 6.5–7.7 (m, 19 H, aryl-H); ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ 49.20 (t, C-2), 53.69 (s, C-3), 58.62 (d, $CHPh_2$), 123.27, 126.15, 126.27, 126.42, 127.15, 127.33, 127.40, 127.67, 128.17, 128.30, 130.18, 130.54, 134.21, 136.24. 140.68, 141.24, 145.42, 160.80 (aryl-C), 204.42 (s, C-1); MS (70 eV), *m/e* 374 (0.1, M^+), 207 (23, $M^+ - C_{13}H_{11}$), 178 (16), 167 (100, $C_{13}H_{11}^+$). Anal. $C_{28}H_{22}O$ (374.5) Calcd: C, 89.81; H, 5.92. Found: C, 89.81; H, 5.80.

Quantitative Photolyses of Enone 2a. A sample of 179 mg (0.477 mmol) of enone **2a** was dissolved in a mixture of 35 mL of absolute methanol, 35 mL of absolute methyl *tert*-butyl ether, and 0.3 mL of acetic acid. The solution was purged with nitrogen for 15 min and then irradiated at 300 nm under nitrogen for 3 h. The solvent was rotoevaporated at 30 °C and 15 torr, the remaining yellow oil was dissolved together with 9.75 mg (0.0535 mmol) of 4,4′-dimethylbiphenyl (internal standard) in $CDCl_3$ and transferred into a NMR tube, and the 90-MHz ^{1}H NMR spectrum was taken. The product distribution (weight %) was calculated from the average of five integrations: methyl 3,3,4,4-tetraphenylbutanoate (**4**), 39 ± 2; methyl 3,3-diphenylacrylate, 3 ± 1; 1,1,2,2-tetraphenylethane, 7 ± 2.

The analogous irradiation of 172 mg (0.459 mmol) of enone **2a** in 70 mL of absolute 2-propanol and 1 mL of acetic acid for 150 min, addition of 11.7 mg (0.0642 mmol) of 4,4′-dimethylbiphenyl, and ^{1}H NMR analysis afforded the following product distribution (weight %): isopropyl 3,3,4,4-tetraphenylbutanoate, 35 ± 2; isopropyl 3,3-diphenylacrylate, ca. 3; 1,1,2,2-tetraphenylethane, 5 ± 2.

In a third run, 153 mg (0.409 mmol) of enone **2a** was dissolved in 35 mL of absolute diisopropyl ether and 35 mL of absolute methanol and irradiated for 100 min. ^{1}H NMR analysis of the photolysate again did not show more than trace amounts of diphenylmethane. Its presence in each of the three photolysates was established by coinjection with an authentic sample by means of capillary GC, with a 50-m Carbowax column, operated at column, injector, and detector temperatures of 160, 180, and 180 °C respectively, and a carrier gas (N_2) flow of 1 mL/min, and HPLC, with a 25 × 0.4 cm LiChroSorb RP C_{18}, 5μ column, eluting with 87:13 MeOH–H_2O at a flow rate of 0.9 mL/min.

Concentation-Time Profiles. A sample of 3 mL of a 5.73 × 10^{-3} M solution of enone **2a** in a 125:125:1 methanol–methyl *tert*-butyl ether–acetic acid mixture was flushed with nitrogen and irradiated at 300 nm under exclusion of air. Samples were taken each 20–30 min and analyzed by HPLC (for conditions, vide supra). The form of the concentration–time profiles indicated that none of the photoproducts resulted from secondary photolyses. Both the butanoate **4** and 1,1,2,2-tetraphenylethane proved stable upon prolonged irradiation, whereas methyl 3,3-diphenylacrylate and indanone **5** underwent rapid subsequent photolysis.

Photolysis of Enone in 2-Propanol and in Benzene at 333.6 nm. Aliquots of 2 mL of a 3.03 × 10^{-3} M solution of enone **2a** in absolute benzene and a 3.15 × 10^{-3} M solution in 2-propanol were flushed with nitrogen for 5 min and irradiated at 333.6 nm under exclusion of air. Samples were taken each 5–10 min and analyzed by HPLC by using a 25 × 0.4 cm LiChroSorb Si 60, 5μ column, eluting with 98:2 hexane–ethyl acetate at a flow rate of 1.5 mL/min. Enone **2a** was found to be consumed at identical rates in both solvents.

Control Experiments. Photostability of Methyl 3,3,4,4-Tetraphenylbutanoate (4) in the Photolysate of Enone 2a. A sample of ca. 2 mg of the butanoate **4** was dissolved in 1 mL of a 125:125:1 methanol–methyl *tert*-butyl ether–acetic acid mixture, flushed with nitrogen for 5 min, and irradiated at 300 nm under exclusion of air. The concentration of the butanoate **4** was monitored by HPLC by using a 25 × 0.4 cm LiChroSorb RP C_{18}, 5μ column, eluting with 87:13 MeOH–H_2O at a flow rate of 0.9 mL/min. After 30 min, ca. 20% of the ca. 2 mg of the enone **2a** starting ester **4** was consumed. To this partial photolysate was added ca. 2 mg of the enone **2a** and the irradition continued. After another 30 min, the enone **2a** was completely consumed and the concentration of the butanone **4** had reached ca. 1.2-fold its initial valve.

Photostability of Diphenylmethane in the Photolysate of Enone 2a. A sample of ca. 12 mg of enone **2a** and ca. 11 mg of diphenylmethane was dissolved in 2 mL of 125:125:1 methanol–methyl *tert*-butyl ether–acetic acid, flushed with nitrogen for 5 min, and irradiated at 300 nm under exclusion of air. The concentrations of the two components were monitored by HPLC (for conditions, vide supra). After 195 min, the enone **2a** was completely decomposed, whereas no consumption of diphenylmethane could be observed.

Photolability of 3,3-Diphenylpropenal in the Photolysate of Enone 2a. A sample of 8.78 mg (0.0235 mmol) of enone **2a** and 10.5 mg (0.0504 mmol) of 3,3-diphenylpropenal was dissolved in 3 mL of 125:125:1 methanol–methyl *tert*-butyl ether–acetic acid, flushed with nitrogen for 5 min, and irradiated at 300 nm under exclusion of air. The concentrations of the two components were monitored by HPLC by using a 25 × 0.4 cm LiChroSorb Si 60, 5μ column, eluting with 96:4 hexane–ethyl acetate at a flow rate of 2 mL/min. After 225 min, 95% of the aldehyde was decomposed, whereas no significant consumption of the enone **2a** could be observed.

X-ray Analysis of the Indanone 5. The cell parameters were determined from a colorless transparent crystal of dimensions 0.08 × 0.15 × 0.05 mm on a SYNTEX-P3 four-circle diffractometer. Measurements of intensities: ω-scan, Mo Kα, 1° range, 2θ maximum = 55°. The intensities of 2183 reflections were measured, 1291 of them with $F > 3\sigma(F)$ were applied for the structure determination. The structure was solved by direct phase determination. The phases of 200 strong reflections were determined and on the resulting *E* map approximate positions of all nonhydrogen atoms could be refined by anisotropic least-squares cycles, $R = 0.073$. The positions of the hydrogen atoms were calculated geometrically and considered isotropically in all refinements. Indanone **5** crystallizes monoclinically in the space group $P2_1/n$ (no. 14) with $a = 1525.3$ (9) pm, $b = 1349.4$ (6) pm, $c = 1006.7$ (7) pm, $\beta = 99.00$ (5)°. The unit cell contains four formula units, the density was calculated to be 1.215 g cm^{-3}.

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Registry No. **3**, 96746-59-7; **4**, 96746-60-0; **5**, 96746-61-1; 1,1-diphenylacetone dianion, 86543-51-3; 1,1,4,4-tetraphenyl-4-hydroxy-2-butanone, 37542-18-0; 1,1-diphenylacetone, 781-35-1; methyl 3,3-diphenylacrylate, 3461-34-5; 1,1,2,2-tetraphenylethane, 632-50-8; benzophenone, 119-61-9.

Supplementary Material Available: A listing of positional and thermal parameters (Table I), bond lengths, and bond angles (Table II) and the perspective drawing (Figure 2) for the indanone **5** (3 pages). Ordering information is given on any current masthead page.