Photochemical Reaction of Ethyl 3-Oxo-2,4-diphenylbutanoate

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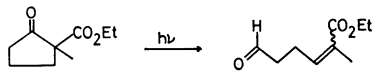
Irradiation of ethyl 3-oxo-2,4-diphenylbutanoate in hexane gave the products formed by recombination of the radicals (Ph–$\dot{C}H_2$ and/or Ph–$\dot{C}H$–CO_2Et) resulting from decarbonylation, together with small amounts of 1,2-diphenylethanol and ethyl α-hydroxyphenylacetate, whereas in benzene no 1,2-diphenylethanol was found. Under oxygen an increased amount of ethyl α-hydroxyphenylacetate and no radical recombination products were observed.

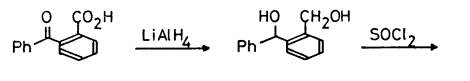
Although the influence of UV-irradiation on the keto-enol equilibrium ratio of β-keto esters has been studied,[1] few reports about the photochemistry of β-keto esters to yield isolatable products have been found.[2,3] Moritur reported[2] that irradiation of the β-keto ester (**1**) gave aldehydes (**2**) resulting from α-cleavage. It is expected that β-keto esters with phenyl group at α-position to both carbonyl groups are easily subject to α-cleavage upon irradiation, and the resulting radicals may couple to yield products. In this paper we wish to report a photolysis of ethyl 3-oxo-2,4-diphenylbutanoate (**3**) which is expected to yield coupling products of radicals resulting from initial α-cleavage of the excited molecule.



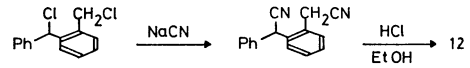
1 2 (E + Z)

Results and Discussion

Irradiation of **3** in hexane with Pyrex filtered light led to the formation of eleven products; bibenzyl (**4**, 13%), ethyl phenylacetate (**5**, 5%), ethyl α-hydroxyphenylacetate (**6**, 5%), 1,2-diphenylethanol (**7**, 2%), ethyl 2,3-diphenylpropionate[4] (**8**, 32%), ethyl *o*-benzylphenylacetate[5] (**9**, 4%), diethyl *meso*-α,α′-diphenylsuccinate[6] (**10**, 7%), diethyl *dl*-α,α′-diphenylsuccinate[6] (**11**, 7%), ethyl *o*-(α-ethoxycarbonylbenzyl)-phenylacetate (**12**, 3%), $PhCH_2C_6H_{13}$ compound (**13**, 4%), and $PhCH(C_6H_{13})CO_2Et$ compound (**14**, 4%). The products **4**, **5**, **6**, and **7** were identified by comparison of their spectroscopic data with those of commercially available authentic samples. The structures of **8**, **9**, **10**, and **11** were established by comparison with the specimens independently synthesized according to published methods.[4–6] The product **12** was confirmed by comparison with an independently synthesized one from *o*-benzoylbenzoic acid by the sequence **15**→**16**→**17**→**18**→**12** (overall yield, 16%).



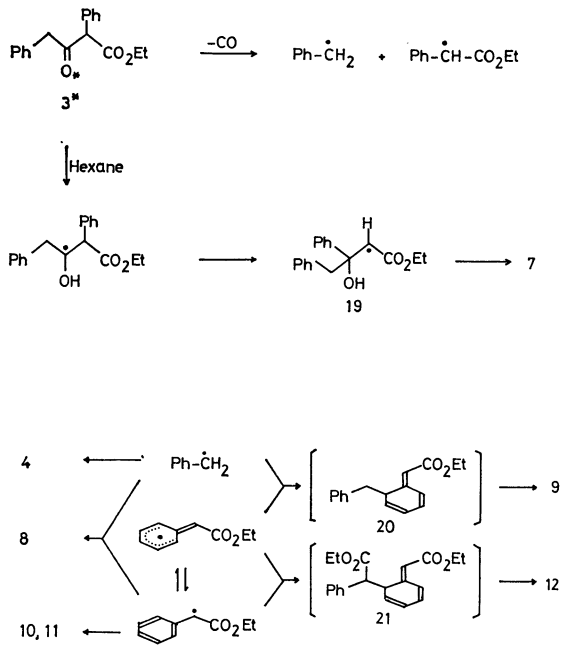
15 16



17 18

The products **13** and **14** were characterized by their spectroscopic data (see Experimental), although the structures of the $-C_6H_{13}$ residues of both **13** and **14** were not clear. ^1H NMR spectrum of **13** shows thirteen hydrogen atoms between $\delta=0.7$ and 1.8 ($-C_6H_{13}$), two hydrogen atoms between $\delta=2.1$ and 2.7 ($-CH_2-$ adjacent to the phenyl group) and five hydrogen atoms between $\delta=7.0$ and 7.3 (phenyl), while that of **14** shows a triplet at $\delta=1.17$ and a quartet at $\delta=4.07$ ascribed to the ethoxycarbonyl group.

The formation of **4**—**6** and **8**—**14** may be explained in terms of cleavage of both the C_2–C_3 and the C_3–C_4 bonds of excited **3** to produce a benzyl radical and an α-ethoxycarbonylbenzyl radical. Homogeneous combination of the benzyl radicals and α-ethoxycarbonylbenzyl radicals yields bibenzyl **4** and two diastereomeric diesters **10** and **11**, respectively. Mixed combination of benzyl radical with α-ethoxycarbonylbenzyl radical yields **8**. Attack of the benzyl radical on a phenyl ring of α-ethoxycarbonylbenzyl radical yields **9** through an intermediate **20**. Similarly, coupling of α-ethoxycarbonylbenzyl radicals yields **12** through an intermediate **21**. Reaction of the α-ethoxycarbonylbenzyl radical with the solvent yields either **5** or **14**. Reaction of benzyl radical with the solvent yields **13**. Ethyl α-hydroxyphenylacetate **6** probably arises *via* the reaction of the α-ethoxycarbonylbenzyl radical with oxygen dissolved in the solvent. In fact, irradiation of **3** under oxygen afforded **6** with an increased yield. The formation of 1,2-diphenylethanol **7** may



be explained in terms of phenyl migration from C-2 to C-3 of the starting β-keto ester. Since irradiation of **3** in benzene, which is inert toward hydrogen abstraction, affords no **7**, the phenyl migration is considered to follow the hydrogen abstraction by excited **3** from the solvent. Therefore, **7** may arise *via* radical **19**. In conclusion, the present work elucidated that photolysis of a β-keto ester having a phenyl group at the C-2 position proceeded predominantly by an α-cleavage and slightly by hydrogen abstraction from the solvent followed by phenyl migration.

Experimental

^{1}H NMR spectra were recorded on a Varian A-60D apparatus in carbon tetrachloride with tetramethylsilane as the internal standard. IR spectra were recorded on a JASCO IRA-2 spectrometer in carbon tetrachloride. Gas liquid chromatography (GLC) was carried out on a Hitachi K-53 (FID) or a Gasukuro Kogyo KOR-70 (TCD) instrument, using a 2 m×3 mm stainless steel (for K-53) or a 5 m×6 mm aluminium column (for KOR-70), both of which were packed with 10% SE-30 on 60—80 mesh Diasolid L. Irradiations were conducted through a Pyrex filter using an Ushio UM-452 high pressure mercury lamp (450 W). Thin layer chromatography (TLC) was carried out on Merck Silica Gel 60 TLC Plates Art. 5737. Column chromatography was carried out on Merck Silica Gel 60 Art. 7734. Ethyl 3-oxo-2,4-diphenylbutanoate (**3**) was prepared by the published method.[7]

Photolysis. a): A solution of 2.64 g of **3** in 1100 cm^3 of hexane (8.5 mmol/dm^3 solution) was irradiated, and the reaction was monitored by TLC. Irradiation was continued until almost all the starting ester was consumed (*ca.* 8 h). The solvent was removed under reduced pressure, and the residue was analyzed by GLC to reveal the following product distribution: **4** (13%), **5** (5%), **6** (5%), **7** (2%), **8** (32%), **9** (4%), **10** (7%), **11** (7%), **12** (3%), **13** (4%), and **14** (4%). These photo-products were separated from the irradiation mixture by a combination of column chromatography using benzene as eluent and preparative GLC. The products **4**—**12** were identical with authentic samples.

b): A solution of 960 mg of **3** in 400 cm^3 of hexane was irradiated under oxygen for 3 h. The solvent was removed under reduced pressure. Column chromatography of the residue gave only **6** with 37% yield.

c): A solution of 10.1 mg of **3** in 1 cm^3 of benzene was placed in a Pyrex tube and irradiated for 1 h. GLC-analysis indicated that the irradiation mixture contained **4** (18%), **5** (2%), **8** (50%), **9** (4%), **10** (10%), **11** (10%), **12** (3%), and no **7**.

$PhCH_2C_6H_{13}$ Compound ***13***. IR 2950, 2900, 695 cm^{-1}. ^{1}H NMR: δ=0.7—1.8 (m, 13H), 2.1—2.7 (m, 2H) and 7.0—7.3 (m, 5H). Found: C, 88.02; H, 11.22%. Calcd for $C_{13}H_{20}$: C, 88.56; H, 11.44%.

$PhCH(C_6H_{13})CO_2Et$ Compound ***14***. IR: 2950, 2920, 1730, 1160, 1030, 700 cm^{-1}. ^{1}H NMR: δ=1.17 (t, J=7.5 Hz, 3H), 0.6—2.4 (m, 13H), 3.0—3.5 (m, 1H), 4.07 (q, J=7.5 Hz, 2H), and 7.1—7.5 (m, 5H). Found: C, 77.64; H, 9.70%. Calcd for $C_{16}H_{24}O_2$: C, 77.37; H, 9.74%.

Synthesis of ***12***. To a suspension of $LiAlH_4$ (2.0 g) in absolute ether (30 cm^3) under reflux was added slowly a solution of *o*-benzoylbenzoic acid (**15**, 5.0 g) in absolute ether (50 cm^3). After the addition was completed, the mixture was heated under reflux for an additional 2 h. After the remaining $LiAlH_4$ had been destroyed by addition of saturated NH_4Cl solution (40 cm^3), the ether layer was separated. The ethereal solution was washed with water, dried over $MgSO_4$, and evaporated. The residue was submitted to chromatography using hexane-ethyl acetate 1:1 as eluent to give 4.1 g (87%) of diol **16**; bp (bath temp) 190 °C/93 Pa. IR: 3300, 700 cm^{-1}. ^{1}H NMR: δ=3.3—3.8 (broad, 1H), 4.1—4.6 (broad, 1H), 4.45 (AB q, J=14.5 and 12.5 Hz, 2H), 5.95 (s, 1H), and 7.15—7.45 (m, 9H). To a solution of **16** (3.0 g) and pyridine (2.3 g) was added slowly $SOCl_2$ (3.4 g) with stirring under cooling with ice. After the addition was completed, the mixture was stirred for 1 h at room temperature and extracted with ether. The ethereal solution was worked up in the usual way. Column chromatography using benzene as eluent gave 1.75 g (50%) of dichloride **17**; bp (bath temp) 155 °C/53 Pa. IR: 3100, 3050, 1500, 1450, 1265, 695 cm^{-1}. ^{1}H NMR: δ=4.68 (AB q, J=18.5 and 12.0 Hz, 2H), 6.68 (s, 1H) and 7.20—7.70 (m, 9H). Dichloride **17** (382 mg) was added at room temperature to the stirred partially soluble NaCN (210 mg) in dimethyl sulfoxide (2 cm^3). The mixture was stirred at room temperature for 90 min, diluted with water (4.5 cm^3), and extracted with ether. The ethereal solution was worked up. Column chromatography eluted with benzene gave 305 mg (86%) of dicyanide **18**; IR: 2260, 1500, 1460, 700 cm^{-1}. ^{1}H NMR: δ=3.63 (s, 2H), 5.35 (s, 1H), and 7.25—7.90 (m, 9H). Dry hydrogen chloride was bubbled through a solution of **18** (252 mg) in ethanol (5 cm^3). The solution was heated under reflux for 50 h. The reaction mixture was cooled with ice, and the precipitated NH_4Cl was filtered off. The filtrate was concentrated. The residue was extracted with ether, and the ether extract was washed with saturated $NaHCO_3$ and water, dried over $MgSO_4$, and evaporated. The residue was submitted to chromatography using benzene as eluent to yield 153 mg (43%) of diester **12**; IR: 1730, 1150, 1030, 690 cm^{-1}. ^{1}H NMR: δ=1.15 (t, J=7.5 Hz, 3H), 1.19 (t, J=7.5 Hz, 3H), 3.56 (s, 2H), 4.03 (q, J=7.5 Hz, 2H), 4.15 (q, J=7.5 Hz, 2H), 5.32 (s, 1H), and 7.1—7.4 (m, 9H). Found: C, 73.83; H, 6.78%. Calcd for $C_{20}H_{22}O_4$: C, 73.59; H, 6.79%.

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