Photoreduction of Acetone by Toluene and Ethylbenzene

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The photoreduction of acetone in toluene gave bibenzyl and 1,1-dimethyl-2-phenylethanol and that in ethylbenzene gave *meso*- and (±)-2,3-diphenylbutane and 1,1-dimethyl-2-phenylpropan-1-ol. Pinacol and propan-2-ol were not formed.

THE photoreduction of ketones with such hydrogen donors as hydrocarbons, alcohols, and compounds that can yield a stable free radical upon loss of hydrogen has been studied.[1–4] Most of the work has been on the photoreduction of aromatic ketones, especially benzophenone;[5,6] the most important reaction is the formation of pinacols. However, less work has been done on the reduction of aliphatic ketones. The irradiation of acetone with isopropyl alcohol is reported to give pinacol as the sole product,[7,8] while its reduction with diphenylmethanol yields only pinacol derived from the latter. We now report results on the reduction of acetone with toluene and ethylbenzene in the presence of u.v. light.

Irradiation of acetone (90 ml) in toluene (90 ml) under nitrogen, through a Pyrex filter, with a 450-W Hanovia lamp for 10 days afforded after work up a brown liquid (2·3 g), which showed two g.l.c. peaks of nearly equal area. These compounds were separated into a crystalline solid and a sweet smelling liquid by column chromatography. The crystalline solid (500 mg), m.p. 47—49°, was identified as bibenzyl (I) (spectroscopy and mixed m.p.).

$$\mathrm{PhMe} + \mathrm{MeCOMe} \xrightarrow[n\to\pi^*]{h\nu} \underset{\text{(I)}}{\mathrm{PhCH_2{\cdot}CH_2Ph}} + \underset{\text{(II)}}{\mathrm{PhCH_2{\cdot}CMe_2{\cdot}OH}}$$

The i.r. spectrum of the liquid fraction (750 mg) showed the presence of hydroxy and monosubstituted phenyl groups. It had n.m.r. signals at δ 1·13 (6H, s), 2·62br (1H, s, concentration-dependent and absent on washing with D_2O), 2·70 (2H, s), and 7·25 (5H, s) p.p.m. Structure (II) is assigned to this alcohol; this assignment was confirmed by spectroscopic comparison with an authentic sample.† In addition to these compounds a low-boiling product was formed which could not be identified.

$$\mathrm{MeCOMe} \xrightarrow[n\to\pi^*]{h\nu} (\mathrm{MeCOMe})^* \tag{1}$$

$$(\mathrm{MeCOMe})^* + \mathrm{PhCH_2R} \rightleftharpoons \underset{\text{(III)}}{\mathrm{Me\dot{C}(OH)Me}} + \underset{\text{(IV)}}{\mathrm{Ph\dot{C}HR}} \tag{2}$$

$$\mathrm{Me\dot{C}(OH)Me} + \mathrm{PhCH_2R} \longrightarrow \mathrm{MeCH(OH)Me} + \mathrm{Ph\dot{C}HR} \tag{3}$$

$$\mathrm{MeCH(OH)Me} + (\mathrm{MeCOMe})^* \longrightarrow 2\mathrm{Me\dot{C}(OH)Me} \tag{4}$$

$$\mathrm{Ph\dot{C}HR} + \mathrm{Me\dot{C}(OH)Me} \longrightarrow \mathrm{PhCHR{\cdot}C(Me)_2{\cdot}OH} \tag{5}$$

(II) R = H
(VIII) R = Me

$$2\mathrm{Ph\dot{C}HR} \longrightarrow \mathrm{PhCHR{\cdot}CHR{\cdot}Ph} \tag{6}$$

(I) R = H
(VI) and (VII) R = Me

The formation of these compounds is represented in reactions (1)—(6). The excited acetone can abstract a proton from hydrocarbons [reaction (2)] to give the radicals (III) and (IV), which by recombination will give products [reaction (5) and (6)] or can give back starting materials. Radical (III), not stable enough to give pinacol, could readily combine with radical (IV) to give the product [reaction (5)] or abstract a proton from the hydrocarbons to give isopropyl alcohol [reaction (3)]. However, the absence of isopropyl alcohol in the photolysis products can be explained on the basis of its greater reactivity than hydrocarbons towards excited ketone molecules.[4] No sooner is it formed than it reacts with excited acetone to give back the free radical (III), which in addition to giving (II) also gives an unidentified product (see Experimental section). The absence of pinacol as one of the photo-products is not surprising as it is known that pinacols are formed only from fairly longe-lived radicals.[8] The formation of pinacol was not observed during the photolysis of acetone in cyclohexene, even though the radical (III) was formed,[9] but pinacol was formed when biacetyl was irradiated in cyclohexene.[10] This is evidently due to the greater stability of the derived radical (V), which is stable

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† Obtained from Sofler Limited, Middlesex.

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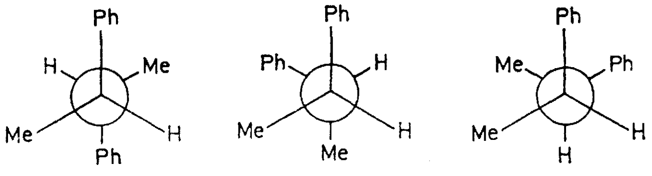
enough to find a second similar radical to give pinacol. The formation of both (±)- and *meso*-forms of 2,3-

$\mathrm{Me\dot{C}(OH){\cdot}COMe}$ (V)

diphenylbutane during irradiation of acetone in ethylbenzene (see later) is a strong evidence for the existence of the free radical (IV).

Radical (IV) will be more stable if R = Me, thereby shifting the equilibrium to the right [reaction (2)], and increasing the overall yield of the photoproducts. This was indeed found to be the case and when acetone was irradiated with ethylbenzene the reaction was faster and the overall yield of the products increased considerably. Thus irradiation of acetone (95 ml) containing an equal volume of ethylbenzene gave, after 8 days, a thick oil (8·5 g) which solidified when set aside. The mixture was separated into three compounds by column chromatography. The earlier eluents with light petroleum–benzene gave a crystalline compound, m.p. 124—126°, which was identified as *meso*-2,3-diphenylbutane (lit.,[11] m.p. 126—128°). Assignment of structure (VI) is supported by its i.r. and n.m.r. spectra. The n.m.r. spectra showed the methine protons as a multiplet at δ 2·6—3·0 p.p.m., which is due to the presence of rotational isomers [(VI), (VIIa and b)].[12] In addition to the crystalline compound (VI) a liquid was obtained in the earlier eluents, which was identified as (±)-2,3-diphenylbutane. Its i.r. spectrum was very similar to that of the *meso*-form but differed in the fingerprint region. The n.m.r. spectra of both these stereoisomers was identical to those in the literature.[12,13]

PhCHMe·CHMe·Ph *meso* (VI) and (±)-(VII) forms

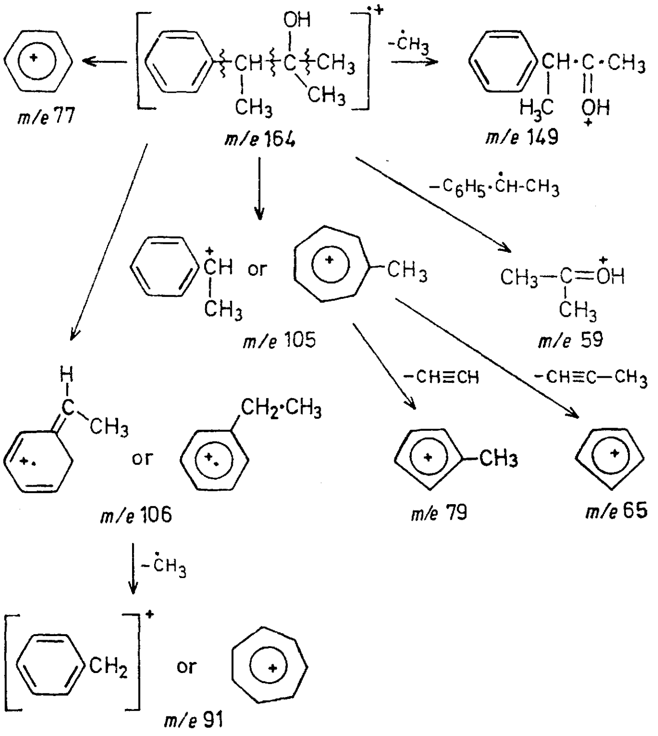


(VI) (VIIa) (VIIb)

Elution with benzene–ether gave a sweet-smelling liquid which showed strong i.r. bands for hydroxy and monosubstituted phenyl groups. On the basis of these spectral data and its n.m.r. spectrum (Experimental section), the mode of formation, and by analogy of the formation of (II), it is assigned structure (VIII). Assignment of structure (VIII) is further supported by its

$\mathrm{PhCHMe{\cdot}C(Me)_2{\cdot}OH}$
(VIII)

mass spectrum, which showed the expected fragmentation pattern[14] (Scheme).



EXPERIMENTAL

I.r. spectra were recorded on a Unicam SP 200 spectrometer. N.m.r. spectra were recorded on a Varian A-60 spectrometer; the values are given in δ p.p.m. downfield from tetramethylsilane as internal standard. Mass spectra were recorded on an MS12 instrument and g.l.c. was run on a Perkin-Elmer F-11 chromatograph.

Freshly distilled and pure (g.l.c.) acetone, toluene, and ethylbenzene were used in the photochemical reactions.

Photolysis of Acetone in Toluene. Formation of (I) *and* (II).—A solution of acetone (90 ml) and toluene (90 ml) was irradiated with a 450-W Hanovia lamp contained in a water-cooled Pyrex well immersed in the solution. Oxygen-free nitrogen, presaturated with acetone, was kept bubbling through the solution. The level of the solution was maintained by addition of acetone–toluene. After irradiation for 10 days, evaporation under reduced pressure afforded an oil (2·3 g), which showed two g.l.c. peaks (silicone gum rubber column) with relative areas 1 : 1. The oil was chromatographed on a silica gel column and elution with benzene–light petroleum (40—60°) (1 : 1) gave (I) as an oil (*ca.* 500 mg, 0·87%), which crystallised when the mixture was set aside. Recrystallisation from methanol afforded white crystals, m.p. and mixed m.p. with authentic bibenzyl 47—49°, $\nu_{\max.}$ (CCl_4) 1950, 1870, 1795, 1745, 1605, and 700 cm^{-1}, δ (CCl_4) 2·80 (4H, s) and 7·08 (10H, s) p.p.m. Elution with benzene–ether (4 : 1) gave compounds (I) and (II) as a brown liquid (750 mg), followed by pure (II) as a light-brown liquid (750 mg, 1·5%), $\nu_{\max.}$ (neat) 3450, 1960, 1880, 1800, 1745, 1605, 740, and 705 cm^{-1}, δ (CCl_4) 1·13 (6H, s), 2·62br (1H, s, removed when shaken with D_2O),

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2·70 (2H, s), and 7·25 (5H, s), mass spectrum, *m/e* 150 (5·4%), 135 (16·5), 132 (6·3), 92 (100, base peak), 91 (57), 77 (5·7), 65 (21), and 59 (60).

The areas under the singlets at δ 2·82 and 2·70 in the n.m.r. spectrum of the crude mixture were in the ratio 2 : 1, giving the ratio of (I) to (II) as 1 : 1. G.l.c., on a polypropylene glycol column at 60°, of the crude mixture before evaporation gave in addition to the peaks due to (I), (II), acetone, and toluene a new peak with a slightly greater retention time than that of acetone, due to an unidentified compound. However, this peak was not due to isopropyl alcohol, mesityl oxide, hexane-2,5-dione, propylene oxide or biacetyl.

Photolysis of Acetone in Ethylbenzene. Formation of (VI), (VII), *and* (VIII).—A solution of acetone (95 ml) and ethylbenzene (95 ml) was irradiated with a 450-W Hanovia lamp, under nitrogen for 8 days. Evaporation under reduced pressure afforded a thick oil (8·5 g), which solidified when set aside. The mixture was chromatographed on silica gel and elution with benzene–light petroleum gave a solid, a mixture of (VI) and (VII) (3·64 g, 6·5%). Recrystallisation from methanol gave (VI) as fluffy crystals, m.p. 124—126° (lit.,[11] 126—128°), $\nu_{max.}$ (CCl_4) 3050, 2980, 1945, 1860, 1790, 1740, 1605, and 705 cm^{-1}, δ (CCl_4) 1·03 (6H, d, *J* 6 Hz), 2·6—3·0 (2H, m), and 7·15 (10H, s) p.p.m., δ (CS_2) 0·97 (6H, d, *J* 6·5 Hz), 2·51—2·87 (2H, m), and 7·20 (10H, s) p.p.m. Evaporation of the mother liquor afforded a semisolid residue, which was treated with methanol (3 ml) and cooled in ice. Quick filtration afforded an additional crop of (VI), and evaporation of the filtrate gave (VII) as a light brown liquid (525 mg, 1%), $\nu_{max.}$ (CCl_4) 3050, 2980, 1945, 1860, 1790, 1740, 1605, and 705 cm^{-1}, δ (CCl_4) 1·22 (6H, d, *J* 6 Hz), 2·6—3·2 (2H, m), and 7·02 (10H, s), δ (CS_2) 1·22 (6H, d, *J* 7 Hz), 2·65—3·03 (2H, m), and 7·02 and 7·05 (10H, each s) p.p.m.

The later eluents with benzene–ether (1 : 1) gave (VIII) as a mobile liquid (3·7 g, 8%), $\nu_{max.}$ (neat) 3010, 2950, 1950, 1880, 1805, 1740, 1605, and 705 cm^{-1}, δ (CCl_4) 1·09 (6H, s), 1·27 (3H, d, *J* 7 Hz), 2·10br (1H, s, concentration dependent, absent on washing with D_2O), 2·70 (1H, q, *J* 7 Hz), and 7·15 (5H, s) p.p.m., mass spectrum, *m/e* 164 (10%), 149 (26·2), 146 (5·0), 106 (99), 105 (90), 91 (100, base peak), 79 (26), 77 (37·5), 65 (8·0), and 59 (100, base peak).

G.l.c. on a polypropylene glycol column, of the crude mixture, before work up, gave in addition to expected peaks a peak whose retention time was identical to that of the unidentified product obtained during the photolysis of acetone and toluene.

The author thanks Professor R. C. Cookson for discussions and encouragement and the S.R.C. for financial assistance.

[0/1155 *Received, May 5th,* 1970]