NOTES

A novel aromatic ketone photoproduct: para-coupling of a phenyl-ketyl radical

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Three minor products from the irradiation of acetophenone in ether are described, and the mechanism of their formation is discussed.

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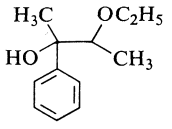
Irradiations of aromatic ketones in hydrogen-donating solvents have long been known to give mixtures of reduction products, predominantly pinacols (1), and recent publications concerning the mechanism of the photoreduction of benzophenone to benzopinacol (2–5) have prompted this report. During the course of other investigations it was found that irradiation of acetophenone in ether/cyclohexane solvent gave, as expected, the acetophenone pinacols in good yield (6). The product mixture also contained three minor constituents which were separated chromatographically and identified.

Two butan-2-ol derivatives were isolated in 6% yield each and the gross structure **1**, for both of them, was assigned from their spectra. The infrared (i.r.) spectra of each showed a monosubstituted phenyl, a hydroxyl group (probably tertiary) and no carbonyl, and differed only in details of the "fingerprint region". The proton magnetic resonance (p.m.r.) spectra, however, differed appreciably. Both showed the presence of one singlet, one doublet, and one triplet methyl group, but in one case (compound **1*a***) the doublet and triplet were well-separated, and in the other (compound **1*b***) almost superimposed. Three protons on carbon adjacent to oxygen appeared as complex multiplets in each, the patterns differing in detail. These were consistent with the A, B, and A′ portion of an ABX_3 pattern superimposed on an $A'X'_3$ (7, 8). Five aromatic protons and one hydroxyl were present in each compound. The compounds **1*a*** and **1*b*** were evidently diastereoisomeric and on the basis of the relative chemical shifts of the methyl groups, and the anticipated preferred conformations (9), the structures were tentatively proposed as shown.



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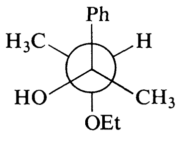
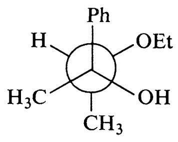
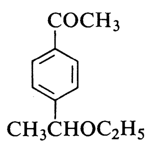


1*a*



1*b*



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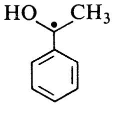

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$CH_3\dot{C}HOCH_2CH_3$

4

The third minor product, **2** (3% yield after purification), was also identified by its spectra. Ultraviolet (u.v.) and i.r. spectra showed that the compound was a substituted aromatic ketone, and all the non-equivalent protons were clearly resolved in the p.m.r. spectrum. The *p*-substitution of the acetophenone was apparent from

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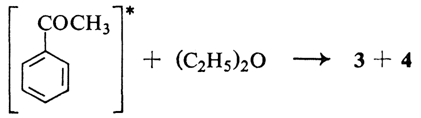
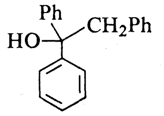
the pattern of the aromatic protons, two symmetrical doublets of two protons each. The possibility of a dimeric structure was considered to be incompatible with the observed p.m.r. spectrum, which was very well-defined.



The generally accepted mechanism for photoreduction of aromatic ketones involves abstraction of a hydrogen atom from the solvent by the ketone in the excited triplet state to give two radicals, in this case **3** and **4**. Subsequent combination of these radicals would give the two butan-2-ol derivatives, **1**, which were observed. Such compounds are well-known as minor products from photoreduction reactions; for example, irradiation of benzophenone in toluene, which acts as a hydrogen donor, gives **5** as well as benzopinacol (10).

The substituted acetophenone, **2**, however, is apparently a photoproduct of a new type. Its formation can be rationalized by postulating that the delocalized ketyl radical, **3**, is attacked at the *p*-position by the ethoxyethyl radical, **4**, to give the enolic intermediate **6**, which would be expected to be oxidized by air to the observed product, **2**, during workup of the reaction mixture. Alternatively the dehydrogenation might have been effected by acetophenone in the excited triplet state. The intermediate is analogous to **7** and **8**, both of which have been reported to be the oxygen-sensitive intermediate in the photoreduction of benzophenone by alcohols (3–5). The isolation of **2**, therefore, tends to confirm the mechanism of benzophenone photoreduction as recently proposed (3–5), and suggests that this mechanism is common to aromatic ketone photoreduction by hydrogen donors other than alcohols.



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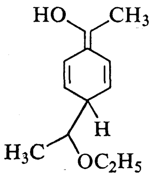

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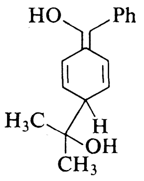

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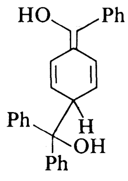

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Experimental

Nitrogen was bubbled through a solution of acetophenone (4.73 g) in 50% ether/cyclohexane (250 ml) for 1 h, and the solution was then irradiated under nitrogen with light of λ_{max} 350 nm ("black light" phosphor lamps through Pyrex; Rayonet reactor) for 2¼ h. Evaporation of the solution and chromatography on a silicic acid column (5% ether/benzene eluent) afforded recovered acetophenone (2.54 g), **1*a*** (162 mg, 7% yield), **1*b*** (150 mg, 6% yield), **2** (70 mg, 3% yield), and a mixture of the acetophenone pinacols (1.30 g).

*Compound **1a*** had p.m.r. peaks at τ 9.16 (3H, d, J = 6.5 Hz), 8.84 (3H, t, J = 7 Hz), 8.49 (3H, s), 7.30 (1H, exchanges with D_2O, s), 6.1–6.9 (3H, m), 2.5–3.0 (5H, m); u.v. λ_{max}^{hexane} at 206 nm (ε 8600), 258 nm (ε 190).

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.17; H, 9.42.

*Compound **1b*** had p.m.r. peaks at τ 9.00 (3H, d, J = 6.5 Hz), 8.93 (3H, t, J = 7 Hz), 8.61 (3H, s), 7.21 (1H, exchanges with D_2O, s), 6.2–7.1 (3H, m), 2.5–3.0 (5H, m); u.v. λ_{max}^{hexane} at 206 nm (ε 8400), 258 nm (ε 200).

Anal. Found: C, 74.35; H, 9.32.

p-(1-Ethoxyethyl)acetophenone, **2**, had i.r. ν_{max} 1685 cm^{-1}; p.m.r. peaks at τ 8.83 (3H, t, J = 7 Hz), 8.62 (3H, d, J = 6.5 Hz), 7.51 (3H, s), 6.69 (2H, q, J = 7 Hz), 5.62 (1H, q, J = 6.5 Hz), 2.68 (2H, d, J = 8 Hz), 2.18 (2H, d, J = 8 Hz); u.v. λ_{max}^{hexane} at 248 nm (ε 15 000), 320 nm (ε 670).

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.07; H, 8.45.

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