Photolysis of α-Chloro-*o*-methylacetophenones

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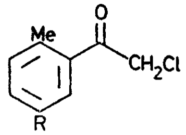
Summary Efficient cyclization (forming an indan-1-one) and solvolysis (forming an *ortho*-methoxymethyl derivative) reactions are apparently derived from photoenols of *o*-methylacetophenones with α-chloro-substituents.

In spite of its apparent simplicity the photoenolization of *o*-methyl-phenyl ketones continues to present a number of puzzling features.[1] Further impetus to study this reaction comes from its potential as a photochromic system and as a reversible photon energy storage system. We have been seeking ways of diverting the ordinarily very rapid thermal enol-to-ketone reversion. Such diversion has been accomplished through α-chloro-*o*-methylacetophenones.

Irradiation of a deoxygenated benzene solution of 2,5-dimethyl-α-chloroacetophenone (**1a**) with a Pyrex-filtered medium-pressure mercury arc lamp provided a 62% yield of 6-methylindan-1-one (**2a**) as the only volatile component, and accompanied by intensely coloured intractable material. Similar results were obtained with (**1b**). Irradiation of (**1a**) in methanol suppressed the formation of coloured material and provided a photosolvolysis product assigned structure (**3**).† Chemical yields determined by g.l.c. were 39% (**2a**) and 57% (**3**).

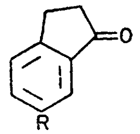
We view these transformations as arising from photoenol intermediates (**4**) and/or (**5**). The behaviour of α-chloro aryl ketones without *ortho*-methyl groups is quite different, involving reduction and rearrangement.[2]



(1)

a; R = Me

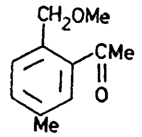
b; R = H



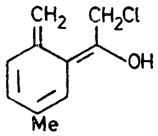
(2)

a; R = Me

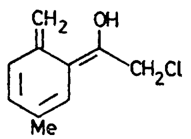
b; R = H



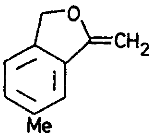
(3)



(4)



(5)



(6)

In methanol the quantum yield for disappearance of (**1a**) is near unity. This fact plus the stereochemical requirements for the processes involved make this photoreaction a useful mechanistic probe. It is not yet known whether the photoproducts arise from excited state or ground state enol. If derived from ground states (**2a**) must be derived from (**4**). The formation of (**3**) indicates that the formation of (**6**) from (**5**) should be possible. That (**6**) is not observed led us to examine it as a possible intermediate. In the presence of sodium hydrogen carbonate the formation of (**3**) is suppressed but the formation of (**2a**) is unchanged, suggesting that (**2a**) and (**3**) arise from different intermediates. No other products are observed under these conditions and the quantum yield for disappearance of (**1a**) is reduced by an amount equivalent to the amount of (**3**) which is not formed. The quantum yield for the formation of (**2a**) in benzene is much lower, 0·11, and unaffected by presence of sodium hydrogen carbonate.

Photolysis of α-bromo-*o*-methylacetophenone provides none of the products observed above but gives instead *o*-methylacetophenone, formed in high yield in both methanol and benzene. This resembles the results of a previous study on α-chloroacetophenones except for the absence of rearrangement products as would be associated with the radical resulting from C–Br bond dissociation.[2,3] ααα-Trifluoro-*o*-methylacetophenone is unchanged on photolysis under these conditions.

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[1] P. G. Sammes, *Tetrahedron*, 1976, **32**, 405; P. J. Wagner and C.-P. Chen, *J. Amer. Chem. Soc.*, 1976, **98**, 239; D. M. Findlay and M. F. Tchir, *J.C.S. Faraday I*, 1976, **72**, 1096.

[2] J. C. Anderson and C. B. Reese, *Tetrahedron Letters*, 1961, 1.

[3] G. Brunton, H. C. McBay, and K. N. Ingold, *J. Amer. Chem. Soc.*, 1977, **99**, 4447.

† The indanone (**2a**) was obtained by sublimation, m.p. 60—61 °C, lit. (W. Miller and W. Rohde, *Chem. Ber.*, 1890, **23**, 1898) 63 °C, and identified by spectral properties: n.m.r. (CCl_4) δ 2·37 (3H, s), 3·00 and 2·55 (2H and 2H, A_2B_2 pattern nearly identical to that of indan-1-one), and 7·40 (3H, m). For the methoxy-ketone (**3**), n.m.r. ($CDCl_3$) δ 2·38 (3H, s), 2·53 (3H, s), 3·38 (3H, s), 4·67 (2H, s), and 7·40 (3H, m). In CD_3OD with a trace of base the singlet at δ 2·53 disappears which distinguishes (**3**) from its isomer, α-methoxy-*o*-methylacetophenone.