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PHOTOADDITION OF BENZOPHENONE TO 2-METHYLPROPAN-2-OL

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2-Methylpropan-2-ol has proved to be a useful solvent in photochemical studies, largely because of the lack of α-hydrogens which imparts a greater resistance to attack by hydrogen-abstracting excited states.[1] We have been using this solvent, with benzophenone as sensitiser, in a study of the triplet excited state chemistry of another substrate. Following the unexpected isolation of 1,1-diphenylethylene, we investigated the photochemistry of benzophenone in 2-methylpropan-2-ol in the absence of added quencher. We have isolated a product which decomposes to 1,1-diphenylethylene under very mild conditions. Our experience has prompted us to alert other workers to this complicating factor which may arise with this sensitiser-solvent system.

Irradiation (Pyrex-filtered light from a Hanovia 250-watt medium pressure mercury vapour lamp) of a solution of benzophenone (500 mg) in 2-methylpropan-2-ol (190 ml) for 2.5 h led to formation of benzpinacol, as previously reported by others,[2] and complete reaction of benzophenone. Removal of the solvent followed by chromatography of the residual material afforded a white solid (m.p. 118 °C; 26%) which was identified as 1,1-diphenyl-3-methylbutan-1,3-diol (I), identical with an authentic specimen.[3]

The diol (I) readily underwent fragmentation at room temperature to 1,1-diphenylethylene and acetone[4] when dissolved in methanol containing a trace of sulphuric acid. Our initial isolation of 1,1-diphenylethylene presumably resulted from fragmentation of diol (I) during work-up of the reaction mixture.

The diol (I) may be formed *via* initial abstraction of a methyl hydrogen atom from 2-methylpropan-2-ol by triplet excited benzophenone to yield the radicals (II) and (III) which then couple:

$$Ph_2CO + Me_3C.OH \xrightarrow{h\nu} \underset{(II)}{Ph_2\dot{C}OH} + \underset{(III)}{\dot{C}H_2CMe_2OH}$$

$$2\ (II) \longrightarrow Ph_2C(OH)CPh_2OH$$

$$(II) + (III) \longrightarrow \underset{(I)}{Ph_2C(OH)CH_2CMe_2OH}$$

$$(I) \xrightarrow{H^+} Ph_2C{=}CH_2 + Me_2CO$$

The isolation of diol (I) is consistent with the occurrence of hydrogen abstraction from a methyl group of 2-methylpropan-2-ol rather than from the hydroxyl group as has recently been suggested[5] for abstraction by an excited β-cyanocyclohexenone. The observed product, arising from addition of a methyl radical to the β-cyanocyclohexenone,[5] is most likely formed following scission of radical (III) to yield acetone enol and a methyl radical.

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