Photochemical Reactions of Acetone with 2,3-Dimethylbut-2-ene

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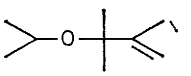
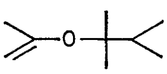
Summary U.v. irradiation of a mixture of acetone and 2,3-dimethylbut-2-ene gives products arising from 1,5-hydrogen atom transfer [(**1**) and (**2**)] and ring closure (**3**) of a biradical intermediate.

The photochemical reactions of carbonyl compounds with olefins have been much studied;[1,2] for ketones, the observed products are generally those arising from cycloaddition, hydrogen abstraction, or triplet energy transfer from ketone to olefin. However, the photochemical reactions of an aliphatic ketone with a simple acyclic olefin have been infrequently investigated.[3,4] We report the photoreactions of acetone with 2,3-dimethylbut-2-ene.



(1)



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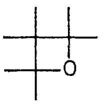
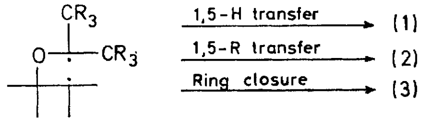


(3)

A deoxygenated solution of 2,3-dimethylbut-2-ene (15 g) and acetone (80 g) in quartz apparatus was irradiated by a medium pressure mercury arc for 13 h. G.l.c. showed the formation of seven major primary photoproducts, separated by preparative g.l.c. and identified as the unsaturated ethers (**1**) and (**2**), oxetan (**3**), two C_9-unsaturated alcohols, and two C_{12}-hydrocarbons.† The same photoproducts were formed in Pyrex apparatus with n-hexane as solvent, and the quantum yields of formation of compounds (**1**)—(**3**) are shown in the Table.

The formation of unsaturated ethers (**1**) and (**2**) along with the oxetan (**3**) suggests the intermediacy of a triplet 1,4-biradical (**4**) in their formation,‡ as shown in the Scheme.



(4) a; R=H
b; R=D

Scheme

Such hydrogen transfer in a 1,4-biradical derived from the photoaddition of a ketone to an olefin has not been observed previously in the reactions of simple ketones, although an α-diketone (biacetyl) on photolysis with acyclic olefins gave allyl ethers analogous to (**1**) in competition with oxetan photocycloaddition products.[5]

Table. *Quantum yields*[a,b] *in the photoreactions of acetone with* 2,3-*dimethylbut*-2-*ene*

	Products		
Ketone	(**1**)	(**2**)	(**3**)
Me_2CO	0·013	0·028	0·042
CD_3COCD_3	0·016	0·018	0·051

[a] Quantum yield values are estimated ±10%; hexan-2-one was used as actinometer.[6] [b] 290—330 nm absorption, *ca.* 45°, acetone (1·02M) and 2,3-dimethylbut-2-ene (0·84M) in n-hexane solvent.

Irradiation of a mixture of CD_3COCD_3 with 2,3-dimethylbut-2-ene led to the formation of similar products, but it was noticeable that the quantum yield of (**2**) decreased, whilst the other products were formed in slightly greater quantum yields (see Table). Thus, formation of (**2**), involving hydrogen abstraction from a methyl group in (**4a**) is hindered by the substitution of trideuteriomethyl groups in (**4b**), indicating an isotope effect (k_H/k_D 1·6) on abstraction.

It is difficult to reconcile the present results with those of Abrahamson and co-workers,[3] in which it is claimed that irradiation of CD_3COCD_3 and 2,3-dimethylbut-2-ene leads only to the formation of acetone and [$^2H_6$]-2,3-dimethylbut-2-ene (quantum yield, $\Phi = 0{\cdot}05$): such a result required the postulation of an unprecedented triplet (n,σ^*) oxetan intermediate. In the present work, irradiations of CD_3COCD_3 and 2,3-dimethylbut-2-ene under similar conditions allowed the formation of the seven products to be followed by n.m.r. spectroscopy, but acetone formation could not be established ($\Phi \leqslant 0{\cdot}005$). In conclusion, the evidence for a triplet (n,σ^*) oxetan intermediate in ketone–olefin photoreactions should be re-examined.

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† Compounds were characterised from n.m.r., i.r. and mass spectra, and elemental analysis.

‡ Experiments using penta-1,3-diene and 2,3-dimethylbuta-1,3-diene as quenchers suggest that reaction occurs predominantly from the triplet state (with formation of (**1**)—(**3**) being quenched at similar rates), in contrast with the singlet complex responsible for alkanal/olefin photochemistry.[2c] Other experiments showed that (**3**) was stable to the photoreaction conditions.

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