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

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U.v. irradiation of acetone in the presence of 2,3-dimethylbut-2-ene (1) leads to the formation in reasonable quantum yields of seven primary photoproducts: two unsaturated ethers [(2) and (3)], an oxetan (4), two unsaturated alcohols [(5) and (6)], and two hydrocarbons [(7) and (8)]. Prolonged irradiation yields a secondary photoproduct, the oxetan (9). Irradiation of hexadeuterioacetone and (1) gives the deuteriated 1:1 adducts (2a)—(6a). The unsaturated ethers (2) and (3) and the oxetan (4) appear to arise from a 1,4-diradical intermediate (15) by competing hydrogen transfers and ring closure, respectively. The results of quenching experiments suggest that both singlet and triplet excited states of acetone are involved in the formation of the adducts (2)—(6).

THERE has been much interest recently in the photocycloaddition of carbonyl compounds to olefins to give oxetans.[1,2] Aliphatic ketones such as acetone have been found to react photochemically with electron-rich olefins (*e.g.* 1-methoxybut-1-enes) to give non-stereospecific cycloaddition products. It is believed the reaction involves 1,4-diradical intermediates arising from both the singlet and triplet excited states of acetone.[3] In contrast, electron-deficient olefins add stereospecifically *via* the singlet ketone excited state.[4,5] As far as simple alkyl-substituted olefins are concerned, most work has involved cyclic olefins: additions of acetone to cyclobutene,[6] cyclopentene,[7] and cyclohexene [8] have been reported. In later mechanistic studies, acetone has been shown to undergo photocycloaddition to cyclooctene by a triplet mechanism,[9] and triplet acetone reacts photochemically with cyclohexene to give an oxetan as one of the seven isolated products.[10] In contrast, the $\gamma\delta$-unsaturated ketone, hept-5-en-2-one, undergoes an intramolecular cycloaddition, apparently from a singlet state.[11] There has been less study of additions to acyclic olefins, and it has generally been assumed that triplet energy transfer from ketone to olefin is the predominant pathway.[1] Aliphatic ketones have therefore been used as photosensitisers of olefin isomerisation.[12,13] However, Abrahamson and his coworkers have claimed that such energy transfer can occur through a triplet (n,σ^*) oxetan species, since they observed isotopic exchange between [$^2H_6$]acetone and 2,3-dimethylbut-2-ene.[14] The present paper examines in more detail the photoproducts arising from u.v. irradiation of acetone and of [$^2H_6$]acetone in solution in the presence of 2,3-dimethylbut-2-ene.[15]

RESULTS AND DISCUSSION

Photoproducts.—A preparative u.v. photoreaction of acetone in solution in the presence of 2,3-dimethylbut-

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[1] D. R. Arnold, *Adv. Photochem.*, 1968, **6**, 301.

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[3] N. J. Turro and P. A. Wriede, *J. Amer. Chem. Soc.*, 1970, **92**, 320.

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[5] J. A. Barltrop and H. A. J. Carless, *J. Amer. Chem. Soc.*, 1972, **94**, 1951.

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[11] S. R. Kurowsky and H. Morrison, *J. Amer. Chem. Soc.*, 1972, **94**, 507.

[12] R. F. Borkman and D. R. Kearns, *J. Amer. Chem. Soc.*, 1966, **88**, 3467.

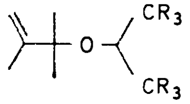
[13] R. B. Cundall and A. S. Davies, *Proc. Roy. Soc.*, 1966, *A*, **290**, 563.

[14] (*a*) S. M. Japar, M. Pomerantz, and E. W. Abrahamson, *Chem. Phys. Letters*, 1968, **2**, 137; (*b*) S. M. Japar, J. A. Davidson, and E. W. Abrahamson, *J. Phys. Chem.*, 1972, **76**, 478.

[15] H. A. J. Carless, *J.C.S. Chem. Comm.*, 1973, 316.

2-ene (1) led to the formation of eight products, detected by g.l.c. analysis. These were separated by preparative g.l.c., and assigned the structures (2)—(9). Quantitative g.l.c. showed the following approximate yields, based on consumed olefin: (2) 8%; (3) 8%; (4) 21%; (5) 5%; (6) 7%; (7) 5%; (8) 2·5%; (9) 5%.

Compound (2) was assigned the allylic ether structure on the basis of its i.r. (=CH_2 at 3100 and 900 cm^{-1}) and n.m.r. spectra (isopropenyl and isopropoxy-groups, and a six-proton singlet at τ 8·75). Mass spectra (weak molecular ion, *m/e* 142) and elemental analytical figures were consistent with this formulation. Compound (3) was identified as the isomeric vinyl ether, by its i.r. (=CH_2 at 3140 cm^{-1}) and n.m.r. spectra (isopropenyl CH_2=C–O signal at τ 6·03, and an isopropyl group, confirmed by double-resonance experiments).



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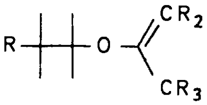
(2a) R = D



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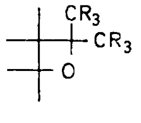

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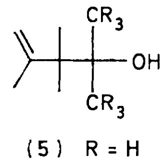
(4a) R = D



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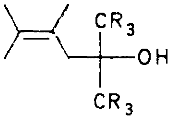

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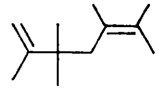
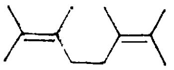
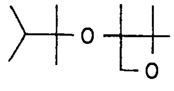


(7)

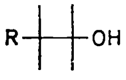


(8)

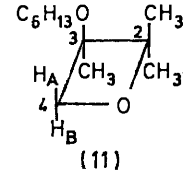


(9)

The compound slowly decomposed (more rapidly on acidic hydrolysis) to give acetone and 2,3-dimethylbutan-2-ol (10), detected by g.l.c. and n.m.r. spectra. Compound (4) was assigned the oxetan structure on the basis of its i.r. (no carbonyl or unsaturated group, but a strong band at 950 cm^{-1})[16] and its simple n.m.r. spectrum [singlets at τ 8·77 (12H) and 8·92 (6H)]. Elemental analytical figures suggested a 1 : 1 adduct of acetone and (1), but the mass spectrum did not show a molecular ion—instead the predominant peaks were due to initial ring cleavage (*m/e* 84 and 58) and subsequent fragmentation, which is common for the oxetan ring.[8,17]



(10) R = H
(10a) R = D



(11)

The structures of the unsaturated alcohols (5) and (6) were apparent from examination and comparison of their n.m.r. spectra. The alcohol (5) showed terminal methylene absorption in the i.r. and n.m.r. spectra, and only one CH_3–C= signal in the n.m.r. spectrum; (6) showed no unsaturation (i.r.), but signals for three CH_3–C= groups and an allylic methylene in the n.m.r. spectrum. Compounds (7) and (8) were apparently hydrocarbons, with fairly simple i.r. spectra. Again, (7) showed the unsaturation of a terminal methylene in the i.r. and n.m.r. spectra, whereas (8) did not. Compound (8)[18] showed a simple n.m.r. spectrum, suggesting a symmetrical structure. Compound (9) gave analytical figures corresponding to a 2 : 1 adduct of acetone and (1), the i.r. spectrum again suggesting an oxetan structure (strong band at 990 cm^{-1}). The n.m.r. spectrum showed a pair of coupled protons (*J* 5·7 Hz) at τ 5·48 and 6·04, assigned to the oxetan C-4 protons, isopropyl signals, a three-proton singlet at τ 8·46 assigned to the oxetan 3-Me, and four other non-equivalent methyl signals. The oxetan C-4 proton, H_A, adjacent to the oxygen atom at C-3 might be expected to be deshielded compared with H_B, and therefore assignable to the τ 5·48 signal [see (11)]. In agreement with this assignment, the H_A signal showed a long-range coupling (*J* 1·0 Hz) to the τ 8·46 methyl protons of the 3-methyl group, as is possible for a W-like four-bond arrangement.[19] Identification as a 3- rather than a 4-alkoxy-oxetan is reasoned on the basis of the chemical shift of the oxetan ring protons (C-4 protons absorb at τ 4·9—6·2; *cf.* the alternative possibility for oxetan ring C-3 protons, τ 6·4—8·0).[20,21] The mass spectrum of the oxetan (9) did not show a molecular ion, but showed several smaller fragments consistent with the structure (9); the main fragmentation pathway appeared to involve fission at the oxetan C(3)–O (*m/e* 99) and C(3)O–C bonds (*m/e* 115 and 85).

Irradiation, under similar conditions, of hexadeuterioacetone and (1) gave products with g.l.c. retention times identical with those of the products arising from acetone and (1). Apart from (9), these were isolated and examined by i.r. and n.m.r. spectroscopy. Comparison with the spectra of non-deuteriated products allowed the

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[16] G. M. Barrow and S. Searles, *J. Amer. Chem. Soc.*, 1953, **75**, 1175.

[17] E. J. Gallegos and R. W. Kiser, *J. Phys. Chem.*, 1962, **66**, 136.

[18] T. S. Cantrell, *J. Amer. Chem. Soc.*, 1973, **95**, 2714.

[19] S. Sternhell, *Quart. Rev.*, 1969, **23**, 236.

[20] D. R. Arnold, R. L. Hinman, and A. H. Glick, *Tetrahedron Letters*, 1964, 1425.

[21] J. A. Barltrop and H. A. J. Carless, *J. Amer. Chem. Soc.*, 1972, **94**, 8761.

positions of deuterium incorporation to be determined, as shown in formulae (2a)—(6a). In the n.m.r. spectrum of (2a), the isopropyl signals of (2) had been replaced by a multiplet (1H) at τ 6·37, assigned to $OCH(CD_3)_2$. In that of (3a), the isopropenyl signal of (3) had disappeared, and the isopropyl signals (J 7 Hz) had been replaced by a six-proton 1 : 1 : 1 triplet (J 1 Hz) assigned to $(CH_3)_2CD$. Like (3), (3a) was susceptible to hydrolysis, and a sample of (10a) was isolated in which the isopropyl CH proton of (10) had been replaced by a deuterium atom (to give a 1 : 1 : 1 triplet, J 1 Hz, 6H, at τ 9·11).

Quantum Yields.—The same photoproducts (2)—(9) were formed in either quartz or Pyrex apparatus, and the quantum yields of formation of (2)—(8) in n-hexane as solvent, under nitrogen, are shown in the Table for two different concentrations of (1). The Table also shows the quantum yields of formation of the (deuteriated) products from [$^2H_6$]acetone and (1). Propan-2-ol formation was tested for, but not confirmed, and an upper limit of $\Phi = 0·03$ was set on its formation.

Quantum yields of acetone–2,3-dimethylbut-2-ene photoreactions [a,b]

Ketone	[Olefin]/ M	Product (2)	(3)	(4)	(5)	(6)	(7)	(8)
Me_2CO	0·84	0·013	0·028	0·042	0·015	0·031	0·016	0·018
	1·56	0·015	0·033	0·046	0·013	0·029	0·020	0·022
[$^2H_6$]-Me_2CO	0·84	0·016	0·018	0·051	0·019	0·041	0·022	0·022

[a] Quantum yield values ±10%. Conditions were: acetone (1·02M) in n-hexane, 290—330 nm absorption, *ca.* 45°, hexan-2-one actinometry. [b] Quantum yields of propan-2-ol formation <0·03.

Reaction Mechanisms.—The oxetan (9) appeared to be a secondary photochemical product, arising by attack of photoexcited acetone on the first-formed vinyl ether (3).[3,22] Thus, the ratio of (9) to the total photoproducts increased with time, in contrast with the other products (2)—(8). In fact, the formation of (9) was not observed until an appreciable concentration of (3) had been formed in solution. Isolation of a sample of (3) and irradiation of it in solution in acetone, followed by g.l.c. analysis, gave a major peak with the same retention time as (9). Rapid and efficient photochemical formation of an oxetan from acetone and a vinyl ether might be anticipated in view of the high rate constant for complexation of vinyl ethers with photoexcited alkyl ketones.[3] In several other known examples, the 3-alkoxyoxetan predominates over the 2-(or 4-)alkoxy-isomer,[23] and in the present case only the 3-alkoxyoxetan was detected.

Although the proportions of products (2)—(8) were constant in the early stages of reaction, there was the possibility that some of the observed photoproducts arose from decomposition of the oxetan (4), perhaps photosensitised by acetone, as in the photosensitised decomposition of 1,2-dioxetans.[24] Experiments were carried out to test the photostability of the oxetan (4): the oxetan was stable on irradiation in acetone–n-hexane under the conditions used in the measurement of quantum yields. It was therefore not responsible for the formation of the other observed products.

The unsaturated alcohols (5) and (6) and hydrocarbons (7) and (8) are products of the type often observed in the photoreactions of ketones with olefins,[1,8,10] and are believed to arise by hydrogen abstraction of the excited (usually triplet) ketone from the olefin. Abstraction in the present case produces a ketyl radical (12) and an allylic radical [represented by (13) $\longleftrightarrow$ (14)], as shown in Scheme 1. Radical recombination within the solvent cage then leads to (5) and (6), and dimerisation of the alkenyl radicals leads to (7) and (8),

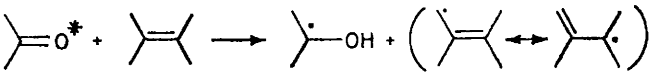
i.e.

$$(12) + (14) \longrightarrow (5)$$

$$(12) + (13) \longrightarrow (6)$$

$$(13) + (14) \longrightarrow (7)$$

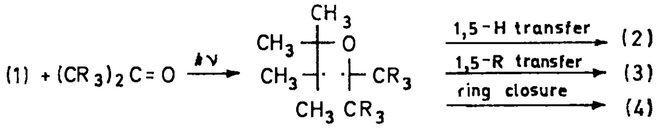
$$(13) + (13) \longrightarrow (8)$$



(1) (12) (13) (14)

SCHEME 1

Diradicals have often been postulated as intermediates in the formation of oxetans from carbonyl compounds and olefins,[1] and it seemed reasonable that the ethers (2)—(4) in the present case were arising from a common intermediate (15), as shown in Scheme 2. Thus, the unsaturated ethers (2) and (3) could arise from the two possible 1,5-hydrogen atom transfers in the diradical intermediate (15; R = H). In support of this hypothesis, the photoproducts from a hexadeuterioacetone–(1) photoreaction were (2a) and (3a), with deuterium incorporated at the positions expected on the basis of the intermediacy of the diradical (15; R = D). These facts imply that the hydrogen transfer reactions compete with ring closure of the diradical, although such transfers have not been observed previously in the photocycloaddition reactions of simple ketones. However, biacetyl has been observed to give allyl ethers [*e.g.* (16)] analogous to (2) in its photoreaction with acyclic olefins;[25] and



(15) R = H or D

SCHEME 2

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[22] N. J. Turro and P. A. Wriede, *J. Org. Chem.*, 1969, **34**, 3562.

[23] S. H. Schroeter and C. M. Orlando, *J. Org. Chem.*, 1969, **34**, 1181.

[24] N. J. Turro and P. Lechtken, *Pure Appl. Chem.*, 1973, **33**, 363; P. Lechtken, A. Yekta, and N. J. Turro, *J. Amer. Chem. Soc.*, 1973, **95**, 3027.

[25] H. S. Ryang, K. Shima, and H. Sakurai, *J. Amer. Chem. Soc.*, 1971, **93**, 5270; *J. Org. Chem.*, 1973, **38**, 2860.

recently benzoic acid has been found to react photochemically with (1) to give a benzoate ester [18] (17) which is mechanistically related to the vinyl ether (3), but

(16)

(17)

formed by hydrogen abstraction from an O–H instead of a C–H bond. The diradical intermediate (15) must have a sufficiently long lifetime for bond rotations to occur before ring closure, thus allowing the molecule to take up suitable conformations for the transfer of a hydrogen atom *via* a six-membered transition state. In support of the idea that the diradical intermediate does have a finite existence, the related diradical derived from the photoaddition of acetone to either *cis*- or *trans*-but-2-ene gives a mixture of *cis*- and *trans*-oxetan products,[26] implying a diradical lifetime sufficient at least for bond rotations to occur competitively with ring closure.

The data in the Table allow the efficiency of formation of products (2)—(4) derived from acetone to be compared with those (2a)—(4a) derived from hexadeuterioacetone. It is noticeable that the quantum yield of vinyl ether [(3) or (3a)] was less from the irradiation of [$^2H_6$]acetone–(1) mixtures, whereas the other products were formed in slightly greater quantum yields. That is, formation of the vinyl ether, involving hydrogen abstraction from a methyl group of the original acetone, is hindered by replacing the methyl groups by trideuteriomethyl groups, indicating an isotope effect on abstraction. If it is assumed that the efficiency of formation of the 1,4-diradical (15) is the same for acetone–(1) as for [$^2H_6$]acetone–(1) systems (since the total quantum yield of diradical-derived products is *ca.* 0·085 in each case), it is possible to calculate an isotope effect for the formation of (3) ($k_H/k_D = 1{\cdot}6 \pm 0{\cdot}3$). Other values for rate constants of hydrogen *vs.* deuterium abstraction involving 1,4-diradicals have been obtained, ranging from 1·7 for formation of the γ-hydroxy-γ-phenylbutyrophenone-derived diradical,[27] to 2·7 and 6·7 for singlet and triplet hexan-2-one-derived diradicals.[28]

As mentioned previously, Abrahamson and his coworkers investigated the photoreaction of [$^2H_6$]acetone with 2,3-dimethylbut-2-ene (1).[14] They observed, by n.m.r. and mass spectral analysis, an isotopic ' molecular exchange ' reaction in degassed solutions to give acetone and [$^2H_6$]-2,3-dimethylbut-2-ene, with quantum yield, $\Phi = 0{\cdot}05$. No other products were detected on irradiation at 313 nm by n.m.r., mass spectral, or g.l.c. analysis. An experiment using light of wavelength greater than 250 nm and a larger extent of conversion allowed the detection of a small amount of a compound tentatively assigned the oxetan structure (4a). The present experiments do not agree with these results. Thus, a mixture of [$^2H_6$]acetone and (1) in a 10 : 1 molar ratio was degassed and irradiated in an n.m.r. tube, with light of wavelength greater than 300 nm; at intervals the tube was removed from the apparatus, and the n.m.r. spectrum was taken. It was possible to see peaks arising from photoproducts, and these were at the τ values of products (2a), (3a), (4a), (7), and (10a); yet acetone was not detected. Finally, the tube was opened and the contents were analysed by g.l.c., which showed products with the retention times corresponding to (2)—(8) and (10). Actinometry showed that the quantum yield of oxetan (4a) was $0{\cdot}03 \pm 0{\cdot}02$, and that the maximum possible quantum yield of formation of acetone was 0·005. A second experiment, using a 1 : 1 molar ratio and slightly different conditions, gave similar products but suggested an even lower maximum quantum yield of acetone production, $\Phi \leqslant 0{\cdot}002$.

Certainly the present results do not support the existence of the novel triplet (n,σ^*) intermediate suggested by Japar, Pomerantz, and Abrahamson.[14a] No complete explanation can be given for the difference between Abrahamson's results and those of the present author. The two sets of experiments were conducted under comparable conditions (degassed solutions, similar molar ratio of reactants, irradiation wavelength, and temperature) and it seems unlikely that small differences in conditions would cause such completely different observations. However, mass spectral analysis is not well suited for distinguishing the carbonyl–olefin reactions of cycloaddition and ' molecular exchange,' since the major mass spectral fragmentation pathway of the oxetan product is cleavage to give carbonyl and olefin, and these are also the products of the ' molecular exchange ' reaction. Observation of the isotopic exchange reaction by mass spectrometry does not necessarily imply that the carbonyl and olefinic fragments were formed in the photochemical step; they could have arisen by mass spectral fragmentation of a photochemically formed (but undetected) oxetan. Such arguments might help to explain a serious discrepancy between the work of Abrahamson's group [14] and that of Yang's group,[29] concerning the acetaldehyde–but-2-ene photoreaction. Abrahamson has reported that the [$^2H_4$]-acetaldehyde–*cis*-but-2-ene system undergoes ' molecular exchange ' ($\Phi = 0{\cdot}009$) and oxetan formation ($\Phi = 0{\cdot}0035$) as well as *cis*- to *trans*-but-2-ene isomerisation ($\Phi = 0{\cdot}023$).[14b] Yang has reported that, in the isotopically related acetaldehyde–*cis*-but-2-ene system, the quantum yields of oxetan formation are $\Phi = 0{\cdot}16$, and

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[26] H. A. J. Carless, *Tetrahedron Letters*, 1973, 3173.

[27] F. D. Lewis, *J. Amer. Chem. Soc.*, 1970, **92**, 5602.

[28] D. R. Coulson and N. C. Yang, *J. Amer. Chem. Soc.*, 1966, **88**, 4511.

[29] N. C. Yang and W. Eisenhardt, *J. Amer. Chem. Soc.*, 1971, **93**, 1277.

there is no detectable *cis-* to *trans*-isomerisation of the starting olefin.[29,30]

It has recently been shown that in photocycloadditions of acetone to certain olefins, there is a strong dependence of the efficiency of formation of oxetan on solvent. Thus, the chemical yields of oxetan from acetone and 3,4,6-tri-*O*-acetyl-D-glucal were greatly increased by the addition of small amounts of propan-2-ol.[31] In an attempt to see if the acetone–(1) system displayed such behaviour, an irradiation was performed in the presence of *ca.* 5% of propan-2-ol. However, the yields of photoproducts (2)—(8) appeared completely unaffected by the presence of the propan-2-ol, and so such solvent effects do not seem important in the present instance.

Irradiations were generally carried out with oxygen-free solutions, prepared by degassing or by passing nitrogen through the solution. It is unlikely, therefore, that any of the photoproducts arose from the acetone-sensitised production of singlet molecular oxygen ($^1\Delta_g$).[32] Essentially similar results were obtained even when the solutions were irradiated in the presence of air; the main difference (by g.l.c. analysis) was the formation of an additional photoproduct. No attempt was made to isolate this product, but it was most likely the allylic hydroperoxide known to be formed efficiently by the photosensitised irradiation of the olefin (1) in the presence of oxygen.[33]

The common mechanism for oxetan formation involves attack of excited ketone on ground-state olefin.[1] However, examples have been found in which oxetan formation has been shown to occur by the unusual mechanism of attack of triplet olefin on ground-state ketone.[34] Evidence that this triplet olefin mechanism does not apply to the present instance was obtained from the following experiment. A solution of acetone and (1) in n-hexane was irradiated at 254 nm in the presence of acetophenone as a photosensitiser, under conditions in which the acetophenone absorbed about 97% of the incident light. Simultaneously, a solution of acetone and (1) was irradiated without sensitiser. G.l.c. analysis showed that no significant amounts of products (2)—(4) were formed in the sensitised reaction (*ca.* 2% of yields in the unsensitised case), nor were compounds (5) and (6) observed (<2%), but compounds (7) and (8) were formed (*ca.* 35%). The acetophenone-sensitised isomerisation of olefins is an efficient process,[35] and so the formation of olefin triplets should occur in both the acetophenone-sensitised and the unsensitised experiments. However, products (2)—(6) are hardly formed on sensitisation, so it is unlikely that the triplet state of the olefin can be responsible for their formation. Nevertheless, it is thought that a diradical intermediate of sensitiser and olefin plays a part in the mechanism of olefin isomerisation;[35] if this is the only mechanism for isomerisation, and does not lead to the triplet olefin, then the present experiment does not conclusively disprove the triplet olefin mechanism. The formation of hydrocarbons (7) and (8) in the sensitised reaction is not surprising, since they can arise by hydrogen abstraction of excited acetophenone from (1), followed by radical combination reactions. The small amounts of (2)—(6) which are formed in the sensitised reaction could arise by competing direct absorption of light by the acetone present, or by inefficient endothermic triplet energy transfer from acetophenone (triplet energy, E_T *ca.* 310 kJ mol^{-1})[36] to acetone (E_T *ca.* 335 kJ mol^{-1}).[37] The same photoproducts (2)—(9) were also detected on irradiation in Pyrex apparatus, conditions which make it improbable that their formation could involve singlet excited olefin, because there is then insufficient excitation energy available.

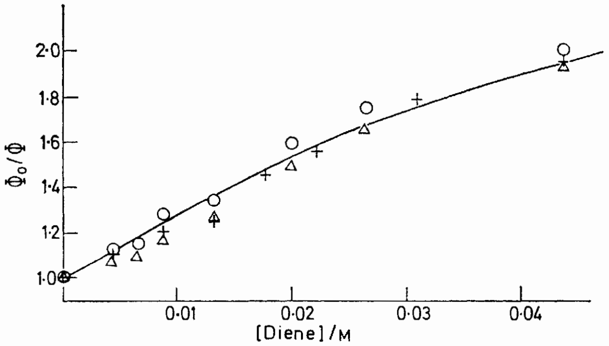

FIGURE 1 Stern–Volmer quenching plot of (relative quantum yield)$^{-1}$ of products (2)—(4) against 2,3-dimethylbuta-1,3-diene quencher concentration; △, allyl ether (2); +, vinyl ether (3); ○, oxetan (4)

A series of quenching experiments was carried out, to see whether product formation arose from the ketone singlet or triplet excited state. The conjugated diene 2,3-dimethylbuta-1,3-diene was used as a triplet quencher; the relative quantum yields of product formation for each of the products (2)—(8) were determined at several different quencher concentrations. The resulting Stern–Volmer plots of (relative quantum yield)$^{-1}$ against quencher molarity are shown in Figures 1—3. Penta-1,3-diene gave qualitatively similar results when used as a quencher, but the production of several pentadiene dimers[38] hindered the g.l.c. analysis of the mixtures. Triplet ketones are efficiently quenched, at up to diffusion-controlled rates, by conjugated dienes.[39]

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[30] N. C. Yang, M. Kimura, and W. Eisenhardt, *J. Amer. Chem. Soc.*, 1973, **95**, 5058.

[31] K. Matsuura, Y. Araki, and Y. Ishido, *Bull. Chem. Soc. Japan*, 1972, **45**, 3496; K. Matsuura, Y. Araki, Y. Ishido, A. Murai, and K. Kushida, *Carbohydrate Res.*, 1973, **29**, 459.

[32] D. R. Kearns, *Chem. Rev.*, 1971, **71**, 395.

[33] G. O. Schenck and K. H. Schulte-Elte, *Annalen*, 1958, **618**, 185; E. C. Blossey, D. C. Neckers, A. L. Thayer, and A. P. Schaap, *J. Amer. Chem. Soc.*, 1973, **95**, 5820.

[34] C. DeBoer, *Tetrahedron Letters*, 1971, 4977, and references therein.

[35] J. Saltiel, K. R. Neuberger, and M. Wrighton, *J. Amer. Chem. Soc.*, 1969, **91**, 3658.

[36] W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, 1964, **86**, 4537.

[37] R. F. Borkman and D. R. Kearns, *J. Chem. Phys.*, 1966, **44**, 945.

[38] G. S. Hammond, N. J. Turro, and R. S. H. Liu, *J. Org. Chem.*, 1963, **28**, 3297.

[39] P. J. Wagner and G. S. Hammond, *Adv. Photochem.*, 1968, **5**, 21.

It was therefore obvious that the products (2)—(8) arose predominantly from a triplet state, because the major part of each product was quenchable by low concentrations of added diene. However, there were clear differences in both the extent and the rapidity of this quenching, and the products behaved according to one of three classes, (i)—(iii).

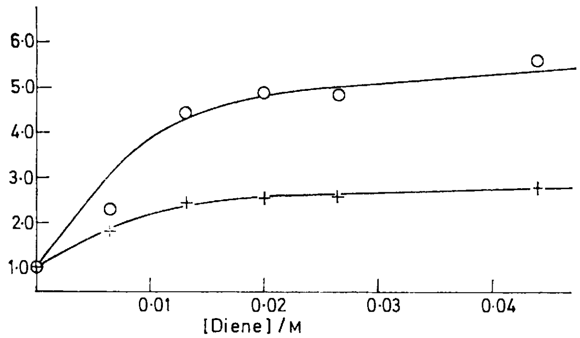

FIGURE 2 Stern–Volmer plot of quenching of products (5) and (6); ○, alcohol (5); +, alcohol (6)

(i) *Products* (2)—(4) (*Figure* 1). The ethers (2)—(4) were all equally quenched, within experimental error, as might be expected if they all arose from a common intermediate. The Stern–Volmer plots were not linear, and appeared to level off at higher quencher concentrations. Such behaviour arises when products are formed by both a singlet (unquenchable) and a triplet (quenchable) mechanism.[40] At higher concentrations of diene, about 25% of the reaction appeared to be coming from an unquenchable state. After subtraction of this unquenchable component, the Stern–Volmer slopes for the remaining quenchable component of reaction were 38 ± 6, 40 ± 8, and 45 ± 8 l mol^{-1}, for (2), (3), and (4) respectively.

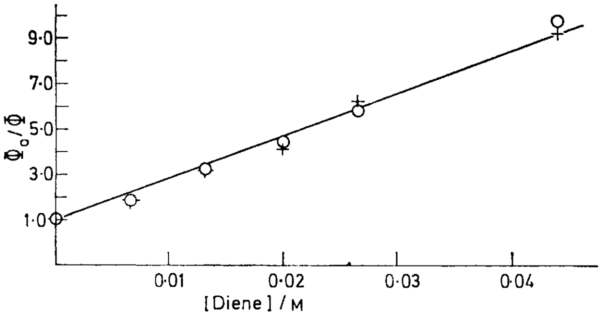

FIGURE 3 Stern–Volmer plot of quenching of products (7) and (8); ○, hydrocarbon (7); +, hydrocarbon (8)

(ii) *Products* (5) *and* (6) (*Figure* 2). Again, the plots for the two alcohols (5) and (6) were non-linear, but in this case the two products were not quenched to the same extent. At higher concentrations of diene, about 10% of the reaction to yield (5) arose from an unquenchable state, whereas this unquenchable fraction was about 25% for alcohol (6). After allowance for the unquenchable component, the corrected Stern–Volmer slopes were 320 ± 130 for (5) and 205 ± 60 l mol^{-1} for (6).

(iii) *Products* (7) *and* (8) (*Figure* 3). Not only did these hydrocarbons appear equally quenched within experimental error, but the plots were linear. The products (7) and (8) arose almost entirely by a triplet mechanism, with certainly less than 3% of an unquenchable component. The Stern–Volmer slope was 185 ± 25 l mol^{-1}.

If we consider the possible experimental errors in these quenching experiments, the slopes of the corrected Stern–Volmer plots therefore fall into two groups: (*a*) products (2)—(4), having slopes *ca.* 40 l mol^{-1}, and (*b*) products (5)—(8), with slopes *ca.* 200 l mol^{-1}; the significance of these figures is discussed later.

Conjugated dienes also quench the singlet excited state of ketones,[21,41,42] although generally at a rate less than diffusion-controlled. At higher concentrations of diene, some singlet quenching may be significant, since the rate constant for acetone singlet quenching by (1) is $1{\cdot}1 \times 10^{8}$ l mol^{-1} s^{-1},[42] and for that by 2,3-dimethylbuta-1,3-diene is $8{\cdot}5 \times 10^{8}$ l mol^{-1} s^{-1},[21] if we assume a singlet lifetime for acetone of 2×10^{-9} s.[4] There is no evidence that this singlet quenching of acetone is important up to 0·044M-diene, since the Stern–Volmer quenching plot for products (7) and (8) appears linear to this concentration (Figure 3). Nevertheless, from the known rate of intersystem crossing and the singlet quenching rate constants for (1) and 2,3-dimethylbuta-1,3-diene, it can be calculated that *ca.* 6% of the acetone singlets are expected to be quenched at 0·044M-diene, and the importance of acetone singlet quenching increases at higher concentrations of quencher.

It is hard to analyse the complex quenching situation quantitatively, because of the likelihood of singlet as well as triplet quenching. It appears that reactions to give (2)—(6) arise from two excited states (acetone singlet and triplet) which are both quenchable at different rates by the diene. Generalised forms of the Stern–Volmer equation have been derived which cover the case of product formation from singlet and triplet reactive states, when the quencher deactivates both singlet and triplet states.[43] The limited precision (±10%) and quencher concentration range of the present results do not make the application of these general equations feasible.

The diene quenches the reactions which give (2)—(4) and (5)—(8) at different rates, so that the quenchable products cannot all simply arise from triplet acetone. A mechanism which has been proposed for certain other oxetan-forming reactions involves complexation of triplet ketone with olefin, leading to a diradical which

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[40] T. R. Evans, in ' Technique of Organic Chemistry,' vol. XIV, eds. P. A. Leermakers and A. Weissberger, Interscience, New York, 1969, p. 338.

[41] F. S. Wettack, G. D. Renkes, M. G. Rockley, N. J. Turro, and J. C. Dalton, *J. Amer. Chem. Soc.*, 1970, **92**, 1793.

[42] N. C. Yang, M. H. Hui, and S. A. Bellard, *J. Amer. Chem. Soc.* 1971, **93**, 4056.

[43] J. C. Dalton and N. J. Turro, *Mol. Photochem.*, 1970, **2**, 133; P. J. Wagner, *ibid.*, 1971, **3**, 23; J. E. Gano, *ibid.*, 1972, **4**, 527.

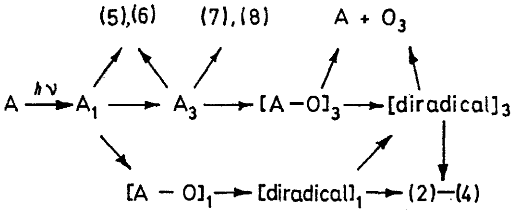
subsequently yields an oxetan.[44] This mechanism as such is not entirely consistent with the present data, because the ethers (2)—(4) arise from a less easily quenchable state than the products (5)—(8), and therefore cannot be arising from a state produced after the formation of triplet acetone. To rationalise the present results, two alternative explanations could be advanced.

(i) Triplet acetone is the precursor of the products (2)—(8). The greater quenching of dimers and unsaturated alcohols (5)—(8) would have to be due to competing chemical reaction of the radical [(13) $\longleftrightarrow$ (14)] with conjugated diene. It may be relevant that methyl radicals do add to olefins and dienes, and reaction with 2,3-dimethylbuta-1,3-diene is very favourable.[45] According to this mechanism, the rate of complexation between triplet acetone and olefin would be *ca.* $2{\cdot}5 \times 10^8$ l mol^{-1} s^{-1}, if we assume a triplet quenching rate by the conjugated diene of 10^{10} l mol^{-1} s^{-1} in hexane,[46] and the Stern–Volmer slope of *ca.* 40 l mol^{-1}.

(ii) The diradical intermediate responsible for (2)—(4) is quenched by diene, but is largely formed by some pathway which avoids the direct involvement of triplet acetone. Acetone triplet is the precursor of (5)—(8), and is quenched by diene. The rate constant for formation of (5)—(8) from the triplet state is the rate constant for hydrogen abstraction by acetone from the olefin, and is *ca.* 5×10^7 l mol^{-1} s^{-1}, from the slope of the Stern–Volmer plot (*cf.* abstraction of acetone from n-hexane, $k = 7 \times 10^4$ l mol^{-1} s^{-1}; from tributyltin hydride, $k = 8{\cdot}5 \times 10^8$ l mol^{-1} s^{-1}).[47] Such an indirect route to the diradical triplet might well be intersystem crossing of the singlet diradical, though there is only limited evidence from other sources to support this notion.[3] A more serious criticism of this alternative mechanism arises from the need for the diradical intermediate to be quenched by conjugated diene. If 1,4-diradicals in general could be quenched by conjugated dienes, then a photoreaction proceeding by way of a ketone triplet state and subsequent 1,4-diradical should be quenched in two ways, and would be expected to show a non-linear Stern–Volmer plot. Such conditions have not been met in the known examples of Norrish type II eliminations or cycloadditions of aromatic ketones.

An overall mechanism for the photoreactions, including intersystem crossing of the diradical, is shown in Scheme 3, where A = acetone, O = olefin, [A–O] represents an acetone–olefin complex, and the subscripts 1 and 3 refer to singlet and triplet states, respectively.

Borrell and Sedlar [10] have studied quenching of the acetone–cyclohexene photoproducts by a conjugated diene (penta-1,3-diene) and they observed Stern–Volmer slopes of *ca.* 50 l mol^{-1} for formation of an oxetan and other addition products, which suggests a similar reactivity of excited acetone towards both cyclohexene and (1). However, a value of *ca.* 10 l mol^{-1} was found for the formation of 3,3′-bi(cyclohexene), the hydrocarbon analogous to products (7) and (8) in the present instance. Thus, Borrell and Sedlar were able to postulate an intermediate complex of cyclohexene and triplet acetone as responsible for the oxetan-forming reaction. Nevertheless, the proposed quenching mechanism was not entirely consistent with their experimental results. It appears that the photochemical reactions of acetone with simple olefins involve several mechanistic paths, and further work is required for a full understanding of such processes.



SCHEME 3

EXPERIMENTAL

G.l.c. was carried out on a Varian Aerograph 2740 instrument equipped with flame ionisation detectors. The following g.l.c. columns were used: SE 30: 10 ft × 1/8 in 3% silicone gum rubber on Diatomite C, or (preparatively) 20 ft × 3/8 in 7% silicone gum rubber on PhaseSep W; DMS: 10 ft × 1/8 in 20% dimethylstearamide on PhaseSep N; QF 1: 20 ft × 3/8 in 15% fluorosilicone oil (FS 1265) on Diatomite C; DNP: 20 ft × 3/8 in 20% dinonyl phthalate on PhaseSep N. N.m.r. spectra were measured on a Varian A60D or a JEOL MH 100 spectrometer: spectra were recorded at 60 MHz for solutions in carbon tetrachloride containing tetramethylsilane as internal standard, unless otherwise noted. I.r. and u.v. spectra were measured on Perkin-Elmer 457 and 402 spectrometers, respectively.

Irradiation of Acetone and 2,3-*Dimethylbut*-2-*ene* (1).—A solution of (1) (15 g; Aldrich) and acetone (80 g; Fison's analytical grade) in a cylindrical, water-cooled quartz reactor was irradiated by a centrally-positioned 450 W medium-pressure mercury arc for 13·5 h at *ca.* 25°, with nitrogen bubbled through the solution. G.l.c. (SE 30; 80°) showed the formation of eight major photoproducts, eluted in the order (2) to (9), relative g.l.c. areas 0·32, 0·33, 1·00, 0·23, 0·41, 0·18, 0·11, and 0·32, respectively. Quantitative g.l.c. (dodecane as an internal standard) showed that 3·5 g of the olefin (1) remained unchanged in the 13·5 h product. The following yields of products were calculated, based on converted olefin: (2), 7·7%; (3), 7·9%; (4), 21%; (5), 4·6%; (6), 6·7%; (7), 4·8%; (8), 2·5%; (9), 5·3%. The ratio of (9) to the total of other photoproducts increased with time, being 0·02, 0·08, and 0·11 at times 4, 10·5, and 13·5 h, respectively.

A portion (62 g) of the product was distilled to give two fractions, (i) b.p. 50—56° at 28 mmHg, 3·7 g; (ii) b.p. 80—105° at 28 mmHg, 3·4 g. Preparative g.l.c. of fraction (i) (DNP; 130°) allowed the separation of products (2)—(4);

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[44] I. E. Kochevar and P. J. Wagner, *J. Amer. Chem. Soc.*, 1972, **94**, 3859; R. A. Caldwell, G. W. Sovocool, and R. P. Gajewski, *ibid.*, 1973, **95**, 2549.

[45] See W. A. Pryor, 'Free Radicals,' McGraw-Hill, New York, 1966.

[46] P. J. Wagner and I. Kochevar, *J. Amer. Chem. Soc.*, 1968, **90**, 2232.

[47] J. C. Dalton and N. J. Turro, *Ann. Rev. Phys. Chem.*, 1970, **21**, 499.

preparative g.l.c. of fraction (ii) (SE 30; 150°) separated compounds (7)—(9), but compounds (5) and (6) were collected together and subsequently separated on an SE 30 column at 80°.

Compound (2) was *isopropyl* 1,1,2-*trimethylprop*-2-*enyl ether*, $\nu_{max.}$ (film) 3100w (=CH), 2985s, 2940s, 1645w (C=C), 1375s (CH_3), 1170s, 1160s, 1110s, 1000s, and 900s (=CH_2) cm^{-1}; τ 5·12 (2H, m, =CH_2), 6·40 (1H, sept, *J* 6 Hz, Me_2CHO), 8·23 (3H, dd, *J* 0·8 and 1·6 Hz, CH_3–C=), 8·75 (6H, s, Me_2C), and 8·95 [6H, d, *J* 6 Hz $(CH_3)_2CH$–O]; *m/e* 142 (1%), 127 (25), 101 (14), 100 (10), 85 (69), 83 (53), 59 (100), 55 (30), and 43 (39) (Found: C, 76·0; H, 12·8. $C_9H_{18}O$ requires C, 76·0; H, 12·8%).

Compound (3), *isopropenyl* 1,1,2-*trimethylpropyl ether*, showed $\nu_{max.}$ (film) 3140w (=CH), 2980s, 2880m, 1650s (C=C), 1375s (CH_3), 1280s, 1150s, 980m, and 800m cm^{-1}; τ (100 MHz) 6·03 (2H, s, =CH_2), 7·90 (1H, m, *J* 7 Hz, Me_2CH), 8·28br (3H, s, =C–CH_3), 8·71 (6H, s, Me_2CO), and 9·10 [6H, d, *J* 7 Hz, $(CH_3)_2CH$]; irradiation (experiments at 100 Hz) of the τ 7·90 (m) signal led to collapse of the 9·10 (d) to a singlet, and irradiation of the 9·10 (d) led to collapse of the 7·90 (m) to a singlet (Found: C, 76·2; H, 12·5. $C_9H_{18}O$ requires C, 76·0; H, 12·8%).

Compound (4), 2,2,3,3,4,4-*hexamethyloxetan*, showed $\nu_{max.}$ (film) 3000s, 2960s, 2925s, 1375s (CH_3), 1225s, 1175s, 1135s, 1115s, 950s (oxetan), 870s, and 845m cm^{-1}; τ 8·77 (12H, s, 2 × Me_2C–O), and 8·92 (6H, s, Me_2C); *m/e* 109 (12%), 84 (65), 69 (100), 67 (12), 58 (26), 55 (21), 43 (62), and 41 (95) (Found: C, 75·8; H, 12·6. $C_9H_{18}O$ requires C, 76·0; H, 12·8%).

Compound (5), 2,3,3,4-*tetramethylpent*-4-*en*-2-*ol*, showed $\nu_{max.}$ (film) 3480s (OH), 3100w (=CH), 2980s, 1630m (C=C), 1375s (CH_3), 1140s, 1110s, 950m, and 890s (=CH_2) cm^{-1}; τ 5·02 and 5·13 (each 1H, m, =CH), 8·12 (3H, m, CH_3–C=), 8·69 (1H, s, OH), and 8·87 and 8·90 (each 6H, s, Me_2C) (Found: C, 75·8; H, 12·8. $C_9H_{18}O$ requires C, 76·0; H, 12·8%).

Compound (6), 2,4,5-*trimethylhex*-4-*en*-2-*ol*, showed $\nu_{max.}$ (film) 3400s (OH), 2975s, 2920s, 2870s, 1375s (CH_3), 1175s, 1150s, 895s, and 760m cm^{-1}; τ 7·75br (2H, s, =C–CH_2–), 8·29 (9H, s, 3 × MeC=), 8·30 (1H, s, OH), and 8·84 (6H, s, Me_2C–O) (Found: C, 76·0; H, 12·8. $C_9H_{18}O$ requires C, 76·0; H, 12·8%).

Compound (7), 2,3,3,5,6-*pentamethylhepta*-1,5-*diene*, showed $\nu_{max.}$ (film) 3100w (=CH), 2970s, 2925s, 2870s, 1635m (C=C), 1375s (CH_3), and 890s (=CH_2) cm^{-1}; τ 5·25 (2H, m, =CH_2), 7·80br (2H, s, =C–CH_2), 8·18 (3H, dd, *J* 0·7 and 1·3 Hz, CH_3–C=CH_2), 8·35br (9H, s, 3 × CH_3–C=), and 8·97 (6H, s, Me_2C) (Found: C, 86·1; H, 13·3. $C_{12}H_{22}$ requires C, 86·7; H, 13·3%).

Compound (8), 2,3,6,7-tetramethylocta-2,6-diene,[48] showed $\nu_{max.}$ (film) 2990s, 2920s, 2865s, 1450s, 1375s (CH_3), 1200m, and 1158m cm^{-1}; τ 7·98 (4H, s, 2 × =C–CH_2), and 8·36 (18H, s, 6 × CH_3–C=).

Compound (9), 2,2,3-*trimethyl*-3-(1,1,2-*trimethylpropoxy*)-*oxetan*, showed $\nu_{max.}$ (film) 2980s, 2940s, 2880s, 1380 and 1370s (CH_3), 1200s, 1165s, 1150s, 1125s, and 990s cm^{-1}; τ (100 MHz) 5·48 (1H, dq, *J* 5·7 and 1·0 Hz, oxetan 4-H), 6·04 (1H, d, *J* 5·7 Hz, oxetan 4-H), 8·34 (1H, m, *J* 7 Hz, Me_2CH), 8·46 (3H, d, *J* 1 Hz, oxetan 3-Me), 8·62 (3H, s, oxetan 2-Me), 8·80, 8·85, and 8·90 (each 3H, s, Me), and 9·08 [6H, d, *J* 7 Hz, $(CH_3)_2CH$]; *m/e* 115 (15%), 99 (22), 86 (70), 85 (57), 84 (43), 69 (45), 59 (39), and 43 (100) (Found: C, 71·7; H, 12·2. $C_{12}H_{24}O_2$ requires C, 72·0; H, 12·1%).

Irradiation of [$^2H_6$]*Acetone and* 2,3-*Dimethylbut*-2-*ene* (1).—(i) A mixture of [$^2H_6$]acetone (5·5 g; Ryvan, >99·5 mole % ^{2}H) and (1) (2·1 g) was irradiated under nitrogen in a stoppered quartz tube for 21 h, next to a 450 W medium-pressure mercury arc contained in a water-cooled quartz jacket. G.l.c. analysis (SE 30; 80°) showed eight products with the retention times corresponding to (2) and (4)—(10), but a product with the retention time of (3) was not apparent. Distillation and preparative g.l.c. of the mixture as before gave samples of the deuteriated products (2a), (4a), (5a), (6a), and (10a): products (7a) and (8a) were identical with (7) and (8), and did not contain deuterium.

(ii) A mixture of [$^2H_6$]acetone (3·7 g) and (1) (1·4 g) in the presence of sodium carbonate (0·01 g) was irradiated for 24 h under the conditions of (i). G.l.c. analysis (SE 30; 80°) showed formation of products with retention times corresponding to (2)—(9), and little of (10). Distillation and preparative g.l.c., as before, gave samples of (2a)—(4a).

Compound (2a), [1,1,1,3,3,3-$^2H_6$]*isopropyl* 1,1,2-*trimethylprop*-2-*enyl ether*, showed $\nu_{max.}$ (film) 3100w (=CH), 2985s, 2230s, 1645w (C=C), 1375s, 1150s, 1045s, and 900s cm^{-1}; τ ([$^2H_6$]acetone) 5·1 (2H, m, =CH_2), 6·37 (1H, m, O–CH), 8·24 (3H, dd, CH_3–C=CH_2), and 8·75 (6H, s, Me_2C).

Compound (3a), [$^2H_5$]*isopropenyl* 1,1,2-*trimethyl*[2-^{2}H]-*propyl ether*, showed τ ([$^2H_6$]acetone) 8·73 (6H, s, Me_2C–O) and 9·10 (6H, 3 lines, *J* 1 Hz, Me_2C–D).

Compound (4a), 2,2-*di*[$^2H_3$]*methyl*-3,3,4,4-*tetramethyl*-*oxetan*, showed $\nu_{max.}$ (film) 3000s, 2960s, 2240m, 2220m, 1375s, 1160s, 1130s, 1050s, 1035s, and 860 cm^{-1}; τ ([$^2H_6$]-acetone) 8·76 (6H, s, Me_2C–O) and 8·88 (6H, s, Me_2C).

Compound (5a), 2-[$^2H_3$]*methyl*-3,3,4-*trimethyl*[1,1,1-$^2H_3$]-*pent*-4-*en*-2-*ol*, showed τ ([$^2H_6$]acetone) 5·14 (2H, m, =CH_2), 7·11 (1H, s, OH), 8·11 (3H, dd, CH_3–C=CH_2), and 8·91 (6H, s, Me_2C).

Compound (6a), 2-[$^2H_3$]*methyl*-4,5-*dimethyl*[1,1,1-$^2H_3$]*hex*-4-*en*-2-*ol*, showed $\nu_{max.}$ (film) 3400s (OH), 2995m, 2920s, 2870m, 2220m, 1375m, 1150s, 1050s, and 820m cm^{-1}; τ ([$^2H_6$]acetone) 7·14 (1H, s, OH), 7·74br (2H, s, CH_2–C=), and 8·34br (9H, s, 3 × CH_3).

Compound (10a), 2,3-*dimethyl*[3-^{2}H]*butan*-2-*ol*, showed $\nu_{max.}$ (film) 3400s (OH), 2970s, 2140w, 1375s, 1130s, 960m, and 875m cm^{-1}; τ ([$^2H_6$]acetone) 7·05 (1H, s, OH), 8·90 (6H, s, Me_2C–O), and 9·11 (6H, 3 lines, *J* 1 Hz, Me_2CD).

Quantum Yields.—Pyrex tubes (20 ml) containing acetone or [$^2H_6$]acetone (1·02M), 2,3-dimethylbut-2-ene (0·84 or 1·56M), and sodium hydrogen carbonate (0·01 g) in n-hexane under nitrogen were irradiated for 2 h in a Rayonet photochemical reactor (model RPR-100; 300 nm lamps; *ca.* 45°), alongside actinometer tubes containing hexan-2-one (0·40 and 0·81M) in n-hexane. After irradiation, internal standard (dodecane) was added to each acetone/olefin tube, and the contents were analysed by g.l.c. (SE 30; 80°). The contents of the actinometer tubes (with added toluene as internal standard) were analysed by g.l.c. (QF 1; 125°) for formation of acetone. Quantum yields of product formation (±10%) were calculated on the assumption that the quantum yield of acetone formation from hexan-2-one is 0·252,[28] and the results are shown in the Table. Analysis for propan-2-ol formation was carried out by g.l.c. (DMS; 50°).

Vinyl Ether (3) *Photoreaction in Acetone*.—A solution of (3) (0·01 g) in acetone (2 ml) under nitrogen was irradiated in a quartz tube for 1·5 h, with a 450 W medium-pressure

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[48] T. Midgely and A. L. Henne, *J. Amer. Chem. Soc.*, 1930, **52**, 2078.

mercury arc. G.l.c. analysis (SE 30; 80°) showed several short-retention-time products, and one major product with retention time identical with that of the oxetan (9).

Oxetan (4) *Photostability*.—Pyrex tubes containing (4) (0·007—0·03M) and acetone (1·4M) in n-hexane were deoxygenated and irradiated at 300 nm alongside acetone–(1)–n-hexane mixtures. G.l.c. (SE 30; 80°) showed that (4) was stable under the photoreaction conditions required to form (2)—(8). At least seven products were detected from the irradiations of (4)–acetone–n-hexane, but these all arose from comparable irradiations of acetone–n-hexane alone, and did not have the same retention times as (2), (3), or (5)—(8).

Photoreaction of $[^2H_6]$*Acetone with Dimethylbutene* (1) *followed by N.m.r. Spectroscopy*.—(i) An n.m.r. tube containing $[^2H_6]$acetone ($1·04 \times 10^{-2}$ mol) and (1) ($1·04 \times 10^{-3}$ mol) was degassed (four freeze–pump–thaw cycles; 5×10^{-3} mmHg), sealed, and irradiated in the Rayonet reactor (300 nm lamps; 15 h). The glass of the n.m.r. tube showed less than 1% transmission below 300 nm. Simultaneously, a degassed and sealed actinometer solution of hexan-2-one in n-hexane was irradiated in an n.m.r. tube with matching transmission properties. After irradiation, toluene (internal standard) was added to the actinometer tube and the contents were analysed for acetone by g.l.c. (QF 1; 125°).

At intervals, n.m.r. spectra of the acetone–(1) tube were run, and these showed steady formation of photoproducts. The major peaks appearing were all assignable, and appeared at the τ values of the isolated photoproducts (2a), (3a), (4a), (7), and (10a). Little increase in intensity of the acetone (or $[^2H_5]$acetone) peak was detected, and a maximum possible quantum yield of formation of acetone, $\Phi = 0·005$, was calculated by reference to the actinometer tube. Finally, the sample was subjected to g.l.c. analysis (SE 30; 80°), which showed formation of products with retention times identical with those of (10) and (2)—(8); relative peak areas 0·14, 0·34, 0·15, 1·00, 0·34, 0·77, 0·60, and 0·72 respectively. The quantum yield of oxetan (4) was calculated to be $0·03 \pm 0·02$.

Similar results were obtained in an experiment in which nitrogen was bubbled through the solution, instead of the degassing procedure being used, and the tube was then sealed and irradiated.

(ii) A mixture of $[^2H_6]$acetone ($3·1 \times 10^{-3}$ mol) and (1) ($3·1 \times 10^{-3}$ mol) was similarly irradiated for 22 h, and the n.m.r. spectrum was taken. The only observed products were those seen in experiment (i). Subsequently the tube was irradiated next to a 450 W medium-pressure mercury arc for 20·5 h. G.l.c. and n.m.r. analysis of the final product was carried out, but the products resembled those from experiment (i) except that (10a) had completely replaced (3a). Hexan-2-one actinometry, on the assumption that the lamp output was constant (since the actinometer solution was only irradiated for a portion of the total time, to avoid too large a conversion), showed that formation of acetone had a quantum yield, $\Phi \leqslant 0·002$. No increase in intensity of the $[^2H_5]$acetone n.m.r. peak was detected.

Effect of Propan-2-*ol on Product Distribution*.—Two Pyrex tubes, containing acetone (1·14M) and (1) (0·70M) under nitrogen in n-hexane or n-hexane containing propan-2-ol (0·54M) were irradiated simultaneously in the Rayonet reactor (300 nm lamps; 4 h; *ca.* 1% conversion). G.l.c. analysis (SE 30; 80°) showed similar product distributions of (2)—(8) in the tubes with and without propan-2-ol, both in relative and absolute (±10%) concentrations of photoproducts.

Photosensitisation Attempt.—Quartz tubes (20 ml) containing acetone (0·68M) and (1) (0·84M) in n-hexane with or without sensitiser (acetophenone, 0·255M) were deoxygenated, sealed, and irradiated for 1 h in a Rayonet photochemical reactor (254 nm lamps). After irradiation, the contents of each tube were analysed by g.l.c. (SE 30; 80°) and the ratios of the yields of products with and without sensitiser, respectively, were found: (2) 0·018; (3) 0·018; (4) 0·019; (5) <0·020; (6) <0·013; (7) 0·34; (8) 0·36. Calculations from u.v. spectra showed that acetophenone should absorb ≥97% of the incident light in the tubes containing it as sensitiser.

Product Quenching Studies.—Pyrex tubes (20 ml) containing acetone (1·36M), (1) (0·84M), and quencher (2,3-dimethylbuta-1,3-diene, 0—0·44M) in n-hexane (to 20 ml) under nitrogen were irradiated for 5 h in a Rayonet photochemical reactor (300 nm lamps). After irradiation, internal standard (dodecane) was added to each tube, and the contents were analysed by g.l.c. (SE 30, 80°). For each product, quantum yields (Φ) of formation at each quencher concentration were measured relative to the tubes without quencher (Φ_0), and Stern–Volmer plots of Φ_0/Φ (±10%) against quencher molarity are shown in Figures 1—3. At higher quencher concentrations, the following approximate Φ_0/Φ values were obtained:

	Product						
	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Diene, 0·22M	3·0	2·3	3·1			32	26
0·44M	4·0		4·6	8·8	3·9		

Stability of the Vinyl Ether (3).—After several weeks, the acetone–(1) photoreaction product showed decomposition of (3) and appearance of another product, (10) which was isolated by preparative g.l.c. (DNP; 130°). Compound (10) had n.m.r. and i.r. spectra identical with those of an authentic sample of 2,3-dimethylbutan-2-ol, prepared from (1).[49] The conversion of (3) into (10) became much more rapid in the presence of water and mineral acid, and the formation of (10) and acetone from (3) was detected by g.l.c. and n.m.r. spectra. Because of the easy decomposition of (3) in the presence of acid, it was found advisable to add sodium hydrogen carbonate (0·01 g per 20 ml tube) to the mixture before irradiation. In this manner, g.l.c. product analysis gave reproducible estimates of (3) concentration. Control experiments with and without added sodium hydrogen carbonate showed that formation of the other photoproducts (2) and (4)—(8) was unaffected by this additive.

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[49] H. C. Brown and P. Geoghegan, *J. Amer. Chem. Soc.*, 1967, **89**, 1522.