Photochemistry of Acyclic $\beta\gamma$-unsaturated Ketones: the Effect of α-Methyl Substitution

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The effect of irradiation of three acyclic $\beta\gamma$-unsaturated ketones (1f—h) at 313 nm has been investigated, with 2,2-dimethylbutane, hexadecane and t-butyl alcohol as solvents. The photoproducts are those formed by recombination of the allyl radicals resulting from initial α-cleavage of the excited ketone, by a 1,3-acyl shift [from (1f)], and by decarbonylation [from (1h)]. With (1f and g) small amounts of biacetyl were found and no carbon monooxide, whereas with (1h) substantial amounts of carbon mono-oxide and no α-diketone were observed. The quantum yields for ketone disappearance and product formation are reported. The effects of α- and α'-methyl substitution on the quantum yield of ketone disappearance is very small. Solvents of higher viscosity (hexadecane and t-butyl alcohol) were found to promote the solvent-cage radical combination reactions. By use of tri-n-butylstannane as a radical scavenger, it was shown (i) that at least 40% of the initially formed *free* radicals from (1f and g) recombine to yield the starting compound, (ii) that with (1f) at least 45% of the 1,3-acyl shift product is formed *via* a *free* radical pathway, (iii) that with (1h) at least 85% of the decarbonylation product is formed from *free* radicals, and (iv) that the decarbonylation of the isobutyryl radical scarcely occurs in the solvent cage. The acetone-photosensitized conversions of (1f—h) are slow in comparison with the photodecomposition of acetone.

THE photochemistry of $\beta\gamma$-unsaturated ketones has received considerable attention.[1] In addition to Z–E isomerization the two specific photoreactions are the 1,3- and 1,2-acyl shifts. The latter is often referred to as the oxa-di-π-methane (ODPM) rearrangement. The former may involve α-cleavage followed by radical combination, or may be concerted, as the process is orbital-symmetry-allowed.[2] CNDO/S calculations[3] indicate that the 1,3-acyl shift results from an excited singlet or triplet[1d,4] state which has mainly n–π^* character, whereas the 1,2-acyl shift results from an excited triplet state of mainly π–π^* character.

Previous photochemical studies have been concerned with $\beta\gamma$-unsaturated ketones in which either the two π-systems had a fixed geometry with respect to each

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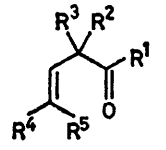
[1] (*a*) S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, 1973, **73**, 531; (*b*) W. G. Dauben, G. Lodder, and J. Ipaktschi, *Fortschr. Chem. Forsch.*, 1975, **54**, 73; (*c*) K. N. Houk, *Chem. Rev.*, 1976, **76**, 1; (*d*) K. Schaffner, *Tetrahedron*, 1976, **32**, 641.

[2] R. B. Woodward and R. Hoffmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 781.

[3] K. N. Houk, D. J. Northington, and R. E. Duke, jun., *J. Amer. Chem. Soc.*, 1972, **94**, 6233.

[4] (*a*) J. C. Dalton, M. Shen, and J. J. Snyder, *J. Amer. Chem. Soc.*, 1976, **98**, 5024; (*b*) D. I. Schuster, J. Eriksen, P. S. Engel, and M. A. Schexnayder, *ibid.*, p. 5025.

other, or the alkene moiety was part of a cyclic system. Little is known of the factors which govern the photochemistry of acyclic βγ-unsaturated ketones. The first report of a 1,2-acyl shift rearrangement of an acyclic βγ-unsaturated ketone was that of compound (1a).[5] Also compounds (1b) [6] and (1c),[7] in contrast to (1d) [1b] and (1e),[8] exhibit the ODPM rearrangement upon triplet sensitization.



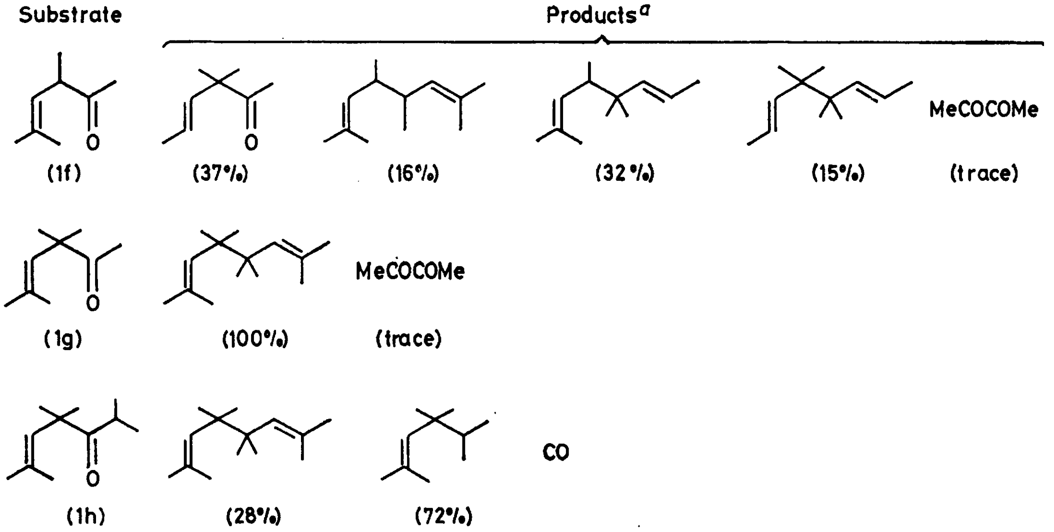
(1)

a; $R^1 = R^2 = R^4 = R^5 = Ph, R^3 = H$
b; $R^1 = Pr^i, R^2 = R^3 = Me, R^4 = Ph, R^5 = H$
c; $R^1 = R^2 = Me, R^3 = Et, R^4 = Ph, R^5 = H$
d; $R^1 = R^2 = Me, R^3 = Et, R^4 = R^5 = Ph$
e; $R^1 = R^2 = R^3 = Me, R^4 = R^5 = Ph$
f; $R^1 = R^2 = R^4 = R^5 = Me, R^3 = H$
g; $R^1 = R^2 = R^3 = R^4 = R^5 = Me$
h; $R^1 = Pr^i, R^2 = R^3 = R^4 = R^5 = Me$
i; $R^1 = R^4 = R^5 = Me, R^2 = R^3 = H$
j; $R^1 = R^2 = R^3 = Me, R^4 = R^5 = H$

At the outset of this study, little systematic work had been performed on the excited-state chemistry of acyclic βγ-unsaturated ketones. However a recent report by Engel and Schexnayder [9] concerns the influence of the type of βγ-unsaturation on the photochemical behaviour. By using 3,4,5,6,7,8-hexahydronaphthalen-2(1*H*)-one as substrate they showed that methyl groups at position 1, *i.e.* the α-position, enhance the α-cleavage.[10]

TABLE 1

Photoproducts of βγ-unsaturated ketones upon irradiation at 313 nm in 2,2-dimethylbutane



[a] Relative yields in parentheses.

The present study was carried out to elucidate the influence of α-methyl substituents on the direct and photosensitized photoreactions of acyclic βγ-unsaturated ketones in the absence of conjugative substituents at the γ-position. In order to gain further insight into the reaction mechanism, the irradiations were also carried out with (i) solvents of higher viscosity, *viz.* hexadecane and t-butyl alcohol, to promote cage radical pair combination reactions, and (ii) addition of tri-n-butylstannane to trap free radicals.

RESULTS AND DISCUSSION

Direct Irradiation.—The products of irradiation of the substrates (1f—h) in 2,2-dimethylbutane at **313** nm are shown in Table 1. Engel and Schexnayder reported that the related compound (1i) upon direct irradiation in benzene yields biacetyl, C_{10} hydrocarbons resulting from recombination of allyl radicals, and minute amounts of (1j).[9]

The formation of the products may be explained in terms of α-cleavage of the singlet or triplet excited βγ-unsaturated ketone. The cage radical pair formed initially [reaction (1)] can combine to give either the starting compound [reaction (2)] or the 1,3-acyl shift product [reaction (3)], or diffuse apart [reaction (4)]. The acyl radical of the cage radical pair can be decarbonylated; the resulting alkyl radical can then combine with the allyl radical in two ways [reaction

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[5] L. P. Tenney, D. W. Boykin, jun., and R. E. Lutz, *J. Amer. Chem. Soc.*, 1966, **88**, 1835.

[6] W. G. Dauben, M. S. Kellog, J. I. Seeman, and W. A. Spitzer, *J. Amer. Chem. Soc.*, 1970, **92**, 1786.

[7] W. G. Dauben, G. Lodder, and J. D. Robbins, *J. Amer. Chem. Soc.*, 1976, **98**, 3030.

[8] H. C. Pratt, *J.C.S. Perkin I*, 1973, 2496.

[9] P. S. Engel and M. A. Schexnayder, *J. Amer. Chem. Soc.*, 1975, **97**, 4825.

[10] P. S. Engel, M. A. Schexnayder, H. Ziffer, and J. I. Seeman, *J. Amer. Chem. Soc.*, 1974, **96**, 924.

(5)]. Combination of the *free* radicals formed by reaction (4) yields either the starting material [reaction (6)] or the 1,3-acyl shift product [reaction (7)]. Recombination of the relatively stable allyl radicals yields

$$(1)^{*} \longrightarrow \overline{\mathrm{R^4R^5C{=}CH\dot{C}R^2R^3 \quad R^1\dot{C}O}} \tag{1}$$

$$\overline{\mathrm{R^4R^5C{=}CH\dot{C}R^2R^3 \quad R^1\dot{C}O}} \longrightarrow (1) \tag{2}$$

$$\overline{\mathrm{R^4R^5C{=}CH\dot{C}R^2R^3 \quad R^1\dot{C}O}} \longrightarrow \mathrm{R^2R^3C{=}CHCR^4R^5COR^1} \tag{3}$$

$$\overline{\mathrm{R^4R^5C{=}CH\dot{C}R^2R^3 \quad R^1\dot{C}O}} \longrightarrow \mathrm{R^4R^5C{=}CH\dot{C}R^2R^3 + R^1\dot{C}O} \tag{4}$$

$$\overline{\mathrm{R^4R^5C{=}CH\dot{C}R^2R^3 \quad R^1\dot{C}O}} \longrightarrow \mathrm{R^4R^5C{=}CHCR^1R^2R^3 + CO} \tag{5a}$$

$$\longrightarrow \mathrm{R^2R^3C{=}CHCR^1R^4R^5 + CO} \tag{5b}$$

$$\mathrm{R^4R^5C{=}CH\dot{C}R^2R^3 + R^1\dot{C}O} \longrightarrow (1) \tag{6}$$

$$\mathrm{R^4R^5C{=}CH\dot{C}R^2R^3 + R^1\dot{C}O} \longrightarrow \mathrm{R^2R^3C{=}CHCR^4R^5COR^1} \tag{7}$$

$$\mathrm{2R^4R^5C{=}CH\dot{C}R^2R^3} \longrightarrow 3 \text{ recombination products} \tag{8}$$

$$\mathrm{2R^1\dot{C}O} \longrightarrow \mathrm{R^1COCOR^1} \tag{9}$$

$$\mathrm{R^1\dot{C}O} \longrightarrow \mathrm{R^{1\cdot} + CO} \tag{10}$$

$$\mathrm{R^4R^5C{=}CH\dot{C}R^2R^3 + R^{1\cdot}} \longrightarrow \mathrm{R^4R^5C{=}CHCR^1R^2R^3} \tag{11a}$$

$$\longrightarrow \mathrm{R^2R^3C{=}CHCR^1R^4R^5} \tag{11b}$$

three different dienes, provided that the allyl radical is asymmetric [reaction (8)]. Recombination of the acyl radicals yields the α-diketone [reaction (9)]. The acyl radicals may undergo decarbonylation [reaction (10)]; the resulting alkyl radicals can combine with the allyl radical [reaction (11)].

Upon irradiation of (1f) the three allyl recombination products are formed in the ratio 1 : 2 : 1, *i.e.* a statistical ratio, indicating that the rates of combination of a secondary and a tertiary allyl radical site are equal. The formation of 3,3-dimethylhex-4-en-2-one illustrates the occurrence of the 1,3-acyl shift. This process cannot be detected with (1g) and (1h) because of the symmetry of the allyl radical intermediate, which also necessitates the formation of only one allyl radical recombination product.

No decarbonylation of the acyl radical is observed upon irradiation of (1f) and (1g), whereas decarbonylation does occur with (1h) (*cf.* Table 1). This difference is as expected in view of the higher rate of decarbonylation of the isobutyryl as compared with the acetyl radical.[11]

The quantum yields for the βγ-unsaturated ketones are shown in Table 2. For the three substrates studied the quantum yield of step (1) will be greater than that of ketone disappearance, in view of the occurrence of steps (2) and (6), which re-form the starting compound. With (1g and h) steps (3) and (7) are indistinguishable from (2) and (6). Accordingly for 2,2-dimethylbutane as solvent, where the quantum yields of ketone disappearance are about the same, the quantum yield of step (1) will be substantially greater for (1g and h) than for (1f). This may be ascribed to a more ready α-cleavage as a result of (i) relief of steric strain, and (ii) the higher stability of the allyl radical resulting from (1g and h) than of that from (1f).

TABLE 2

Quantum yields (λ 313 nm) for disappearance of starting material and for product formation

		ϕ			
Substrate	Solvent [a]	Ketone	Allyl recomb.	1,3-Acyl shift	Decarb.
(1f)	DMB	0.38_5	0.09_5	0.05_7	
	DMB + TBS	0.52_5	0.08_4	0.03_2	
	HD	0.40_5	0.09_3	0.07_3	
	Bu^{t}OH	0.38_5	0.05_7	0.13_3	
(1g)	DMB	0.40	0.05_7		
	DMB + TBS	0.59_5	0.05_4		
	HD	0.29_6	0.00_8		
	Bu^{t}OH	0.11_2	0.02		
(1h)	DMB	0.41	0.02_5		0.06_5
	DMB + TBS	0.42_5	0.02_1		0.00_8
	HD	0.19_7	0.01_6		0.07_4
	Bu^{t}OH	0.32	0.01_2		0.06_2

[a] DMB = 2,2-dimethylbutane; TBS = tri-n-butylstannane; HD = hexadecane.

Solvent Variation.—The quantum yields of the photoreactions of (1f—h), all both in hexadecane and in t-butyl alcohol, are given in Table 2. It appears that the quantum yield for the formation of the allyl recombination product(s) is lower for hexadecane and t-butyl alcohol than for the less viscous 2,2-dimethylbutane. This is in line with expectation as the rate of formation of the *free* radicals by step (4) will be significantly less in the solvent of higher viscosity. The 1,3-acyl shift product is formed both by a cage process [step (3)] and by a free radical pathway [step (7)]. The increased quantum yield of the 1,3-acyl shift product with (1f) in hexadecane and t-butyl alcohol as compared with 2,2-dimethylbutane as solvent may therefore be explained by a reduction in the rate of step (4). The quantum yield of decarbonylation is only slightly affected by the viscosity of the solvent [*cf.* (1h)]. The quantum yield for ketone disappearance is independent of the viscosity of the solvent with (1f), whereas there is a strong dependence with (1g and h). This is due to the fact that step (3) yields the 1,3-acyl shift product with (1f), but the starting compound with (1g and h). For (1g and h) the quantum yield for ketone disappearance is markedly affected by the solvent viscosity. This illustrates that steps (2) and (3), which yield starting material, are much faster than step (5).

Irradiations in the Presence of Tri-n-butylstannane.—Tri-n-butylstannane is a well known radical scavenger. It is also a reducing agent for electronically excited carbonyl compounds, which then yield the corresponding

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[11] M. J. Perkins and B. P. Roberts, *J.C.S. Perkin II*, 1974, 297

alkanols.[12] Irradiation of (1f—h) in 2,2-dimethylbutane in the presence of tri-n-butylstannane did not lead to photoreduction, as no additional products were observed by g.l.c. This indicates that the lifetime of the triplet excited state is much smaller for $\beta\gamma$-unsaturated ketones than for simple ketones, *e.g.* acetone.[12a] The quantum yields for the photochemical products of the $\beta\gamma$-unsaturated ketones in the presence of tri-n-butylstannane are given in Table 2. With (1f and g) the enhanced ketone disappearance (*ca.* 40%) in the presence of the stannane indicates that, in the absence of stannane, 40% of the *free* radicals formed recombine again with formation of the starting compound [step (6)]. With (1h), the quantum yield of ketone disappearance is not affected by the presence of the stannane, indicating that the rate of step (10) is very much greater than that of step (6).

The quantum yield for the decarbonylation product decreases by *ca.* 85% in the presence of the stannane. This indicates that step (4) is considerably faster than step (5). The stannane quenches the 1,3-acyl shift product by *ca.* 45%, indicating that at least 45% of this product is formed *via* step (7). There is little effect of the stannane on the formation of allyl recombination product, indicating that these relatively stable radicals are hardly scavenged by the stannane.

The formation of a substantial amount of ethanal upon irradiation of (1f and g) in the presence of the stannane illustrates the ability of the acetyl radicals to abstract hydrogen from the stannane. Upon irradiation of (1h) in the presence of the stannane, a substantial amount of propane was formed and no 2-methylpropanal. This illustrates that the decarbonylation of the isobutyryl radical is faster than its reaction with the stannane.

Acetone Sensitization.—The acetone-sensitized irradiation of the compounds (1f—h) at λ 313 nm was also investigated. However, it appeared that the conversion of the $\beta\gamma$-unsaturated ketones is slow as compared with the photodecomposition of acetone. This low reactivity may be ascribed to the efficient deactivation of excited triplet (π–π^*) states by *E–Z* isomerization (the so-called 'free rotor effect'[13]), which cannot be detected [since $R^4 = R^5$ (= Me)]. With related substrates in which $R^4 \neq R^5$ this isomerization is in fact observed.[14]

EXPERIMENTAL

Synthesis of $\beta\gamma$-Unsaturated Ketones.—*4-Methylpent-3-enoic acid.* A solution of 2-carboxyethyl(triphenyl)phosphonium chloride[15] (0.22 mol) and dry acetone (0.22 mol) in tetrahydrofuran–dimethyl sulphoxide (1 : 1; 400 ml) was added dropwise at 0 °C under nitrogen to powdered sodium hydride (0.42 mol). After 20 h stirring the resulting yellow mass was hydrolysed with ice (600 g) and 98% sulphuric acid (45 g). The organic layer was separated and the aqueous layer extracted with chloroform. The combined organic layers were washed with brine till neutral, dried ($MgSO_4$), and evaporated. The residue was distilled to afford a clear liquid, b.p. 112° at 15 mmHg (lit.,[16] 77—85° at 2.4—2.7 mmHg); yield 13.2 g (54%); δ ($CDCl_3$) 11.45 (1 H, s), 5.30br (1 H, t, *J* 7 Hz), 3.05br (2 H, d, *J* 7 Hz), 1.73br (3 H, s), and 1.63br (3 H, s); $\nu_{max.}$ ($CHCl_3$) 3 000, 2 800, 1 705, 1 420, 1 380, and 1 300 cm^{-1}.

5-Methylhex-4-en-2-one (1i). A solution of 4-methylpent-3-enoic acid (0.12 mol) in water was made alkaline with lithium hydroxide (to pH 9). The solvent was removed under reduced pressure and the residue dried *in vacuo* at 100 °C for 24 h. To the lithium salt in dry ether (150 ml) was added under nitrogen at −20 °C an ethereal solution of methyl-lithium [from methyl iodide (0.25 mol) and lithium (0.4 mol) in dry ether (300 ml)]. The mixture was left refluxing overnight and after cooling poured on ice. The organic layer was separated and the aqueous layer extracted with ether. The combined organic layers were washed with brine till neutral, dried ($MgSO_4$), and evaporated. The residue was distilled; b.p. 66° at 28 mmHg (lit.,[17] 61—62° at 28 mmHg); yield 9 g (70%); δ (CCl_4) 5.27br (1 H, t, *J* 7 Hz), 3.00br (2 H, d, *J* 7 Hz), 2.03 (3 H, s), 1.74br (3 H, s), and 1.60br (3 H, s); $\nu_{max.}$ ($CHCl_3$) 3 010, 2 910, 1 700, 1 625, 1 450, 1 380, 1 355, 1 300, and 1 245 cm^{-1}; $\lambda_{max.}$ (cyclohexane) 287 nm (ε 80).

3,5-Dimethylhex-4-en-2-one (1f)[18] *and 3,3,5-Trimethylhex-4-en-2-one* (1g).[19]—A solution of 5-methylhex-4-en-2-one (45 mmol) in dry dimethyl sulphoxide (10 ml) was added dropwise to a suspension of potassium t-butoxide (51 mmol) in dry dimethyl sulphoxide (35 ml) under nitrogen. The solution was stirred for 15 min at room temperature, then methyl iodide was added slowly (in order to keep the temperature below 30 °C) until the solution was (almost) colourless, and the mixture was stirred for 2 h at room temperature. It was then poured on ice and extracted with ether. The combined ethereal solutions were washed with aqueous 5% hydrogen chloride, then saturated aqueous sodium hydrogen carbonate and finally brine till neutral. After drying ($MgSO_4$), the solvent was removed and the residue distilled; b.p. 74—76° at 26 mmHg [lit.,[19] for (1g) 61—63° at 15 mmHg]; yield of (1f) + (1g) 5 g. The two compounds were separated by g.l.c. on two columns (5 m × 1/4 in; 15% SE-30 or 10% Reoplex-400; 135 °C). G.l.c. analysis revealed that (1f) and (1g) were present in the ratio 3 : 1. The *ketone* (1f) showed δ (CCl_4) 5.10br (1 H, d, *J* 10 Hz), 3.39 (1 H, d of q, J_d 10, J_q 7 Hz), 2.09 (3 H, s), 1.77br (3 H, s), 1.72br (3 H, s), and 1.12 (3 H, d, *J* 7 Hz); $\nu_{max.}$ (CCl_4) 2 980, 2 920, 2 860, 1 705, 1 450, 1 380, 1 350, and 1 160 cm^{-1}; $\lambda_{max.}$ (cyclohexane) 294 (ε 187), 287 (183), and 285 nm (258); *m/e* 126 (M^+) and 83 (base) (Found: C, 76.2; H, 11.3. Calc. for $C_8H_{14}O$: C, 76.15; H, 11.2%). The *ketone* (1g) showed δ (CCl_4) 5.33br (1 H, s), 2.10 (3 H, s), 1.72 (3 H, d, *J* 1 Hz), 1.48 (3 H, d, *J* 1 Hz), and 1.20 (6 H, s); $\nu_{max.}$ (liquid) 3 000, 2 950, 1 705, 1 665, 1 450, 1 390, 1 350, 1 230, 1 110, 1 070, 1 020, 960, 880, and 820 cm^{-1}; $\lambda_{max.}$ (cyclohexane) 293

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[12] (*a*) P. J. Wagner, *J. Amer. Chem. Soc.*, 1967, **89**, 2503; (*b*) E. Baggiolini, H. P. Hamlow, and K. Schaffner, *ibid.*, 1970, **92**, 4906.

[13] H. E. Zimmerman and P. S. Mariano, *J. Amer. Chem. Soc.*, 1969, **91**, 1718.

[14] P. S. Engel and M. A. Schexnayder, *J. Amer. Chem. Soc.*, 1972, **94**, 9252.

[15] D. B. Denney and L. C. Smith, *J. Org. Chem.*, 1962, **27**, 3404.

[16] E. Caspi and K. R. Varna, *J. Org. Chem.*, 1968, **33**, 2181.

[17] K. Uehara, F. Kitamura, and M. Tanaka, *Chem. Letters*, 1973, 279.

[18] D. R. Paulson, G. Korngold, and G. Jones, *Tetrahedron Letters*, 1972, 1723.

[19] J. L. Dolby and C. L. Wilkins, *Tetrahedron*, 1969, 2381.

(ε 92) and 287 nm (90) (Found: C, 77.2; H, 11.55. Calc. for $C_9H_{16}O$: C, 77.1; H, 11.5%).

2,4,4,6-*Tetramethylhept*-5-*en*-3-*one* (1h).—To a solution of 5-hydroxy-2,4,4,6-tetramethylheptan-3-one [20] (47 mmol) in dry pyridine (100 ml), thionyl chloride (59 mmol) was added slowly at 10—15 °C. The mixture was stirred for 7.5 h at room temperature, poured into ice–water, acidified with cold aqueous 20% hydrogen chloride, and extracted with ether. The combined ethereal solutions were washed with saturated aqueous sodium hydrogen carbonate and brine till neutral, and dried ($MgSO_4$). The solvent was distilled off and the residue was purified by g.l.c. (4 m × 1/4 in; 10% GE-XE-60; 100 °C); δ (CCl_4) 5.25br (1 H, s), 2.90 (1 H, sept, J 6.5 Hz), 1.70br (3 H, s), 1.50 (3 H, s), 1.18 (6 H, s), and 0.98 (6 H, d, J 6.5 Hz); $\nu_{max.}$ ($CHCl_3$) 3 000, 2 890, 1 700, 1470 1 385, 1 370, and 1 340 cm^{-1}; $\lambda_{max.}$ (cyclohexane) 296 nm (ε 113) (Found: C, 78.6; H, 12.05. Calc. for $C_{11}H_{20}O$: C, 78.5; H, 12.0%).

Irradiations.—The irradiations were carried out in a Rayonet RPR-208 photoreactor equipped with eight RUL 300 nm lamps at room temperature. The solutions of the ketones (0.10—0.14M) in 2,2-dimethylbutane, hexadecane, or t-butyl alcohol, contained in Pyrex tubes closed with a septum, were first saturated with nitrogen. For the scavenging experiments two tubes were irradiated simultaneously in a ' merry-go-round ' in which one of the two also contained freshly distilled tri-n-butylstannane (0.3M).

The quantum yields were determined by valerophenone actinometry [21] with use of the merry-go-round and a potassium chromate filter to isolate the 313 nm group of lines. The solutions of the ketones were in this case degassed three times prior to the irradiation; the maximum conversion of starting material was 25%.

For the irradiations in acetone as sensitizer the ketone concentration was 7 × 10^{-3}M.

Analysis, Product Isolation, and Identification.—The photoreactions were monitored by g.l.c. The product yields were determined from g.l.c. peak areas relative to that of internal *p*-dichlorobenzene. The products were isolated by preparative g.l.c. (5 m × 1/4 in; 10% Reoplex-400, T_0 80 °C, ΔT 2° min^{-1}). The presence of biacetyl was demonstrated by comparing the g.l.c. retention time with that of an authentic sample and also by its characteristic odour. The ^1H n.m.r. spectra were recorded with tetramethylsilane as internal reference.

3,3-*Dimethylhex*-4-*en*-2-*one* showed δ (CCl_4) 5.47 (2 H, m), 1.97 (3 H, s), 1.69 (3 H, d, J 5 Hz), and 1.13 (6 H, s); $\nu_{max.}$ (CCl_4) 2 980, 2 860, 1 705, 1 465, 1 445, 1 380, 1 365, 1 350, and 1 115 cm^{-1}; *m/e* 126 (M^+) and 83 (base). 2,4,5,7-*Tetramethylocta*-2,6-*diene* showed δ (CCl_4) 4.92 (2 H, m), 2.10 (2 H, m), 1.66 (6 H, s), 1.56br (6 H, s), and 0.90 (6 H, d, J 7 Hz); $\nu_{max.}$ (CCl_4) 2 980, 2 920, 2 880, 1 670, 1 455, 1 380, 1 055, and 840 cm^{-1}; *m/e* 166 (M^+) and 83 (base). 2,4,5,5-*Tetramethylocta*-2,6-*diene* showed δ (CCl_4) 5.37 (2 H, m), 5.20 (1 H, m), 2.10 (1 H, m), 1.60 (9 H, m), and 0.90 (9 H, m); $\nu_{max.}$ (CCl_4) 2 970, 2 910, 2 860, 1 450, 1 375, 1 060, 970, and 850 cm^{-1}; *m/e* 166 (M^+) and 83 (base). 4,4,5,5-*Tetramethylocta*-2,6-*diene* showed δ (CCl_4) 5.45 (2 H, d, J 16 Hz), 5.25 (2 H, d of q, J_d 16, J_q 6 Hz), 1.65 (6 H, d, J 6 Hz), and 0.87 (12 H, s); $\nu_{max.}$ (CCl_4) 2 980, 2 860, 1 450, 1 375, 1 125, 1 110, and 975 cm^{-1}; *m/e* 166 (M^+) and 83 (base). 2,4,4,5,5,7-*Hexamethylocta*-2,6-*diene* showed δ (CCl_4) 5.14br (2 H, s), 1.67 (12 H, s), and 1.04 (12 H, s); $\nu_{max.}$ (CCl_4) 2 980, 2 920, 1 650, 1 450, 1 370, 1 125, 1 060, and 830 cm^{-1}; *m/e* 194 (M^+) and 97 (base). 2,4,4,5-*Tetremethylhex*-2-*ene* [22] showed δ (CCl_4) 5.04br (1 H, s), 1.66br (6 H, s), 1.60 (1 H, septet, J 7 Hz), 1.00 (6 H, s), and 0.83 (6 H, d, J 7 Hz).

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