Homolytic Organometallic Reactions. Part X.[1] Kinetics of the Homolytic Photoreductions of Aromatic Ketones by Trialkylboranes

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The kinetics of the homolytic photoreductions of a series of ring-substituted acetophenone triplets with trialkylboranes in benzene have been investigated by comparing the rate of the S_H2 process [equation (i)] with those of the quenching of the triplets by piperylene or of the sensitized isomerization of *trans*- to *cis*-piperylene. Rate constants

$$\mathrm{ArMeCO^{*} + BR_3 \longrightarrow ArMe\dot{C}OBR_2 + R\cdot} \qquad \text{(i)}$$

for the S_H2 process are of the order of 10^8 l mol^{-1} s^{-1} at 28° for both $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ triplets. Quantum yields vary from *ca.* 0·3 to 0·7 and decrease when t-butyl alcohol is present in the solvent. It is suggested that the ketone triplets form a polar complex with the borane, which can then decompose by loss of the alkyl radical R· or can revert to trialkylborane and a ground-state ketone.

In Part V [2] it was shown that ketone triplets react with organoboron compounds according to equation (1).

$$\mathrm{R^1R^2CO^{*} + R_3^3B \longrightarrow R^1R^2\dot{C}OBR_2^3 + R^3\cdot} \qquad (1)$$

If the reactions are carried out in the cavity of an e.s.r. spectrometer, the spectra of the two product radicals can be observed, and the rate constants for the reactions can be obtained by monitoring the concentrations of the radicals under different experimental conditions.

These studies were limited to simple dialkyl ketones. We have now examined the reactivity of aromatic ketones, particularly substituted acetophenones, towards several organoboranes and analysed the results in terms of substituent and solvent effects.

RESULTS AND DISCUSSION

In the absence of a triplet quencher, the principal elementary processes which need to be considered are as follows, where the superscripts *s* and * denote excited singlet and triplet states. Reaction (5*c*) can be ignored

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[1] Part IX, A. G. Davies, D. Griller, and B. P. Roberts, preceding paper.

[2] Part V, A. G. Davies, B. P. Roberts, and J. C. Scaiano, *J. Chem. Soc.* (*B*), 1971, 2171.

for aromatic ketones with no γ hydrogen atoms. In addition to these reactions, a series of combination and disproportionation reactions among the radicals finally

$$R^1R^2CO \longrightarrow R^1R^2CO^s \tag{2}$$

$$R^1R^2CO^s \begin{cases} \xrightarrow{a} R^1R^2CO \\ \xrightarrow{b} R^1R^2CO + h\nu' \end{cases} \tag{3}$$

$$R^1R^2CO^s \longrightarrow R^1R^2CO^* \tag{4}$$

$$R^1R^2CO^* \begin{cases} \xrightarrow{a} R^1R^2CO \\ \xrightarrow{b} R^1R^2CO + h\nu'' \\ \xrightarrow{c} \text{products} \end{cases} \tag{5}$$

$$R^1R^2CO^* + BR_3^3 \begin{cases} \longrightarrow R^1R^2\dot{C}OBR_2^3 + R^3\cdot & (6) \\ \longrightarrow R^1R^2\dot{C}OH + BR_3^3(-H) & (7) \\ \longrightarrow R^1R^2CO + BR_3^3 & (8) \end{cases}$$

leads to molecular products. Unless otherwise indicated, we shall assume that reaction (7) is very slow compared with reaction (6); the justification of this will be discussed later in the light of our kinetic results.

For the aromatic ketones, it was experimentally more convenient to determine the rate constants by conventional methods rather than by e.s.r. spectroscopy, since the latter technique would involve the measurement of radical concentrations for species with rather complex spectra, and under conditions where it is difficult to pick out strong individual lines. Two different methods were used to measure the rate constants of reactions (6).

Method A.—The measurements were carried out causing reaction (6) to compete with the quenching

$$R^1R^2CO^* + Q \longrightarrow R^1R^2CO + Q^* \tag{9}$$

process of reaction (9), where Q was the commercially available mixture of *cis*- and *trans*-piperylene.*

The experimentally measured quantum yield of ketone disappearance (Φ_{-k}) can be related to the rate constants of reactions (6) and (9) by equation (10) where $\alpha = k_6/(k_6 + k_8)$, which can be fitted by suitable least squares treatment in order to determine the coefficients $\Phi^{-1}_4\alpha^{-1}$, $\Phi^{-1}_4(k_5/k_6)$, and $\Phi^{-1}_4(k_9/k_6)$.

$$\Phi^{-1}_{-k} \equiv \Phi^{-1}_6 = \Phi^{-1}_4\alpha^{-1} + \Phi^{-1}_4\left(\frac{k_5}{k_6}\right)\frac{1}{[BR_3]} + \Phi^{-1}_4\left(\frac{k_9}{k_6}\right)\frac{[Q]}{[BR_3]} \tag{10}$$

In fact, one can determine Φ_6 on an arbitrary, rather than an absolute scale; then the combination of the first and last coefficients allows the evaluation of $(k_6 + k_8)/k_9$. If the individual rate constants are required these can be obtained using the limiting quantum yields [equation (11)].

$$\left(\lim_{[BR_3]\to\infty} \Phi_6\right)_{[Q]=0} = \Phi_4\alpha \tag{11}$$

Therefore, this limiting quantum yield is the only one which need be determined absolutely. It should be noticed that if reaction (8) could be neglected, then $\alpha \doteqdot 1$, and it would be enough to normalise the first coefficient to the reciprocal of the quantum yield of intersystem crossing [reaction (4)].

Frequently the second term of equation (10) can be neglected, and the value of $\Phi^{-1}_4(k_5/k_6)$ was usually checked to see if it was within its own error limits. Equation (10) then reduces to equation (12) which corresponds to a straight line and can be fitted by the least squares method.

$$\Phi^{-1}_6 = \Phi^{-1}_4\alpha^{-1} + \Phi^{-1}_4\left(\frac{k_9}{k_6}\right)\frac{[Q]}{[BR_3]} \tag{12}$$

Method B.—In this method, reaction (6) was made to complete with the sensitization of the isomerization of *trans*-piperylene (*t*-Q) to *cis*-piperylene (*c*-Q), which was measured by g.l.c. Under these conditions, the reaction scheme can be represented by equations (2)—(6), (8), and (13)—(15).

$$R^1R^2CO^* + t\text{-}Q \longrightarrow R^1R^2CO + Q^* \tag{13}$$

$$Q^* \longrightarrow t\text{-}Q \tag{14}$$

$$Q^* \longrightarrow c\text{-}Q \tag{15}$$

If the conversion is kept low enough so as to suppress any quenching by *cis*-piperylene produced in reaction (15), then equation (16) will hold where $\beta = k_{15}/(k_{14} + k_{15})$, and has been measured under a variety of experimental conditions.[4]

$$\Phi^{-1}_{c\text{-}Q} \equiv \Phi^{-1}_{15} = \Phi^{-1}_4\beta^{-1}\left(1 + \frac{k_5}{k_{13}}\frac{1}{[Q]} + \frac{k_6 + k_8}{k_{13}}\frac{[R_3B]}{[Q]}\right) \tag{16}$$

The value of $(k_6 + k_8)/k_{13}$ can be obtained from equation (16) in a similar way to $(k_6 + k_8)/k_9$ from equation (10). In fact, if the *cis*- and *trans*-isomers of piperylene are taken to have identical quenching efficiencies, then $k_{13} \equiv k_9$.

Table 1 shows the rate constants for the interaction of several ketone triplets with tri-n-butylborane, taking k_9 as 5×10^9 l mol^{-1} s^{-1}. These rate constants are in general much larger than the values usually observed in hydrogen abstraction [reaction (17)].

$$PhCOMe^* + RH \longrightarrow Ph\dot{C}(OH)Me + R\cdot \tag{17}$$

For example if RH is cyclohexane, $k_{17} \doteqdot 5 \times 10^5$ l mol^{-1} s^{-1}, and if it is toluene, $k_{17} \doteqdot 2 \times 10^5$ l mol^{-1} s^{-1}.[5,6]

An increase in steric hindrance (*e.g.* acetophenone ⟶ propiophenone) or a decrease in triplet energy (*e.g.* acetophenone ⟶ benzophenone) produces a decrease

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* Piperylene has a triplet energy of *ca.* 58·8 kcal mol^{-1}, and is a diffusion-controlled triplet quencher for the ketones used here (except fluorenone).[3]

[3] G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, 1964, **86**, 3197.

[4] G. S. Hammond and A. A. Lamola, *J. Chem. Phys.*, 1965, **43**, 2129; J. Saltiel, L. Metts, A. Sykes, and M. Wrighton, *J. Amer. Chem. Soc.*, 1971, **93**, 5302.

[5] H. Lutz and L. Lindqvist, *Chem. Comm.*, 1971, 493; P. J. Wagner and R. A. Leavitt, *J. Amer. Chem. Soc.*, 1970, **92**, 5806.

[6] C. M. Previtali and J. C. Scaiano, to be published.

in the rate of reaction in a mode which parallels the hydrogen abstraction reactions.

TABLE 1

Rate constants for the reaction of aromatic ketone triplets with tri-n-butylborane at 28 ± 2° in benzene

Ketone [a]	Method	No. exp.[b]	$k_9/(k_6 + k_8)$	$(k_6 + k_8) \times 10^{-8}$ [c]
Acetone	e.s.r.			0·07
ACP	A	10	20 ± 5	2·5
ACP	B	4	33 ± 10	1·5
p-Methyl-ACP	A	17	10 ± 6	5·0
m-Methoxy-ACP	A	28	7 ± 1	7·0
m-Methoxy-ACP	B	8	11 ± 5	4·6
p-Methoxy-ACP	A	14	7 ± 4	7·0
p-Methoxy-ACP	B	6	12 ± 5	4·2
p-Phenyl-ACP	A	8	16 ± 10	3·1
Benzophenone	B	4	110 ± 30	0·46
Propiophenone	B	3	85 ± 30	0·60
p-Cyano-ACP	B	8	9 ± 4	5·5
m-Nitro-ACP	A		No reaction	
m-Nitro-ACP	B		No reaction [d]	

[a] Acetophenone = ACP. [b] Number of experiments. [c] In $l\ mol^{-1}\ s^{-1}$. [d] No triplet input, see text.

m-Nitroacetophenones does not significantly react with organoboranes; this can be associated with a negligible triplet input.*

The effects of substitution in the aromatic ring on the rate of the S_H2 process are not easy to understand. In general, the following factors might be expected to be relevant. (*a*) Change in the triplet energy. (*b*) Change in the relative energies, and/or the energy gap, between $n \longrightarrow \pi^*$ and $\pi \longrightarrow \pi^*$ triplet states, as well as in the degree of 'mixing'. (*c*) Change in Φ_4. (*d*) Change in the reactivity of the triplet state, due to substitution effects similar to those usually described in terms of the Hammett relationships. It is unfortunate that this factor cannot be isolated and examined separately. (*e*) Steric effects.

An examination of equations (10) and (16) shows that factor (*c*) can be isolated from the others, and therefore we do not need to be concerned with it unless Φ_4 is so small that the triplet reactivity (*e.g. m*-nitroacetophenone) cannot be measured.

The change in the triplet energy can be a very important factor, but the change associated with substituents like methyl or methoxy-groups is small and the effect here should not be very significant.

The steric effects of substituents are not likely to be important in the reactions considered here, since all the substituents studied are rather small and are located in *para*- or *meta*-positions.

In Norrish type II photoeliminations, the main factor which determines the reactivity is (*b*), *e.g.* triplet valerophenone is *ca.* 230 times more reactive than *p*-methoxyvalerophenone,[7] the former being $n \longrightarrow \pi^*$ in character, and the latter $\pi \longrightarrow \pi^*$. Similar results have been obtained in the study of intermolecular photoreductions.[8]

Table 1 suggests that reaction (6) is not as selective as the Norish type II reaction in the intermolecular hydrogen abstraction. One possible explanation could be that both triplet states ($n \longrightarrow \pi^*$ and $\pi \longrightarrow \pi^*$) are reactive.

Quantum Yields.—We have measured the quantum yield for the S_N2 process [reaction (6)] for all the ketones for which method A was applicable.

TABLE 2

Absolute quantum yields

Ketone	R in R_3B	$[R_3B]/M$	Φ_6/Φ_4
ACP	Bu^n	0·28	0·59
ACP	Bu^n	0·56	0·62
ACP	Bu^n	0·14	*ca.* 0·55
ACP	Bu^i	0·14	0·26
ACP	Bu^s	0·14	0·29
p-Methyl-ACP	Bu^n	0·14	0·48
p-Methyl-ACP	Bu^n	0·28	0·47
m-Methoxy-ACP	Bu^n	0·07	0·73
m-Methoxy-ACP	Bu^n	0·28	0·66
p-Phenyl-ACP	Bu^n	0·07	0·53
p-Phenyl-ACP	Bu^n	0·28	0·59
p-Methoxy-ACP	Bu^n	0·07	*ca.* 0·54
p-Methoxy-ACP	Bu^n	0·28	*ca.* 0·44

The experimental conditions were such that the second term in equation (10) could be neglected, and there was no significant dependence of quantum yield on organoborane concentration.† Equation (11) therefore holds, and the only important mechanism for the removal of triplets is their interaction with the organoborane.

All the quantum yields which were measured are consistently and significantly lower than unity. This can be taken to mean that reaction (8) is playing an important role in the mechanism, *i.e.* under these conditions equation (18) holds. This is a rather surprising

$$\Phi_6/\Phi_4 = k_6/(k_6 + k_8) \equiv \alpha \qquad (18)$$

result, since it implies that the organoborane, having only σ bonds and no low-lying excited electronic state, is behaving as a good physical triplet quencher with rate constants of the order of $10^8\ l\ mol^{-2}\ s^{-1}$.

Solvent Effects.—The energy gap between the $n \longrightarrow \pi^*$ and $\pi \longrightarrow \pi^*$ triplets has been shown to be dependent on the polarity of the medium.[9,10] For some ketones the addition of a polar solvent (*e.g.* an alcohol) to the medium can result in an inversion of states, leading to a low-lying $\pi \longrightarrow \pi^*$ triplet; such is the case with acetophenone. We thought than an examination of this effect might lead to a better understanding of the importance of factor (*b*). The effect of changes in the composition of the solvent (benzene–t-butyl alcohol) on the quantum yield of reaction under selected experimental conditions was therefore investigated.

Table 3 illustrates two series of results. The first refers to experiments in the absence of quencher, and again under conditions where equation (11) holds. The second refers to conditions of partial quenching by

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* At least of triplets which will sensitize the isomerization of *trans*-piperylene. This is probably due to a low value of Φ_4.

† Equating Φ_{-k} and Φ_6 implies the assumption that the products of reaction (6) do not revert to the organoborane and ground-state ketone.

[7] P. J. Wagner, *Accounts Chem. Res.*, 1971, **4**, 168.

[8] *E.g.*, N. C. Yang and R. L. Dusenberry, *J. Amer. Chem. Soc.*, 1968, **90**, 5899.

[9] H. Lutz, M. C. Duval, E. Beheret, and L. Lindqvist, VI International Conference on Photochemistry, Bordeaux, 1971, Abstract No. 19.

[10] R. Rusakowicz, G. W. Byers, and P. A. Leermakers, *J. Amer. Chem. Soc.*, 1971, **93**, 3263.

piperylene. In both, the quantum yield decreases on addition of the alcohol, but the effect is larger in the absence of quencher. Only relative quantum yields are quoted in Table 3, since they are more accurate and easier to obtain than absolute values. They can be put on an absolute basis using the data from Tables 1 and 2.

TABLE 3

Solvent dependence of the quantum yield in the acetophenone–tri-n-butylborane reaction

$[\mathrm{Bu^tOH}]/\mathrm{M}$ [a]	[Piperylene]/M	Φ_6/Φ_6^0 [b]
0		1·0
1·8		0·54
3·6		0·48
6·5		0·39
0	0·0067	1·0
0·5	0·0067	0·92
1·7	0·0067	0·81
2·5	0·0067	0·78
4·9	0·0067	0·67

[a] The co-solvent is benzene. [b] Φ_6^0 Is the quantum yield in the absence of t-butyl alcohol for the same concentration of piperylene.

Reactivity of Different Boranes.—Our previous results showed that the S_H2 reactions of acetone and of di-isopropyl ketone triplets with organoboranes are sterically controlled.[2] We have now measured the rate of reaction of acetophenone triplets with the three isomeric (n, s, and iso) tributylboranes. The results are given in Table 4; the figure for tri-s-butylborane is much less accurate than the others as a result of difficulties which are discussed in the Experimental section. Comparable figures are included in Table 4 for acetone triplets and for t-butoxyl radicals. The three reactions have very similar features.

TABLE 4

Rate constants for the quenching (chemical and physical) of acetophenone triplets by several organoboranes

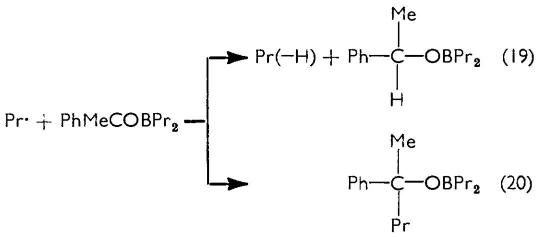
	k [a]		
R_3B	$PhCOCH_3$* [b]	Me_2CO * [c]	$\mathrm{Bu^tO\cdot}$ [d]
$\mathrm{Bu_3^nB}$	2×10^8	7×10^6	3×10^7
$\mathrm{Bu_3^iB}$	$3{\cdot}5 \times 10^7$	8×10^4	1×10^6
$\mathrm{Bu_3^sB}$	*ca.* 5×10^6	$<10^4$	2×10^5

[a] In units of l mol^{-1} s^{-1}. [b] $k_6 + k_8$ or k_{21a}. [c] Ref. 2. [d] Ref. 11.

The Significance of Hydrogen Abstraction.—If hydrogen abstraction by reaction (7) made a similar contribution to homolytic substitution at boron by reaction (6) the values of k_6 and of Φ_6 which are given in the tables would be overestimates, corresponding in fact to $k_6 + k_7$ and $\Phi_6 + \Phi_7$ respectively. The following facts suggest that k_7 can be neglected under our experimental conditions. (*a*) No ketyl radicals, $\mathrm{PhMe\dot{C}OH}$, could be detected by e.s.r. when mixtures of acetophenone and tri-n-butylborane were irradiated. (*b*) t-Butoxyl radicals, which are good analogues of ketone triplets, react only at the boron centre.[11,12] (*c*) The rate constants we obtained are larger than those which are observed in the abstraction, by carbonyl triplets, of hydrogen from even very weak C–H bonds.

The S_H2 reaction at the boron centre in tri-s-butylborane is comparatively slow, and a combination of experimental difficulties precluded a detailed examination of this system. Here, then, we cannot fully rule out some contribution from reaction (7).

The Reaction which Removes Radicals.—The radicals $R^1R^2\dot{C}OBR^3_2$ and $R^3\cdot$ are removed from the system by a series of combination and disproportionation reactions which lead to molecular products. In the photolysis of mixtures of acetophenone and tri-n-propylborane in benzene solution we were able to measure the relative yields of 1-phenylethanol and 2-phenylpentan-2-ol, which were obtained when the products were hydrolysed. The ratio of these two compounds, 0·25 ± 0·05, can be taken to correspond to the value of k_{19}/k_{20}.



$$\mathrm{Pr\cdot + PhMeCOBPr_2} \longrightarrow \mathrm{Pr(-H) + Ph{-}CH(Me){-}OBPr_2} \quad (19)$$

$$\mathrm{Pr\cdot + PhMeCOBPr_2} \longrightarrow \mathrm{Ph{-}C(Me)(Pr){-}OBPr_2} \quad (20)$$

Mechanism.—The following results tend to suggest that the actual reaction mechanism is not as simple as shown in reactions (6)—(8). (*a*) $\pi \longrightarrow \pi^*$ Triplets have a reactivity similar to those of $n \longrightarrow \pi^*$ triplets (see Table 1). (*b*) The limiting quantum yield of the S_H2 reaction [equation (11)] is less than unity, implying that the organoborane behaves as both a chemical and a physical quencher. (*c*) The rate constants for aromatic ketone triplets are *ca.* 30 times larger than for acetone.[2] (*d*) The limiting quantum yield of equation (11) is decreased by the addition of t-butyl alcohol implying that k_8/k_6 is increased. The effect of the alcohol is smaller for the partially quenched reaction than in the limiting case; this can be taken to mean that $k_6 + k_8$ is increased by the addition of the alcohol. (*e*) Tri-isobutylborane is more reactive than tri-s-butylborane but the latter gives the larger quantum yield.

The first of these points deserves to be re-emphasised. Even fluorenone, having a typically $\pi \longrightarrow \pi^*$ triplet and a rather low triplet energy (53·3 kcal mol^{-1})[13] undergoes significant photoreduction in the presence of tri-n-butylborane; *p*-phenylacetophenone is another clear example.*

We believe that the mechanism (21) which is consistent with all our experimental observations, probably

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* Butyrophenone undergoes a triplet type II reaction with a high quantum yield at room temperature, but *p*-phenylbutyrophenone does not.[14]

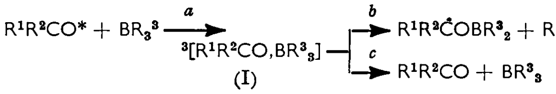
[11] Part III, A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc.* (*B*), 1971, 1823.

[12] J. Grotewold, E. A. Lissi, and J. C. Scaiano, *J. Chem. Soc.* (*B*), 1971, 1187.

[13] J. G. Calvert and J. N. Pitts, 'Photochemistry,' Wiley, New York, 1967, p. 298.

[14] E. J. Baum, J. K. S. Wan, and J. N. Pitts, *J. Amer. Chem. Soc.*, 1966, **88**, 2652.

describes best the reaction between aromatic ketones and boranes. Although we do not understand fully the



$$R^1R^2CO^* + BR^3_3 \xrightarrow{a} {}^3[R^1R^2CO,BR^3_3] \begin{cases} \xrightarrow{b} R^1R^2\dot{C}OBR^3_2 + R^3\cdot \\ \xrightarrow{c} R^1R^2CO + BR^3_3 \end{cases} \quad (21)$$

(I)

type of interaction involved in (I) it is clear that two unpaired electrons are involved with parallel spins: it could be a transition state or a true intermediate. The presence of an aromatic ring favours reaction (21*a*), and may even be a necessary condition for the formation of (I). Reaction (21*c*), unlike reaction (21*b*), involves spin inversion and leads to two ground-state singlets; spin flip probably occurs as a first step, giving a ground-state pair which then dissociates.

The rate of reaction (21*a*) is then determined by the complexing power of the triplet rather than by its radical-like characteristics. From Table 1 it would seem that $\pi \longrightarrow \pi^*$ rather than $n \longrightarrow \pi^*$ triplets undergo this process preferentially.

The solvent effect can be interpreted as follows. The limiting quantum yield, previously written as $\alpha = k_6/(k_6 + k_8)$ can be rewritten as $\alpha = k_{21b}/(k_{21b} + k_{21c})$.

The decrease in limiting quantum yield should therefore be associated with a change in the relative rate of the dissociative processes undergone by (I). The possible increase of k_{21a} mentioned above would be consistent with (*a*) an enhancement of the reactivity due to an increase in $\pi \longrightarrow \pi^*$ character, and (*b*) a stabilization of (I) due to solvation as a result of its polar character.

The value of k_{21a} is larger for tri-isobutylborane than for tri-s-butylborane, as expected for a sterically controlled process. The limiting quantum yield is larger for tri-s-butylborane probably because k_{21b} is determined by the thermochemistry of the process, *i.e.* by the stability of the alkyl radical which is produced.

EXPERIMENTAL

Reagents.—Trialkylboranes were prepared by standard methods from the appropriate Grignard reagents and were stored and handled under oxygen-free nitrogen. N.m.r. spectroscopy showed that they contained <2% of the oxidation product R_2BOR. All the ketones were used as purchased except benzophenone and fluorenone which were recrystallised twice. Fisons A.R. grade benzene was used as solvent without further purification. The commercial piperylene (Aldrich) contained 23·5% of the *cis*-isomer. The pure *cis*- (Fluka) and *trans*- (Aldrich) compounds were shown by g.l.c. to be free from isomeric material.

Preparative Experiments.—Acetophenone (0·26 mmol) in benzene (3 ml) containing tripropylborane (0·51 mmol) was irradiated for 8 h using a 125 W Hanovia medium pressure mercury arc. The sample was contained in a Pyrex tube located 3—4 cm from the source. After the irradiation, water (0·05 ml) was added and the sample was examined by g.l.c. using a Perkin-Elmer F11 instrument (Antarox CO990 on Chromosorb W at 200 °C). The product contained unreacted acetophenone (4%), 2-phenylpentan-2-ol (15%), and 1-phenylethanol (4%) as well as n-hexane and heavier non-identified products.

Quantum Yields.—Quantum yields used in equations (10) and (16) were determined using a ' merry-go-round ' apparatus immersed in water at 28 ± 2 °C.[15] Unfiltered light from a Hanovia 125 W medium pressure mercury arc was used to irradiate samples (3 ml) contained in matched Pyrex tubes. The concentration range of the ketones was chosen so as to ensure a maximum absorption of the 313 nm line and a very small absorption of the 365/6 nm lines.

For acetophenone the initial concentration was always about 4×10^{-2}M, and for all the other ketones was within a factor of two of this figure. Irradiation times were of the order of 10^4 s in method A, and about 2×10^3 s in method B. Radiation doses were about $1{\cdot}25 \times 10^{15}$ quanta ml^{-1} s^{-1}. Ketones were analysed by g.l.c. using a 2 m column of Apiezon L on Chromosorb P (15 : 85) between 180 and 240°. A similar 4 m column at 65° was used to determine *cis* : *trans* ratios of piperylene.

Absolute Quantum Yields.—These were determined using the sensitization of the isomerization of *cis*-piperylene as actinometer,[4] and taking the efficiency of the *cis* $\longrightarrow$ *trans* isomerization as 0·55. This technique in fact measures triplet input rather than radiation dose. The two quantities are related by Φ_4, therefore the quantum yields of Table 2 are given as Φ_6/Φ_4.

The quantum yields were reproducible to *ca*. ±0·04. The main reason for this rather large error is that the results are derived from g.l.c. measurements of ketone consumption, which presented a series of experimental difficulties. These were caused by the rather high temperatures needed in the g.l.c. injector which caused the organoborane to decompose to a certain extent into olefin and dialkylborane; this latter can add to the carbonyl double bond leading to an unwanted consumption of ketone. Under these conditions, the injector temperature becomes a critical factor. These difficulties were most serious with the less volatile ketones and the more unstable organoboranes, particularly tri-s-butylborane, and the values derived for this compound are subject to rather large errors.

Some error may be introduced by absorption of light by traces of peroxide formed during transfer of the organoborane, but this cannot be serious in reactions involving long irradiations.

E.s.r. Experiments.—These were carried out using a Varian E4 spectrometer with auxilliary equipment as described in our earlier papers [2,11]

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[15] The experimental set-up has been described previously, A. G. Davies, B. P. Roberts, and J. C. Scaiano, *J.C.S. Perkin II*, 1972, 803.