Homolytic Substitution at Boron by the Triplet State of Ketones

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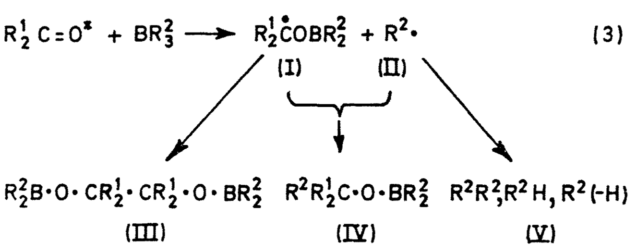
Summary In the triplet state, ketones (R^1_2CO) will react with trialkylboranes (R^2_3B) by a bimolecular homolytic substitution to give the radicals $R^1_2\dot{C}OBR^2_2$ and $R^2\cdot$.

ALKOXYRADICALS have recently been shown to react with a variety of organometallic compounds to displace the organic radicals by the S_H2 process of equation (1).[1]

$$R^1O\cdot + MR^2_n \rightarrow R^1OMR^2_{n-1} + R^2\cdot \qquad (1)$$

The reactions and reactivities of alkoxyradicals and of ketones which are excited to the $n \rightarrow \pi^*$ triplet state are often similar.[2] We have now shown that the triplet state of ketones will react with organoboranes to displace an organic radical by equation (3).



If the reactions are carried out in the cavity of an e.s.r. spectrometer, the superimposed spectra of the radicals (I) and (II) can be observed. For example, irradiation of a solution of acetone (2·4 M) and tri-n-butylborane (0·7 M) in toluene at −85° with u.v. light from a Mazda ME/D 1000 W high-pressure mercury arc gives (Figure 1) the butyl radical (*cf.* ref. 1a) and the radical $Me_2\dot{C}OBBu_2$ [*a*(H) 20·6, $a(^{11}B)$ 8·3 G;† $g(I) - g(Bu^n\cdot) = 0{\cdot}00071$]. Identical spectra were obtained in cyclopentane solvent. The overall concentrations of the two radicals are equal,‡ implying that the rate of self-reaction of the radical $Me_2\dot{C}OBBu_2$ is similar to that of the butyl radical, *i.e.* approximately $2 \times 10^9 M^{-1} s^{-1}$.[3] Pinacol (from III; R^1 = Me, R^2 = Bu), 1,1-dimethylpentanol (from IV; R^1 = Me, R^2 = Bu), and octane (V; R^1 = *Bu*), were identified in the product after hydrolysis.

Under the same conditions, hexadeuterioacetone gave the superimposed spectra of the butyl radical and of the radical (I; $R^1 = CD_3$, R^2 = Bu) with a value of *a*(D) of 3·2 G [calc. from $g(D)/g(H) = 0{\cdot}1531$, 3·16 G].

Tri-isobutylborane and tri-s-butylborane reacted with acetone in the same way; the coupling constants in the radical (I; R^1 = Me) were *a*(H) = 20·6, $a(^{11}B)$ = 8·3 G, for $R^2 = Bu^i$, and *a*(H) = 20·6, $a(^{11}B)$ = 7·9 G, for $R^2 = Bu^s$ (at −85°). In the reaction of tri-s-butylborane the spectra were less intense than for $R^2 = Bu^n$ or Bu^i. In preliminary competition experiments of the type carried out for t-butoxyradicals,[4] tri-isobutylborane was shown to be about 10 times less reactive than tri-n-butylborane towards the acetone triplet at −80°. This might be taken to imply that the various boranes show the same sequence of reactivity towards triplet state ketones and t-butoxy radicals, *viz.* $Bu^n_3B > Bu^i_3B > Bu^s_3B$.[4]

Signals of the n-butyl radical, superimposed on a second radical, were also observed when samples of tri-n-butylborane and diethyl ketone, acetophenone, benzophenone, fluorenone, biacetyl, or benzil were irradiated. With the aromatic ketones, the intensity of the spectrum of the radical (I) was stronger than that of the butyl radical, suggesting that the self-reaction of the radical (I; R = Aryl) is relatively slow. Spectrophotofluorimetric measurements showed that the phosphorescence of benzophenone and of fluorenone in benzene was markedly quenched by the addition of tributylborane.§

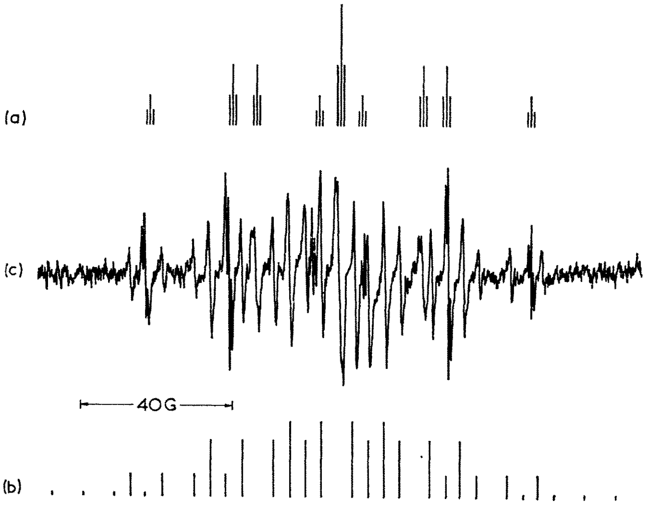


FIGURE 1. *E.s.r. spectrum from irradiation of acetone–tributylborane mixture.* (a) *Calculated spectrum of* Bu·; (b) *calculated spectrum of* $Me_2\dot{C}{\cdot}O{\cdot}BBu_2$; (c) *observed superimposed spectra.*

To check the suggested mechanism, the concentration of the butyl radical was determined, by e.s.r. spectroscopy, as a function of the concentration of tetramethylethylene (Q) which was added as a quencher to the reaction between acetone and tributylborane (0·76 M) in toluene solution.

$$R^1_2CO^* \left\{ \begin{array}{l} \xrightarrow{\ a\ } R^1_2CO \\ \xrightarrow{\ b\ } R^1_2CO + h\nu \\ \xrightarrow{\ c\ } \text{products} \end{array} \right. \qquad (4)$$

If the triplet state ketone can undergo processes (4) and (5), as well as react by equation (3), and it is assumed that

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† For the radical $\dot{C}H_2OB(OMe)_2$, $a(^{11}B)$ = 0·35 G at −34°.[1c] This difference might be ascribed to the larger Lewis acidity of the boron atom, or to some deviation from planarity, in the radical (I).

‡ Only the species (I) which contains the ^{11}B isotope (81·17% abundance, $I = 3/2$) is observed.

§ Grotewold and Lissi[5] showed that the phosphorescence of biacetyl in the gas phase is quenched by triethylborane, and suggested that chemical quenching is involved.

the rate of formation of the ketone triplet state is identical in the presence and absence of quencher, the behaviour of

$$R^1_2CO^* + Q \left\{ \begin{array}{l} \xrightarrow{\text{a}} R^1_2CO + Q \\ \xrightarrow{\text{b}} R^1_2CO + Q^* \\ \xrightarrow{\text{c}} \text{products} \end{array} \right. \qquad (5)$$

the system can be described by equation (6), where $[R^2\cdot]_0$ is the concentration of $R^2\cdot$ in the absence of Q.

$$[R^2\cdot]_0^2/[R^2\cdot]^2 = 1 + k_5[Q]/(k_4 + k_3[R^2_3B]) \qquad (6)$$

The results are shown in Figure 2, where the value of $k_5/(k_4 + k_3[R^2_3B])$ is $0{\cdot}75\text{M}^{-1}$ at −80°. If k_4 is neglected, and k_5 is assumed to be temperature independent at $5 \times 10^7\ \text{M}^{-1}\,\text{s}^{-1}$,[6] an upper limit for k_3 can be estimated to be approximately $9 \times 10^7\ \text{M}^{-1}\,\text{s}^{-1}$ at −80°. This is to be compared with a value of $3 \times 10^7\ \text{M}^{-1}\,\text{s}^{-1}$ for the equivalent S_H2 reaction of the t-butoxyradical at the same temperature.[4]

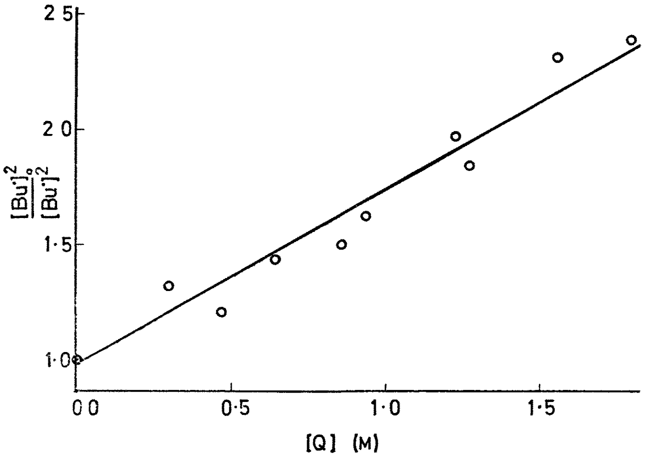

FIGURE 2. *Dependence of* $[Bu\cdot]^2_0/[Bu\cdot]^2$ *on* $[Me_2C{:}CMe_2]$, [Q], *in the reaction of* Me_2CO^* *with* Bu_3B *in toluene at* −80°.

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