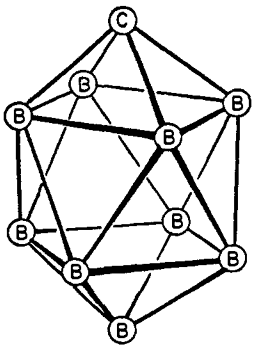

Figure 1. Skeletal Structure of $1\text{-}B_9H_9CH$.

polyhedron with one apical boron atom replaced by a carbon atom (Figure 1). The B^{11} spectrum of $CsB_{11}H_{11}CH$ in acetonitrile consists of three doublets which, though poorly resolved even at 32.1 Mc, appear to be of relative intensities 1:5:5 as required for an icosahedral monocarborane.

Todd and co-workers have recently reported the reaction of decaborane with isocyanides to form aminocarboranes of the general formula $B_{10}H_{12}CNH_2R$, and the N-alkylation of these compounds.[5] The melting point reported for $B_{10}H_{12}CN(CH_3)_3$ (344–345° dec) is close to that which we find (345–350°) for this compound as prepared in eq 1. The B^{11} nmr spectrum at 32.1 Mc reported by Todd is compatible with one determined on our sample at 19.2 Mc. Additionally, and more conclusively, the benzylation of $B_{10}H_{12}CNH_3$ (from eq 1) gives $B_{10}H_{12}CNH_2CH_2C_6H_5$ which is identical by mixture melting point and infrared and powder X-ray analysis with $B_{10}H_{12}CNH_2CH_2C_6H_5$ as prepared from decaborane and benzyl isocyanide.[6] It is clear, therefore, that Todd's route and the mild acidification of $B_{10}H_{13}CN^{2-}$ lead to the same class of aminocarboranes. Boron[11] nmr analysis shows that the carborane skeleton is not affected by the deamination to $B_{10}H_{12}CH^-$. It appears probable from B^{11} nmr spectroscopy that $B_{10}H_{11}(OH)CNH_3$ and its N-methylated derivative (eq 4) are also members of this structural class.

The aminocarboranes $B_9H_{11}CNH_3$ and $B_9H_{11}CN(CH_3)_3$ (eq 4 and 5) as well as $B_{10}H_{10}CH^-$ (eq 1) represent other new carborane series, which will be discussed in more detail in a subsequent paper. Boron[11] nmr analysis suggests a highly symmetrical structure for $B_{10}H_{10}CH^-$; this anion is isoelectronic with $B_9C_2H_{11}$.[7]

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[6] Acknowledgment for a sample of the decaborane–benzyl isocyanide product is made to Dr. W. R. Hertler, who independently discovered the decaborane–isocyanide reaction.

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Reactivity of Triplet States

Sir:

The relative reactivities of the n,π* triplet states of several ketones have been compared with that of *t*-butoxy radicals[1,2] in hydrogen abstraction reactions. We wish to report a comparison of the absolute reactivities of the triplet states of diethyl ketone and of benzophenone in hydrogen abstraction reactions under oxidative conditions. This comparison is made possible by the recent finding of Borkman and Kearns[3] that the triplet yield of acetone, like that of benzophenone,[4,5] is nearly unity.

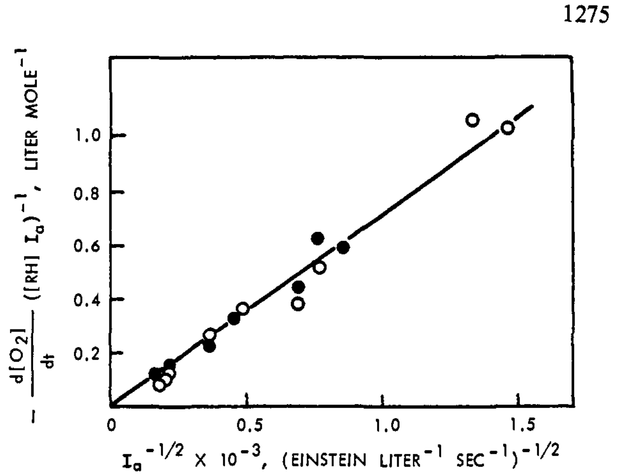

Figure 1. Photooxidations of cumene sensitized by benzophenone and by diethyl ketone, at 62.5° and 3130 A: ○, benzophenone; ●, diethyl ketone.

A solution of the ketone in 1:2 cumene–chlorobenzene was irradiated by either 3130- or 3650-A light under a constant oxygen pressure of 1 atm. The rate of oxidation was recorded automatically and the incident light intensity was measured before and after each irradiation. The purification of the compounds used, the optical system with associated filters, the oxygen absorption equipment, and the actinometry have been described elsewhere.[6] Over 95% of the light absorbed was absorbed by the ketone in all the experiments. Only the constant initial rates of oxidation, corresponding to less than 10% of the ketone reacted, were recorded. At very long irradiation times, the rates become faster or slower than the initial rate depending upon the amount of ketone initially present. The amount of unreacted benzophenone was determined spectrophotometrically; the amount of unreacted diethyl ketone was determined by gas chromatography. The results are summarized in Tables I and II.

Assuming quantitative intersystem crossing efficiencies for both diethyl ketone and benzophenone, using the usual mechanism for autoxidation,[6] we derive an expression for the initial rate of oxidation as

$$-\frac{d[O_2]}{dt} = \Phi^T I_a + \frac{k_p}{k_t^{1/2}}[RH](\Phi^T I_a)^{1/2} \qquad (1)$$

where I_a is the absorbed light intensity, Φ^T is the quantum yield of initiation by the triplet state, k_p and k_t are the rate constants of propagation and termination, respectively, and [RH] is the cumene concentration. To calculate the values of Φ^T, we plot $(-d[O_2]/dt)/[RH]I_a$ *vs.* $I_a^{-1/2}$ in Figure 1. The results

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[2] C. Walling and M. Gibian, *J. Am. Chem. Soc.*, **86**, 3902 (1964).

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[5] W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961).

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Table I. Benzophenone-Initiated Photoxidation of Cumene at 62.5° and 3130 A

[Benzophenone], M	[Cumene], M	$I_0 \times 10^8$, einsteins cm^{-2} sec^{-1}	$I_a \times 10^5$, einsteins l.$^{-1}$ sec^{-1}	$-$d[O$_2$]dt $\times 10^6$, moles l.$^{-1}$ sec^{-1}
1.0	1.98	2.14	2.14	4.48
0.3	2.25	1.96	1.96	6.57
0.09	2.34	2.02	2.02	6.88
0.0081	2.38	2.97	2.51	6.52
0.0024	2.38	4.96	2.14	6.67
0.00073	2.38	4.62	0.71	4.55
0.00060	2.38	3.92	0.428	3.64
0.00022	2.38	4.23	0.207	1.86
0.00020	2.38	3.72	0.167	2.02
0.000066	2.38	3.77	0.0566	1.43
0.000060	2.38	3.55	0.049	1.20

Table II. Diethyl Ketone Initiated Photooxidation of Cumene at 62.5° and 3130 A

[Diethyl ketone], M	[Cumene], M	$I_0 \times 10^8$, einsteins cm^{-2} sec^{-1}	$I_a \times 10^5$, einsteins l.$^{-1}$ sec^{-1}	$-$d[O$_2$]dt $\times 10^6$, moles l.$^{-1}$ sec^{-1}
1.03	2.13	3.13	3.28	8.42
0.50	2.25	3.40	2.24	8.26
0.226	2.31	2.06	0.77	4.17
0.10	2.37	2.64	0.494	4.05
0.0503	2.38	2.06	0.208	2.25
0.0224	2.38	3.72	0.171	2.60
0.0104	2.38	4.10	0.088	1.26

of diethyl ketone and of benzophenone sensitized photooxidations thus plotted are seen to be superimposable. The slope of the common line in Figure 1 is simply $k_p(\Phi^T/k_t)^{1/2}$. The rate constant ratio $k_p/k_t^{1/2}$ for cumene oxidation has been found[7] to be 4.5×10^{-3} (l./mole sec)$^{1/2}$, from which we obtained a value of $\Phi^T =$ 0.0255 for both systems.

The quantum yield Φ^T is defined as $k_r[\mathrm{RH}]/(k_r[\mathrm{RH}] + k_q[\mathrm{O_2}] + k_d + k_{sol}[\mathrm{sol}])$, where k_r, k_q, k_d, and k_{sol} are the rate constants for the hydrogen abstraction, oxygen quenching, decay, and solvent quenching reactions of the triplet state, respectively. The values of these rate constants for benzophenone have been estimated by Hammond, *et al.*:[8] $k_d = 2.6 \times 10^5$ sec^{-1}; $k_q = 10^9$ l. mole^{-1} sec^{-1}; $k_r = 7 \times 10^4$ l. mole^{-1} sec^{-1}; $k_{sol}{}^9 = 3 \times 10^4$ l. mole^{-1} sec^{-1}. The solubility of oxygen in a 1:2 mixture of cumene and chlorobenzene at 62.5° was determined to be 5.5×10^{-3} mole l.$^{-1}$. Substitution of these values into the definition for the quantum yield gives a value of $\Phi^T = 0.027$ for benzophenone, in agreement with the value of 0.025 found here.

Closer examination of the expression for quantum yield shows that the value of $k_q[\mathrm{O_2}]$ is about ten times the sum of the other three terms. Quenching of the triplet state by oxygen has been found to be diffusion limited for many compounds.[11] If one assumes the oxygen quenching of the diethyl ketone triplet state is also diffusion limited and large compared to other triplet decay processes, the reactivities of the triplets states of these ketones can be calculated. The values of the diffusion-limited quenching rate constants were first obtained from known relationships.[15] These are $(k_q)_{\mathrm{BP}} = 1.2 \times 10^9$ l. mole^{-1} sec^{-1} and $(k_q)_{\mathrm{DEK}} = 1.4 \times 10^9$ l. mole^{-1} sec^{-1}. From these values, the triplet state of diethyl ketone is found to be about 20% more reactive than the benzophenone triplet state, with values of k_r estimated to be 8×10^4 l. mole^{-1} sec^{-1} and 7×10^4 l. mole^{-1} sec^{-1}, respectively. Even though the absolute values of these rate constants are subject to some uncertainty, it is safe to conclude that *the triplet states of diethyl ketone and benzophenone abstract hydrogen with comparable reactivities.*

Experiments were also carried out at 3650 A for benzophenone-sensitized photooxidations. The quantum yields of initiation at this wavelength are found to be indistinguishable from the results obtained at 3130 A.

The method described above can be extended to determine the reactivities of other ketones, for example, the derivatives of benzophenone. The values of diffusion-limited k_q's for these derivatives should be closely similar; ratios of k_r's can be obtained with good accuracy. Those results will be reported shortly.

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(8) G. S. Hammond, W. P. Baker, and W. M. Moore, *ibid.*, **83**, 2795 (1961).

(9) This value was given for toluene. Even though chlorobenzene is expected to quench benzophenone triplet with somewhat higher efficiency[10] than toluene and cumene, the three were assumed here to have equal efficiencies. The error thus introduced would not be appreciable because solvent quenching is small compared to oxygen quenching.

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(15) See references cited by Hammond, *et al.*[5]

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Inner-Sphere Reduction of an Azidocobalt(III) Complex by Vanadium(II). Kinetics of Formation and Decomposition of the Metastable Monoazidovanadium(III) Ion[1]

Sir:

The question of whether vanadium(II) reductions of cobalt(III) complexes proceed by inner-sphere or outer-sphere mechanisms has been considered previously by several workers.[2-6] The evidence has been indirect, however, with arguments based largely on comparisons of reactivity patterns toward different complexes. This situation stands in contrast to that for chromium(II) reductions, where the very slow decomposition of the metastable monosubstituted chromium(III) complex, primary product of the inner-sphere pathway, permits its isolation and identification. The high rate at which vanadium(III) substitution processes come to equilibrium has hitherto prevented the finding of similar direct evidence for vanadium(II).

Consider the alternate mechanisms for reduction of the cobalt(III) complex $\mathrm{CoL_5X^{2+}}$ by V(II). In an outer-sphere process (eq 1), the immediate product is the stable

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(1) Work performed in the Ames Laboratory under the auspices of the U. S. Atomic Energy Commission. Contribution No. 2007.

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