(90% of the data available) were observable and were estimated visually. The crystal used was small with approximate dimensions 0.40 $\times$ 0.13 $\times$ 0.05 mm; absorption corrections were therefore neglected.

Positions for the five bromine atoms were obtained from the Patterson projection and were confirmed by means of difference Fourier syntheses. After refinement using a full-matrix least-squares program[3] with isotropic temperature parameters, an electron density synthesis was computed which showed the whole structure to consist of a tribromo-substituted five-membered ring linked by one bond to a dibromo-substituted six-membered having a third substituent light atom.

Both rings were assumed to be unsaturated; this was supported both by the empirical formula and by the projected distances between the bromine atoms. The interpretation of the ultraviolet spectrum was assumed to be correct and the nitrogen was placed as the unsubstituted atom in the five-membered ring. The oxygen atom could not be identified on the basis of peak heights in the synthesis. However, only one position was consistent with an unsaturated six-membered ring and the oxygen was assigned, therefore, as the light atom substituent to the ring, establishing the structure of the molecule as 2-(3,5-dibromophenyl)-3,4,5-tribromopyrrole (Figure 1).

The complete structure was refined by least-squares and the final discrepancy factor was 0.13. The final electron density synthesis is shown in Figure 2 with the structure superimposed.

The proposed structure, which is consistent with all the physical properties of the antibiotic, has been synthesized and shown to be identical in all respects with the antibiotic material.[4]

Acknowledgment. This work was supported through Research Grant GB 2898 from the National Science Foundation.

[3] W. R. Busing and H. A. Levy, personal communication, 1959. A crystallographic least-squares refinement program for the IBM 704, U. S. Atomic Energy Commission Publication ORNL 59-4-37.

[4] S. Hanessian and J. S. Kaltenbronn, *J. Am. Chem. Soc.*, **88**, 4509 (1966).

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Deuterium Isotope Effects in the Photochemistry of 2-Hexanone

Sir:

Substitution of hydrogen with deuterium in organic compounds may exert a marked effect on certain properties of their excited states. Hutchison and Mangrum[1] have demonstrated that substitution of hydrogen in naphthalene by deuterium increases the lifetime of its triplet state 8–9-fold. The deuterium isotope effect on the physical behavior of excited states may, at least in part, be attributed to the differences in the magnitude of the vibrational overlap integral between the ground and the excited states.[5,6] In addition, the usual isotope effect involved in the breaking of a C–D bond may cause a modification in the photochemical behavior of an organic compound. The extent of these isotope effects may depend on how extensively the C–D bond interacts with the excited states. Under the influence of ultraviolet light, ketones with γ hydrogens undergo the type II process and cyclobutanol formation, *i.e.*, the excited carbonyl function interacts with the γ hydrogens exclusively.[7] Recent contributions from various laboratories have demonstrated that these reactions proceed *via* both the n $\rightarrow$ π^* singlet and triplet states.[8–11] It was felt that substitution of the γ hydrogen with deuterium may exert an effect on these reactions. This communication deals with the photochemistry of 2-hexanone, 2-hexanone-5-*d*, 2-hexanone-5,5-d_2, and 2-hexanone-d_{12}.[12,13]

The labeled 2-hexanones were synthesized *via* the acetoacetic ester synthesis with the appropriate starting material. The photochemical apparatus used was similar to the one reported by Wagner and Hammond.[8] The filter system consisted of a potassium chromate solution (0.6 g/l. with 0.17 g/l. of KOH added) and Corning 7-54 filters to isolate the 3130-A emission of mercury. The emission intensity was monitored with a ferrioxalate actinometer and found to be 2.4 $\times$ 10^{17} quanta min^{-1} cm^{-2}. Multiple runs were carried out with 2-hexanones in pentane at variable quencher concentrations. The irradiations were interrupted when approximately 10% of the 2-hexanones were decomposed in the absence of the quencher. At this point, negligible amounts of by-products were detected. The progress of reaction and the quantum yields of formation of individual products were followed by quantitative gas chromatography. The reproducibility was found to be better than ±0.003 on the quantum yield determinations. The quencher used was *cis*-1,2-dichloroethylene. When piperylene was used as the quencher, chemical reactions between the deuterated 2-hexanones and piperylene were observed although this was not true in the case of 2-hexanone. The quantum yields of the type II process of the 2-hexanones began to level off and remained constant at moderate to high quencher concentrations. The quantum yields remaining at high quencher concentrations were attributed to the reactivities of the n $\rightarrow$ π^* singlet states.[8] The differences between the total quantum yields ($[\Phi]_{\text{total}}$) and the quantum yields attributed to the n $\rightarrow$ π^* singlet states ($[\Phi]_S$) were taken as the quantum yields due to the triplet states ($[\Phi]_T$). The data for the quantum yields of the type II processes and cyclobutanol formations are summarized in Table I. The Stern–Volmer plots for the type II

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[1] For examples, see ref 2–4, and C. A. Hutchison, Jr., and W. M. Mangrum, *J. Chem. Phys.*, **32**, 1261 (1960).

[2] M. R. Wright, R. P. Frosch, and G. W. Robinson, *ibid.*, **33**, 934 (1960).

[3] S. G. Hudley, H. E. Rast, and R. A. Keller, *ibid.*, **39**, 705 (1963).

[4] R. E. Kellogg and R. P. Schwenker, *ibid.*, **41**, 2860 (1964).

[5] R. P. Frosch and G. W. Robinson, *ibid.*, **38**, 1187 (1963).

[6] W. Siebrand, *ibid.*, **44**, 4055 (1966).

[7] N. C. Yang and D. H. Yang, *J. Am. Chem. Soc.*, **80**, 2913 (1958).

[8] P. J. Wagner and G. S. Hammond, *ibid.*, **87**, 4010 (1965); **88**, 1245 (1966).

[9] T. J. Dougherty, *ibid.*, **87**, 4011 (1965).

[10] P. Ausloos and R. E. Rebbert, *ibid.*, **86**, 4512 (1964).

[11] J. L. Michaels and W. A. Noyes, Jr., *ibid.*, **85**, 1027 (1963).

[12] Some aspects of the photochemistry of 2-hexanone-5,5-d_2 has been reported by R. Srinivasan, *ibid.*, **81**, 5061 (1959).

[13] Photochemistry of 2-pentanone-4,5,5-d_3 and the relative reactivities of its γ-H and γ-D atoms have been reported by R. P. Borkowski and P. Ausloos, *J. Phys. Chem.*, **65**, 2257 (1961).

Table I

Compound	$\Phi_{-\text{ketone}}$[a] Total	S	T	$\Phi_{\text{type II}}$[b] Total	S	T	$\Phi_{\text{cyclobutanols}}$[c] Total	S	T
2-Hexanone	0.327	0.104	0.233	0.252	0.097	0.155	0.075	0.007	0.068
2-Hexanone-5-*d*	0.369	0.078	0.291	0.273	0.072	0.201	0.096	0.006	0.090
2-Hexanone-5,5-d_2	0.411	0.052	0.359	0.298	0.047	0.251	0.113	0.005	0.108
2-Hexanone-d_{12}	0.409	0.047	0.362	0.294	0.043	0.251	0.115	0.004	0.111

[a] The sum of $\Phi_{\text{type II}}$ and $\Phi_{\text{cyclobutanols}}$. [b] The values given are from the formation of acetone, although the same values within experimental error are obtained from the formation of propene. [c] The values given are the sums of both stereoisomers, IIIa and IIIb. A constant ratio of IIIa:IIIb of 1.00:1.25 was observed in all cases.

process from the irradiation of 2-hexanone, hexanone-5-*d*, and hexanone-5,5-d_2 are presented in Figure 1, and those for cyclobutanol formation in Figure 2.

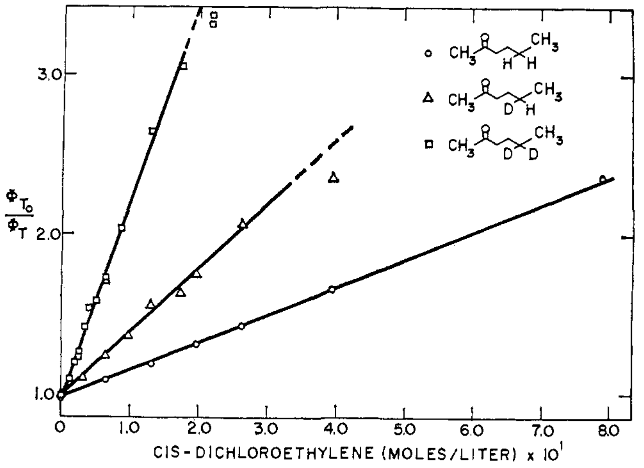
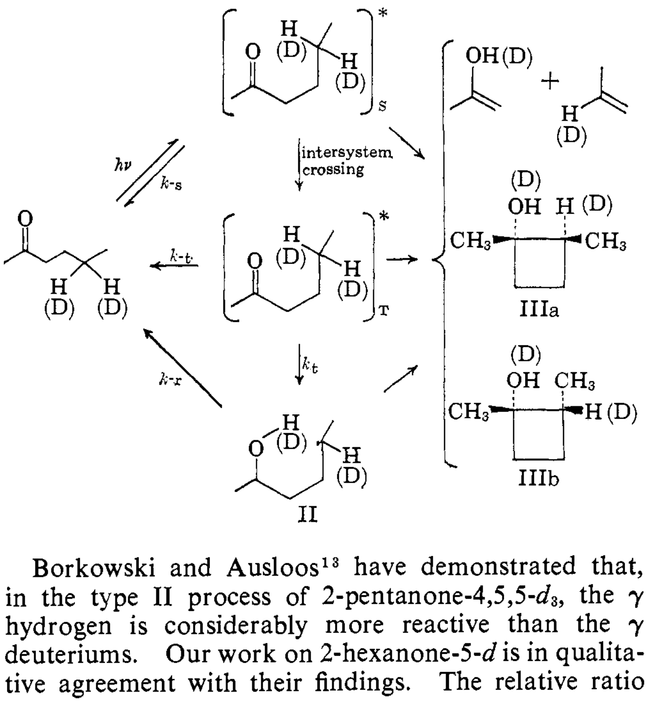


Figure 1. The Stern–Volmer plots for the type II process of the 2-hexanones.

The relative standard deviations of the least-square slopes in these figures are less than 0.02 l. mole^{-1} in all cases.



Borkowski and Ausloos[13] have demonstrated that, in the type II process of 2-pentanone-4,5,5-d_3, the γ hydrogen is considerably more reactive than the γ deuteriums. Our work on 2-hexanone-5-*d* is in qualitative agreement with their findings. The relative ratio of propene-2-*d* to propene resulting from the irradiation of this ketone was determined by mass spectrometry. A ratio of 5.7 was observed in the absence of quencher, while a ratio of 2.7 was observed when the ketone was irradiated in the presence of 5 *M* piperylene. These values, coupled with the fact that only 26% of the reaction proceeds *via* the n → π^* singlet state, imply that the triplet-state reaction would give a ratio of 6.7.[14]

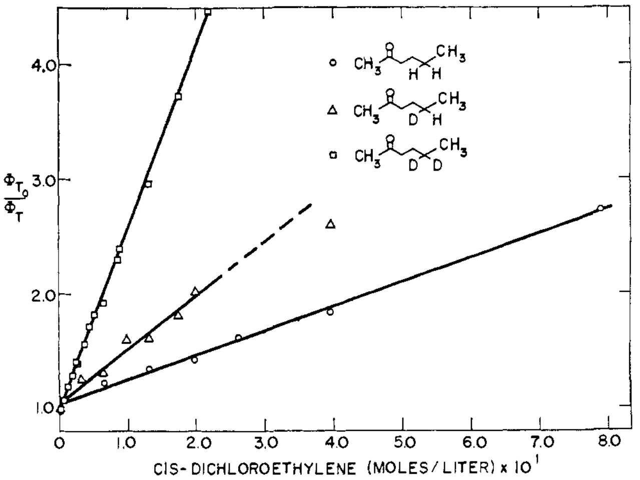


Figure 2. The Stern–Volmer plots for cyclobutanol formation from the 2-hexanones.

Although these results suggest that a γ hydrogen is considerably more reactive than a γ deuterium in the type II process of 2-hexanones, we have found that the photochemical reactions of 5-deuterio-2-hexanones proceed with enhanced quantum yields, i.e., 5-deuterio-2-hexanones are photochemically more reactive than 2-hexanone. While the quantum yields from the n → π^* singlet state, $[\Phi]_S$, for all processes decrease with deuterium substitution at the 5 position, the quantum yields from the triplet state, $[\Phi]_T$, increase substantially with deuterium substitution. $[\Phi_{-\text{ketone}}]_T$ increases from 0.223 for 2-hexanone to 0.359 for 2-hexanone-5,5-d_2! These results indicate that the triplet states of 5-deuterio-2-hexanones may have considerably longer lifetimes than that of 2-hexanone. The relative lifetimes of the triplet states may be estimated from the relative ratios of the Stern–Volmer slopes in Figures 1 and 2. Indeed, it follows that the lifetime of the 2-hexanone-5-*d* triplet state is about 2.3 times longer than that of

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(14) These values have not been corrected for the isotopic purity of the 2-hexanone-5-*d* used. Analyses by mass spectrometry and by nmr showed it to be 92 ± 2% pure.

2-hexanone while the lifetime of the 2-hexanone-5,5-d_2 triplet state is over seven times longer!

In order to account for this observed increase in quantum yields from the triplet states of 5-deuterio-2-hexanones, at least three factors may be considered. (1) It may be noted in Table I that deuterium substitution retards the photochemical reactions of the excited singlet states. Thus, one would expect a more efficient intersystem crossing in the 5-deuterio-2-hexanones resulting in an increase in the steady-state concentration of the triplet state. (2) Evidence has accumulated to support the possibilities that the photochemical reactions of ketones possessing γ hydrogens proceed through a biradical intermediate (II) and that this intermediate may also revert back to the ground-state ketones.[8,15,17] Deuterium substitution at the 5 position will reduce the rate of this reverse reaction (k_{-r}) since it will require the breaking of an O–D bond instead of an O–H bond, whereas it will have a negligible isotope effect on the rates of product formation. (3) It is possible that the γ-C–D and γ-C–H bonds may interact strongly with the excited carbonyl group in a manner analogous to hydrogen bonding in the ground state. This interaction could cause a reduction in the rates of radiationless decay upon deuterium substitution due to the participation of the Franck–Condon factor.[6] The relative importance of these factors will depend upon the relative magnitude of the rates of radiationless decay (k_{-t}) compared to those of γ-hydrogen or -deuterium abstraction. If the rates of decay (k_{-t}) are small compared to those of abstraction, the efficiency of intersystem crossing (factor 1) and the rate of reverse reaction from II (factor 2) will assume more important roles in enhancing the quantum yields from the triplet states. However, since these explanations could not be differentiated by kinetic analysis, it is not possible to choose among them. In fact, it is possible that all these factors may be operating.

A preliminary investigation on 2-hexanone-d_{12} indicated that perdeuteration of 2-hexanone had no measurable increase in isotope effect over the case of 2-hexanone-5,5-d_2 (Table I). Another interesting observation is that over 90% of cyclobutanol formation from 2-hexanones may be quenched by triplet-state quenchers. Therefore, cyclobutanol formation in saturated aliphatic ketones may be primarily a triplet-state reaction. The effects of deuterium substitution on other photochemical reactions are currently under progress in our laboratory.

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(18) National Science Foundation Postdoctoral Fellow, 1964–1965; National Institutes of Health Postdoctoral Fellow, 1965–1966.

(19) The authors wish to thank the National Science Foundation for the support of this work, the National Science Foundation and the Louis P. Block Fund of the University of Chicago for the funds granted to purchase the AEI MS-9 mass spectrometer used in this work, and Mr. S. Murov for many helpful discussions.

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The Crystal and Molecular Structure of $B_9C_2H_9(CH_3)_2$

Sir:

A detailed investigation by three-dimensional single-crystal X-ray diffraction techniques has established the molecular structure of $B_9C_2H_9(CH_3)_2$ shown in Figure 1. We believe this to be the first example of a carborane in which carbon atoms within a cage framework are nonvicinal. The carbon atoms are in the 6 and 9 positions and have methyl substituents, clearly distinguishing them from boron. We emphasize this structural feature since, as pointed out by Lipscomb,[1] the possibility of an isomeric configuration with carbon atoms in the 2 and 4 positions could not be eliminated on a basis of previous physical and chemical evidence.

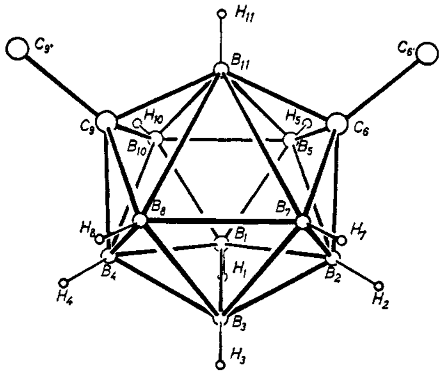

Figure 1. The structure and labeling convention for the designation of atoms in Table I. The methyl group hydrogen atoms have been omitted from $C_{6'}$ and $C_{9'}$.

We conclude from our results that the unsubstituted carborane, $B_9C_2H_{11}$, and the isoelectronic anion, $B_{11}H_{11}^{2-}$, have the structure shown in Figure 2 as proposed by Hawthorne and co-workers[2,3] with the B_{11} atom effectively bridging a decaborane-like framework.

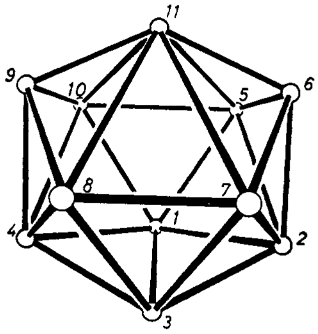

Figure 2. The structure of $B_9C_2H_{11}$ or $B_{11}H_{11}^{2-}$. For $B_9C_2H_{11}$ positions 6 and 9 are occupied by C–H units and all other positions represent B–H units. For $B_{11}H_{11}^{2-}$ all positions represent B–H units.

A colorless crystal, grown from the melt of a small sample sealed in a capillary, gave 668 out of an estimated 695 possible unique reflections in the Cu Kα

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(1) See referee's comments in footnote 3 of ref 2.

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(3) F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **86**, 4222 (1964).