



of its analysis and infrared ( $\lambda$  (film) 6.10, 6.90, 9.80, and 12.85  $\mu$ ) and n.m.r. spectra. The n.m.r. spectrum of the neat olefin showed the following peaks: a broad doublet, area 1, at  $\tau$  4.02 ( $J = 10$  c.p.s.), a sharp doublet, area 1, at 4.37 ( $J = 10$  and 4 c.p.s.), a sharp doublet, area 3, at 8.96 ( $J = 7.0$  c.p.s.), a multiplet, area 1, centered at 9.95, and two remaining broad multiplets, combined area 6. Thus the spectrum can be interpreted as showing two olefinic protons ( $\tau$  4.02 and 4.37) of a disubstituted double bond, a secondary methyl group (8.96), and a cyclopropyl ring (9.95). Similar decarboxylation of *trans*-Ia gave a poorer yield of II (62% isolated) identical in all respects (infrared, n.m.r., and vapor phase chromatography) with that from *cis*-Ia.

The preparation of these acids brought to light an interesting and useful bit of knowledge concerning the Simmons-Smith reaction.<sup>5</sup> When methyl 1,4-dihydrobenzoate<sup>6</sup> was treated with an excess of the Simmons-Smith reagent,<sup>5</sup> the major product (*ca.* 80%) was composed of two isomeric, bis adducts A and B, evidenced by vapor phase chromatography, in the relative proportions of 80% A and 20% B. If pure A, pure B, or the reaction mixture above was refluxed with a catalytic amount of sodium methoxide in dry methanol, an identical equilibrium mixture containing 30% A and 70% B was obtained. Three bis adducts could have been formed in the cyclopropanation reaction: two meso compounds, *cis*- and *trans*-Ib, and a *dl* pair III. The equilibration of A and B excludes III as a possible structure for either A or B, since such an equilibration of III would produce no new compound. Thus A and B must be the *cis* and *trans* forms of Ib. Assignment of the correct relative stereochemistry to A and B was accomplished by inspection of Dreiding models of *cis*- and *trans*-Ib, from which it was clear that the carbomethoxyl group is significantly more hindered in *cis*-Ib than in *trans*-Ib. In the analogous case of 2,5-dimethylcyclopentanecarboxylic acid, it has been shown<sup>7</sup> that the all *cis* acid is less stable thermodynamically than the acid in which the two methyl groups are *trans* to the carboxyl group. On this basis isomer A is *cis*-Ib and isomer B is *trans*-Ib. When the above stereochemical result is compared with that obtained by carrying out the Simmons-Smith reaction on 1,4-dihydrobenzene, which results in the predominately *trans* configuration of cyclopropyl rings,<sup>8</sup> it is seen that

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(7) T. L. Jacobs and W. H. Florsheim, *J. Am. Chem. Soc.*, **72**, 256, 261 (1950).

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the carbomethoxyl group has exerted a profound directing influence on the reaction. The similar directive influence of allyl alcohols, their methyl ethers, and homoallyl alcohols has previously been observed.<sup>9</sup>

Careful saponification of the reaction mixture from the cyclopropanation and fractional crystallization of the mixture of acids so obtained yielded *cis*-Ia, m.p. 106–107°,  $\lambda_{C=O}$   $\text{CHCl}_3$  5.85  $\mu$ . The n.m.r. spectrum of *cis*-Ia in  $\text{CCl}_4$  showed the following peaks: a singlet, area 1, at  $\tau$  -2.33 (acid OH), a triplet, area 1, at 6.51,  $J = 6$  c.p.s. (assigned to the proton  $\alpha$  to the carboxyl group), a multiplet, area 2, at 7.82 (assigned to the cyclohexane methylene), and two multiplets, each of area 4, at 8.6–9.2 and 9.3–10.1 (assigned to the cyclopropane protons). Saponification of the equilibrated mixture of esters from the cyclopropanation with a limited amount of potassium hydroxide produced the epimeric acid *trans*-Ia, m.p. 87–88°,  $\lambda_{C=O}$   $\text{CHCl}_3$  5.85  $\mu$ . Its n.m.r. spectrum contained the following peaks: a singlet, area 1, at  $\tau$  -2.30 (acid OH), a multiplet, area 1, at 7.45 (proton  $\alpha$  to carboxyl group), a multiplet, area 8, from 8.2 to 9.7, and a multiplet, area 2, centered at 9.95.

The possibility that the acids Ia might equilibrate under the conditions of the decarboxylation prevents any conclusions at this time about the stereochemical requirements of the reaction. However, the relative yields of olefin from both acids compel one to consider as highly likely a cyclic transition state such as IV, at least for decarboxylation of the *cis*-acid. Experiments are currently in progress to test this hypothesis and to exploit this new, high yield decarboxylation as a synthetic tool.<sup>10</sup>

(9) W. G. Dauben and G. H. Berezin, *ibid.*, **85**, 468 (1963); S. Winstein and J. Sonnenberg, *ibid.*, **83**, 3235 (1961); P. C. Radlick and S. Winstein, *ibid.*, **86**, 1866 (1964).

(10) S. Winstein and co-workers have independently observed an example of this decarboxylation. We are grateful to Professor Winstein for communication of his results prior to publication.

(11) Address correspondence to Department of Plant Pathology, University of California, Riverside, Calif. 92502.

James J. Sims<sup>11</sup>

Department of Chemistry, University of California  
Riverside, California 92502

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## The Photolysis of 2,3-Dicarbaheptaborane(8)

The compounds 1,5-dicarbaloopentaborane(5) ( $\text{C}_2\text{B}_3\text{H}_5$ ), 1,2-dicarbaloheptaborane(6) ( $1,2\text{-C}_2\text{B}_4\text{H}_6$ ), 1,6-dicarbaloheptaborane(6) ( $1,6\text{-C}_2\text{B}_4\text{H}_6$ ), and 2,4-dicarbaloheptaborane(7) ( $\text{C}_2\text{B}_3\text{H}_7$ ) have been synthesized and characterized.<sup>1-3</sup> However, further work with these carboranes has been hampered by the extremely low yields obtained, especially for the first three compounds. We have found that ultraviolet irradiation of 2,3-dicarbaheptaborane(8) ( $\text{C}_2\text{B}_4\text{H}_8$ ) vapor gives greatly improved yields of  $\text{C}_2\text{B}_3\text{H}_5$ ,  $1,2\text{-C}_2\text{B}_4\text{H}_6$ , and  $1,6\text{-C}_2\text{B}_4\text{H}_6$ .

(1) I. Shapiro, C. D. Good, and R. E. Williams, *J. Am. Chem. Soc.*, **84**, 3837 (1962).

(2) I. Shapiro, B. Keilin, R. E. Williams, and C. D. Good, *ibid.*, **85**, 3167 (1963).

(3) T. Onak, R. P. Drake, and G. B. Dunks, *Inorg. Chem.*, **3**, 1686 (1964).

**Table I.** Photolysis of  $C_2B_4H_8^a$ 

Expt. no.	$C_2B_4H_8$ , mmoles	Added gas, mmoles	$C_2B_4H_8$ consumed, mmole	Products, mole % of $C_2B_4H_8$ consumed		
				$C_2B_3H_5$	1,6- $C_2B_4H_6$	1,2- $C_2B_4H_6$
1	1.010	None	0.292	17.1	22.3	14.0
2	0.544	$B_5H_9$ (0.544)	0.204	15.2	23.5	13.7
3	1.082	$B_2H_6$ (1.093)	0.423	0.9	15.8	11.5
4	1.141	$C_2H_2$ (2.237)	0.321	21.0	16.8	6.7
5	0.951	$H_2$ (10)	0.407	18.0	24.4	17.2
6	1.072	$N_2$ (11)	0.391	12.2	19.7	10.3

<sup>a</sup> 2-hr. periods, 60°.

The  $C_2B_4H_8$  was prepared from  $C_2H_2$  and  $B_5H_9$  by previously described methods.<sup>3</sup> Samples were condensed into a 4.0 × 30 cm. fused silica tube sealed with a Teflon needle valve and clamped in front of a 360-w., quartz, medium pressure, mercury arc lamp<sup>4</sup> for irradiation. The tube was placed in the same position in front of the lamp for each experiment and an arrangement was made for cooling the tube in a stream of tap water for some of the experiments. The products were separated by high vacuum distillation and vapor phase chromatography (10-ft. column, 30% Kel-F on firebrick) and identified by their retention volumes<sup>3</sup> and infrared spectra.<sup>1,2</sup>

In a typical experiment 1.385 mmoles of  $C_2B_4H_8$  was irradiated for 2.0 hr. at 23°. During this time 0.295 mmole of material was consumed, giving (in mmoles)  $H_2$ , 0.139;  $B_2H_6$ , 0.042;  $B_5H_9$ , 0.032;  $C_2B_3H_5$ , 0.067; 1,6- $C_2B_4H_6$ , 0.058; and 1,2- $C_2B_4H_6$ , 0.036. Changing the temperature (0 to 60°) did not alter the yield of carboranes or appreciably change the distribution of products. Longer irradiation time resulted in decreased yield of product, especially 1,2- $C_2B_4H_6$ , and the rate of  $C_2B_4H_8$  consumption decreased, probably because the coating which formed on the tube absorbed light.

If some reactive intermediate is produced in the course of this reaction, it might react with other gases giving a change in the distribution of products or different products. Several experiments are outlined in Table I in which various gases were added to the tube. These experiments were all done without controlling the temperature of the reaction; however, the temperature came to about 60°. The effects are rather minor, except in experiment 3, where the yield of  $C_2B_3H_5$  decreased. In this case 40% of the  $B_2H_6$  was not recovered and, in a separate experiment, approximately the same proportion of  $B_2H_6$  was consumed when it was irradiated alone under the same conditions.

Apparently no  $C_2B_5H_7$  was produced in this work. Since it is difficult to separate from the recovered  $C_2B_4H_8$ , the n.m.r. spectrum, infrared spectrum, and gas density of the recovered starting material were carefully checked, but no evidence was found for  $C_2B_5H_7$ .

An attempt was made to produce carboranes by irradiating a mixture of  $B_5H_9$  and  $C_2H_2$ . When 1.50 mmoles of  $B_5H_9$  and 7.50 mmoles of  $C_2H_2$  were irradiated for 18.5 hr., 0.21 mmole of  $B_5H_9$  and 0.29 mmole of  $C_2H_2$  were consumed, but no other volatile material was recovered.

(4) G. W. Gates and Co., Franklin Square, L. I., N. Y., Model No. 420-U1.

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John R. Spielman, James E. Scott, Jr.

Department of Chemistry  
California State College at Los Angeles  
Los Angeles, California 90032

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### A Six-Boron Carborane, $(CH_3)_2C_2B_6H_6$ , and $B_6H_{10}-P(C_6H_5)_3$ from Hexaborane(10)

Sir:

The carborane containing six boron atoms,  $C_2B_6H_8$  (dicarbaoclovoctaborane(8)), was expected to be thermally quite stable;  $B_6H_{10}$  and acetylene(s) were considered the most likely candidate reagents for its synthesis. Accordingly, several hundred millimoles of  $B_6H_{10}$  were prepared<sup>1</sup> and a number of reactions which paralleled the successful synthesis of carboranes from  $B_5H_9$ <sup>4-8</sup> and  $B_{10}H_{14}$ <sup>9,10</sup> were undertaken.  $B_6H_{10}$  was therefore treated with acetylene at elevated temperatures in the presence and absence of several Lewis bases and with Lewis bases alone. Although trace amounts of the six-boron carborane were prepared by heat treatment, the subsequent utilization of ultraviolet irradiation resulted in a "reasonable yield" synthesis.

$B_6H_{10}-CH_3C\equiv CCH_3$ . The mass spectrum of the least volatile fractions isolated from the reactions of a

- (1)  $B_6H_{11}$  was prepared<sup>2</sup> from  $B_5H_9$  and converted to  $B_6H_{10}$ .<sup>3</sup>
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