

will depend on the extent to which the strength of the nonreacting bonds of  $H_3O^+$  changes as the proton transfer transition state is reached, and this, in turn, will be a function of the amount of proton transfer at the transition state. An upper limit of 1.00 for this isotope effect can be set for the (hypothetical) case of no proton transfer and no change in the nonreacting bonds. A lower limit is harder to fix, but an argument can be made for its being  $l^2$  or 0.48.<sup>2b</sup> It seems likely that the position which the isotope effect on a given reaction occupies with respect to these limits will constitute a valuable criterion of the extent of proton transfer at the transition state of that reaction.

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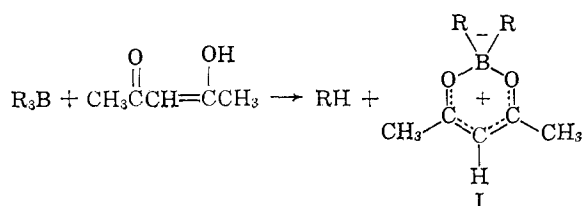
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### Cyclic Dialkylboronium Acetylacetonates

Sir:

We wish to report the general synthesis of cyclic dialkylboronium acetylacetonates of structure I and related cyclic compounds.<sup>1</sup> The reaction of trialkylboranes with acetylacetonate produces the corresponding dialkylboronium acetylacetonate and the hydrocarbon derived from the trialkylborane in virtually quantitative yield. The reaction undoubtedly proceeds through



the enol form of the  $\beta$ -dicarbonyl compound in a manner analogous to the known reaction of carboxylic acids with trialkylboranes.<sup>2</sup> Other  $\beta$ -dicarbonyl compounds such as dibenzoylmethane and ethyl acetoacetate gave products analogous to I with trialkylboranes as did 2-imino-4-pentanone.

In a typical preparation, the trialkylborane is mixed with a 50% excess of acetylacetonate and heated under nitrogen at 70–75° for 24 hr. The excess acetylacetonate, hydrocarbon product, and dialkylboronium acetylacetonate are recovered by fractional distillation at reduced pressure. Yields of chelate and hydrocarbon most often exceed 95%. Triphenylborane did not react with acetylacetonate under these conditions. Table I reports pertinent characterization data. All products gave satisfactory elemental analyses.

The simple dialkylboronium acetylacetonates are bright yellow, distillable liquids or low melting solids. They are stable toward water and atmospheric oxygen for moderate periods of time. Treatment of these compounds with aqueous base at the reflux temperature followed by acidification and distillation afforded the

(1) W. Gerrard, M. F. Lappert, and R. Shafferman, *J. Chem. Soc.*, 3648 (1958), have prepared di-*n*-butylboron ethyl acetoacetate and diphenylboron ethyl acetoacetate from the corresponding organoboron chlorides and ethyl acetoacetate.

(2) H. C. Brown and K. Murray, *J. Am. Chem. Soc.*, **81**, 4108 (1959).

TABLE I

Trialkylborane	Dicarbonyl compound	Yield, %	B.p. (mm.) or m.p., °C.
<i>n</i> -Butyl	Acetylacetonate	98.3	86 (0.1)
Isobutyl	Acetylacetonate	98.3	75 (0.1)
2-Butyl	Acetylacetonate	98.5	71 (0.15)
<i>n</i> -Hexyl	Acetylacetonate	98.3	120 (0.1)
Cyclohexyl	Acetylacetonate	98.5	65.5–66.0
<i>n</i> -Butyl	2-Imino-4-pentanone	89.6	84 (0.1)
Isobutyl	Dibenzoylmethane	90	70–71
Isobutyl	Ethyl acetoacetate	92	87 (1.0)

corresponding dialkylborinic anhydrides in high yield. This method is attractive for the large scale synthesis of the latter compounds.

Bromination of dialkylboronium acetylacetonates with elemental bromine in carbon tetrachloride solution at room temperature apparently produces unstable dibromides which spontaneously dehydrobrominate to produce monobromo derivatives which contain no vinylic hydrogen and two equivalent methyl groups in their <sup>1</sup>H n.m.r. spectra. Unsubstituted dialkylboronium acetylacetonates exhibited vinylic hydrogen at  $\tau$  4.6 to 4.8 and two equivalent methyl groups at  $\tau$  8.00 relative to tetramethylsilane. These results confirm the cyclic structure I assigned to the dialkylboronium acetylacetonates and the monobromo derivatives. The infrared spectra of the dialkylboronium acetylacetonates contained absorption bands at 6.25, 6.55, 7.25, 9.00, and 13.0  $\mu$ . Their ultraviolet spectra were characterized by two principal absorption bands between 320–345 and 220–270  $m\mu$ .

Further work dealing with the chemistry of the dialkylboronium acetylacetonates is in progress and will be reported elsewhere.

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(3) Alfred P. Sloan Research Fellow.

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### The Thermal Isomerization of C-Phenyldicarbaundecaborate(12)

Sir:

We wish to report the thermal rearrangement of the C-phenyldicarbaundecaborate(12) (I) derived from C-phenyl-*o*-dicarbaclvododecaborane(12)<sup>1</sup> (II) to an isomeric ion III which was also prepared directly by basic degradation of C-phenyl-*m*-dicarbaclvododecaborane(12) (IV). The latter material (m.p. 55.1–55.6°) was prepared in 70% yield by thermal rearrangement<sup>2</sup> of the *ortho* isomer at 410° and was characterized by its mass spectrum. The mass spectrum contained a sharp cutoff at  $m/e = 223$  which corresponds to <sup>11</sup>B<sub>10<sup>12</sup>C<sub>7</sub><sup>13</sup>C<sub>1</sub>H<sub>16</sub>. The ratios of the  $m/e = 222$  and 223 intensities for this material and the *ortho* isomer</sub>

(1) R. A. Wiesboeck and M. R. Hawthorne, *J. Am. Chem. Soc.*, **86**, 1642 (1964).

(2) (a) D. Grafstein and J. Dvorak, *Inorg. Chem.*, **2**, 1128 (1963); (b) H. Schroeder and G. D. Vickers, *ibid.*, **2**, 1317 (1963).