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.[2b] 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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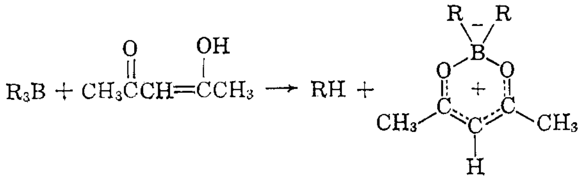
Cyclic Dialkylboronium Acetylacetonates

Sir:

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



I

the enol form of the β-dicarbonyl compound in a manner analogous to the known reaction of carboxylic acids with trialkylboranes.[2] Other β-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 acetylacetone and heated under nitrogen at 70–75° for 24 hr. The excess acetylacetone, 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 acetylacetone 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 corresponding dialkylborinic anhydrides in high yield. This method is attractive for the large scale synthesis of the latter compounds.

TABLE I

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

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 ^1H n.m.r. spectra. Unsubstituted dialkylboronium acetylacetonates exhibited vinylic hydrogen at τ 4.6 to 4.8 and two equivalent methyl groups at τ 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 μ. Their ultraviolet spectra were characterized by two principal absorption bands between 320–345 and 220–270 mμ.

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

Acknowledgment.—The authors wish to thank the Petroleum Research Fund administered by the American Chemical Society for generous financial support.

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[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).

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RECEIVED SEPTEMBER 8, 1964

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*-dicarbaclovododecaborane(12)[1] (II) to an isomeric ion III which was also prepared directly by basic degradation of C-phenyl-*m*-dicarbaclovododecaborane(12) (IV). The latter material (m.p. 55.1–55.6°) was prepared in 70% yield by thermal rearrangement[2] 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 $^{11}B_{10}{}^{12}C_7{}^{13}C^1H_{16}$. The ratios of the m/e = 222 and 223 intensities for this material and the *ortho* isomer

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[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).

were identical. The basic degradation reaction of IV to III was accomplished with ethanolic potassium hydroxide in an autoclave at 200° for 10 hr.

$$m\text{-}C_6H_5B_{10}C_2H_{11}\ (IV) + C_2H_5O^- + 2C_2H_5OH \longrightarrow C_6H_5B_9C_2B_{11}^-\ (III) + B(OC_2H_5)_3 + H_2$$

A 60% yield of III was obtained as its cesium salt. *Anal.* Calcd. for $CsB_9C_8H_{16}$: B, 28.44; H, 4.71; C, 28.06. Found: B, 28.15; H, 4.78; C, 27.97. The infrared spectrum of cesium–III contained characteristic absorption bands at 3.98 (s), 7.93 (m), 8.96 (m), 10.22 (m), 11.86 (m), 13.40 (w), 13.62 (m), 13.88 (m), and 14.17 μ (s). The 19.3-Mc./sec. ^{11}B n.m.r. spectrum of III is complex, but has the over-all appearance of three doublets centered at 4.70, 22.5, and 35.3 p.p.m. from boron trifluoride diethyl etherate, with splittings of 130, 130, and 141 c.p.s., respectively. Treatment of III with polyphosphoric acid under an atmosphere of 500 mm. of nitrogen at 135° produced the recently reported[3] C-phenyldicarbaundecaborane-(11) (V) in 54% yield. The carborane product was identified by its characteristic infrared and ^{11}B n.m.r. spectra and melting point.

The cesium salt of I, when fused *in vacuo* at 300°, produced III in virtually quantitative yield after 3 hr. Purification was accomplished by recrystallization from water. The cesium–III produced by this route was identical with III obtained by degradation of IV as shown by infrared and ^{11}B n.m.r. spectra and X-ray powder diagrams. All interconversions are presented below.

$$\begin{tikzcd}
o\text{-}C_6H_5B_9C_2H_{11}^-\ (I) \arrow[rr, "300°"] \arrow[dr, "H^+", "-H_2"'] & & C_6H_5B_9C_2H_{11}^-\ (III) \arrow[dl, "H^+"', "-H_2"] \\
& C_6H_5B_9C_2H_{10}\ (V) & \\
o\text{-}C_6H_5B_{10}C_2H_{11}\ (II) \arrow[uu, "\text{degrade}"] \arrow[rr, "410°"] & & m\text{-}C_6H_5B_{10}C_2H_{11}\ (IV) \arrow[uu, "\text{degrade}"']
\end{tikzcd}$$

If the basic degradation reactions of II and IV proceed without motion of the two carbon atoms relative to each other, III might reasonably be described as an 11-particle icosahedral fragment with the two carbon atoms in the periphery of the pentagonal face, separated by a boron atom. Conversion of I and III to the carborane V strengthens the view[3] that the carbon atoms of V are separated and that the conversion of I to V proceeds with motion of the carbon atoms relative to each other.

The thermal rearrangement of I to III may involve an 11-particle cuboctahedral fragment as an intermediate or transition state analogous to the pathway suggested[4] for the rearrangement of *o*- to *m*-dicarbaclovododecaborane(12).

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

[4] (a) R. Hoffmann and W. N. Lipscomb, *Inorg. Chem.*, **2**, 231 (1963); (b) A. Kaczmarczyk, R. D. Dobrott, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **48**, 729 (1962).

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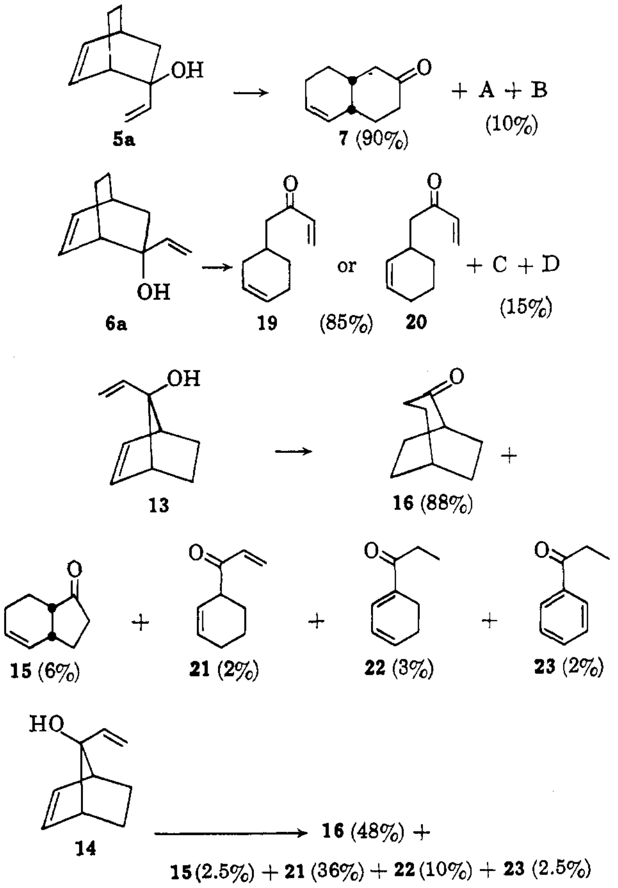
RECEIVED SEPTEMBER 14, 1964

Stepwise Mechanisms in the Oxy-Cope Rearrangement[1]

Sir:

A comparison of the behavior on pyrolysis of 2-*exo*-vinyl-2-*endo*-hydroxybicyclo[2.2.2]octene (**6a**)[2] and *syn*-7-vinyl-*anti*-7-hydroxynorbornene (**13**) with that of their respective epimers **5a** and **14** provides some insight into the mechanisms of the oxy-Cope rearrangements.[3] The products shown here from such experiments are derived from gas phase pyrolyses in evacuated vessels at 320°, although the distributions are rather insensitive to temperature and to large increases in surface-volume ratio. The indicated figures refer to percentages of volatile materials as determined by vapor chromatographic areas.



Grounds for the assignments of structure to products **7**, **15**, and **16** have already been given.[3] Structure

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[1] This work was supported in part by the Directorate of Chemical Sciences, Air Force Office of Scientific Research Grant No. AF-AFOSR 389-63, and by funds provided by the Wisconsin Alumni Research Foundation.

[2] The formula numbers correspond to those of the accompanying paper.[3]

[3] J. A. Berson and M. Jones, Jr., *J. Am. Chem. Soc.*, **86**, 5019 (1964).