energy of activation for the thermal decomposition of alkyl hydroperoxides is similarly insensitive to the nature of the alkyl group.[13]

The energies of activation (*ca.* 27 kcal./mole) reported here for the silyl hydroperoxides are slightly less than the 29-kcal./mole values for alkyl hydroperoxides.[13] This lower value can be readily explained in that silicon is more electropositive than carbon and thus produces a higher electron density on the attached oxygen. In general it has been found that factors leading to high electron densities on peroxidic oxygens promote thermal dissociation.[14] This explanation leads to a prediction that in hydroperoxides of the group IV elements, with increasing atomic weight of the elements, the hydroperoxides should be less stable. Quantitative data are generally not available but trimethyltin hydroperoxide does have an energy of activation of only 11.04 kcal./mole for its first-order thermal dissociation in acetonitrile.[15] A similar decrease in stability of the bisperoxides should be encountered with an increase in the atomic weight of the peroxidic element. The present knowledge of the stability of silicon,[2] germanium[16], tin,[17] and lead[17] bisperoxides seems to substantiate qualitatively this hypothesis excepting for the tin compound. Alleston and Davies' tentative suggestion[18] that the alternate elements (*e.g.*, C, Ge, and Pb) in group IV might possess the most stable peroxides must now be rejected because of the stability of the silicon compounds.

Hiatt[9] has postulated that, owing to dπ–pπ bonding, silyl peroxides should be more stable than their carbon analogs. He proposed that the 27-kcal. value reported[1c] is too low and suggested that the decompositions yielding this value do not involve an uncomplicated cleavage of the oxygen-to-oxygen bond. Hiatt's selection of *t*-butyl hydroperoxide as a reference compound is unfortunate in that its energy of activation (39 kcal./mole[19]) is anomalous to those of the other alkyl hydroperoxides. It is true, however, that the data here presented do not rigorously prove that an uncomplicated homolysis of the peroxide link is being observed.

Effect of Acid.—The absence of acid catalysis of the silyl hydroperoxide decompositions is surprising in that alkyl hydroperoxides and *t*-butyl trimethylsilyl peroxide are so susceptible to such catalysis. Simple first-order kinetics in *o*-dichlorobenzene were observed in the present work in contrast to the autocatalytic behavior of *t*-butyl trimethylsilyl peroxide in chlorobenzene caused by formation of trace quantities of hydrogen chloride.[9] Hydrogen chloride may similarly have been formed from the silyl hydroperoxides in *o*-dichlorobenzene, but obviously no enhancement in rate would result.

Base-Catalyzed Decomposition of the Hydroperoxides.—The base-catalyzed decomposition of the hydroperoxides (Table II, Figure 3) accounts for the inability of several investigators to synthesize the compounds in alkaline media. As would be expected, the rate increases with greater concentrations or larger K_b values of the amine used as a catalyst. The decomposition probably proceeds through the silylperoxy anion. The zero-order rate dependence upon the peroxide is consistent with this hypothesis, but the lack of a first-order dependence on base requires clarification. More data are needed before a mechanism may be proposed on a secure basis.

Photolytic Decomposition of Triphenylsilyl Hydroperoxide.—The pronounced enhancement of rate obtained by photolysis indicates a homolytic mechanism of decomposition. Its first-order kinetics support a free-radical mechanism for the similarly first-order thermal dissociation.

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Dialklyboronium Acetylacetonates

M. FREDERICK HAWTHORNE[1] AND MARTEN REINTJES

Department of Chemistry, The University of California, Riverside, California 92502

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Dialkylboronium acetylacetonates were prepared in quantitative yields from the reaction of the corresponding trialkylboranes with acetylacetone. Other β-dicarbonyl compounds as well as 2-imino-4-pentanone produced analogous products with trialkylboranes. The cyclic structure of these compounds was established by n.m.r. and infrared spectral analyses. Alkaline hydrolysis of the acetylacetonates afforded the dialkylborinic anhydrides in good yield.

In a preliminary communication[2] we described a general synthesis of dialkylboronium acetylacetonates. With the exception of boron, the acetylacetonates of the group III elements have been known for some time. Menzies, *et al.*,[3] reported the preparation of dimethylthallium acetylacetonate in 1928. In more recent work, Coates[4,5] described the synthesis of dimethylgallium acetylacetonate and dimethylindium acetylacetonate. Gerrard, *et al.*,[6] prepared diphenylboronium ethyl acetoacetate and di-*n*-butylboronium ethyl acetoacetate from the corresponding organoboron chlorides and ethyl acetoacetate. Mikhailov[7] re-

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TABLE I

PHYSICAL CONSTANTS AND CHARACTERIZATION DATA OF DIALKYLBORONIUM ACETYLACETONATES AND OTHER CHELATES

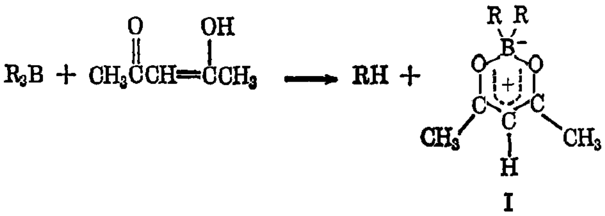
Trialkylborane	Dicarbonyl compd.	Yield, %	B.p. (mm.) or m.p., °C.	$n^{20}D$	Calcd.		Found	
					% C	% H	% C	% H
n-Butyl	Acetylacetone	98	86 (0.1)[a]	1.4670[a]	69.64	11.16	69.51	11.13
Isobutyl	Acetylacetone	98	75 (0.1)	1.4619	69.64	11.16	69.35	10.99
2-Butyl	Acetylacetone	98	71 (0.15)	1.4709	69.64	11.16	69.62	11.12
n-Hexyl	Acetylacetone	98	120 (0.1)	1.4662	72.86	11.79	73.04	11.82
Cyclohexyl	Acetylacetone	99	65.5–66.0		73.91	10.51	73.68	10.64
n-Butyl	2-Imino-4-pentanone	90	84 (0.1)	1.4848	69.96[b]	11.66	70.07	11.90
Isobutyl	Dibenzoylmethane	90	70–71		79.31	8.33	78.97	8.28
Isobutyl	Ethyl acetoacetate	92	87 (1.0)	1.4547	66.14	10.63	65.94	10.65

[a] Lit.[7] b.p. 134–135° (13 mm.), $n^{20}D$ 1.4667. [b] *Anal.* Calcd.: N, 6.28. Found: N, 6.12.

ported the preparation of di-*n*-propylboronium acetylacetonate and di-*n*-butylboronium acetylacetonate from the corresponding trialkylboranes and acetylacetone. This author also prepared di-*n*-propylboronium acetylacetonate from methyl di-*n*-propylborinate and acetylacetone, and di-*n*-butylboronium acetylacetonate from the reaction of *n*-butyl di-*n*-butylthioborinate with acetylacetone. In this article, the preparation, characterization, and reactions of a series of dialkylboronium acetylacetonates are described. In addition, the hydrolysis of dialkylboronium acetylacetonates to the corresponding dialkylborinic acids is demonstrated.

Results and Discussion

The reaction of trialkylboranes with acetylacetone produced the corresponding dialkylboronium acetylacetonates and the hydrocarbon derived from the trialkylborane in virtually quantitative yield. As mentioned above, Mikhailov[7] previously reported this reaction using tri-*n*-propylborane and tri-*n*-butylborane. Other β-dicarbonyl compounds such as dibenzoylmethane and ethyl acetoacetate produced analogous products with trialkylboranes as did 2-imino-4-pentanone. The reaction most likely proceeds through the enol form of the β-dicarbonyl compound in a manner analogous to the known reaction of carboxylic acids,[8] alcohols,[9] or mercaptans[10] with trialkylboranes. Similar ideas have been expressed regarding the reaction of organoboron chlorides and ethyl acetoacetate.[6]



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The trialkylborane–acetylacetone reaction was carried out using 25–50% excess of acetylacetone, and heating under nitrogen at 75–80° for 24–48 hr. Mikhailov[7] reported that after a brief induction period a vigorous reaction began and was accompanied by a strong exotherm. This was observed by us only in the case of tri-*n*-butylborane after warming the reaction mixture to about 70°. With the isomeric butylboranes (Table I) there was a gradual evolution of hydrocarbon over a period of several hours while the higher trialkylboranes reacted even more slowly. Care was taken to prevent the reaction temperature from exceeding 80° since retrohydroboration occurs above that temperature and the resulting dialkylborane reduces the carbonyl function of the substrate. The reaction products were isolated in high yield by fractional distillation. Triphenylborane did not react with acetylacetone under these conditions. Table I reports the physical constants and characterization data obtained for the compounds prepared in this study.

The dialkylboronium acetylacetonates are stable toward water and atmospheric oxygen for moderate periods of time. The stability of these compounds may be attributed to the cyclic structure I. This structural assignment is based upon infrared and ^1H n.m.r. spectra. All of the compounds show two strong bands in the infrared at 1600 and 1528 cm.$^{-1}$ which are due to chelated C=O and to >C=C< stretching modes.[6,11] Unsubstituted dialkylboronium acetylacetonates exhibited n.m.r. signals due to vinylic hydrogen at δ 5.2 to 5.48 and due to two equivalent methyl groups at δ 2.00 relative to tetramethylsilane. The two methyl groups remained equivalent in the temperature range of 40 to −40°.

Bromination of dialkylboronium acetylacetonates with elemental bromine in carbon tetrachloride solution at room temperature produced monobromo derivatives which contained no vinylic hydrogen and had two equivalent methyl groups in their ^1H n.m.r. spectra at δ 2.31 relative to tetramethylsilane.

TABLE II

ULTRAVIOLET SPECTRAL DATA OF DIALKYLBORONIUM CHELATES

Trialkylborane	Dicarbonyl compd.	λ_{max} (ϵ) in acetonitrile, mμ		
n-Butyl	Acetylacetone	332 (1260)		270 (4250)
Isobutyl	Acetylacetone	330 (1295)		270 (6010)
2-Butyl	Acetylacetone	341 (2430)		236 (4410)
n-Hexyl	Acetylacetone	330 (1145)		270 (5550)
Cyclohexyl	Acetylacetone	343 (2220)		244 (4020)
n-Butyl	2-Imino-4-pentanone	337 (3150)	330 (1985)	222 (4240)
Isobutyl	Ethyl acetoacetate	298 (2300)		225 (3830)

The ultraviolet spectra of the dialkylboronium acetylacetonates and related compounds were characterized by two principal absorption bands between 320–345 and 220–270 mμ. These data are shown in Table II.

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Dialkyl-substituted boron compounds, *e.g.*, halide, ester, borane, etc., are potential starting materials for the preparation of borinic acids.[12] The availability of trialkylboranes *via* hydroboration[13] has suggested their use as precursors to dialkylborinic acids. Accordingly, Mikhailov[9] has reported that the hydrolysis and alcoholysis of trialkylboranes yields dialkylborinic acids and esters, respectively. The former reaction requires temperatures in the 160–180° range and the latter reaction gives yields of the order of 65–80%. As an alternative procedure, the hydrolysis of dialkylboronium acetylacetonates was investigated.

Treatment of dialkylboronium acetylacetonates with aqueous base at the reflux temperature followed by acidification and distillation afforded the corresponding dialkylborinic anhydride in good yield. Representative results are presented in Table III. This method may be adapted to large-scale syntheses.

TABLE III

PHYSICAL CONSTANTS AND CHARACTERIZATION DATA FOR THE DIBUTYLBORINIC ANHYDRIDES

Dialkylborinic anhydride	Yield, %	B.p., °C. (mm.)	$n^{20}D$
n-Butyl[a]	79.8	82–84 (0.1)	1.4277
Isobutyl[a]	71.4	64 (0.07)	1.4226
sec-Butyl[b]	67.7	84–86 (0.15)	1.4392

[a] Lit.[9] b.p. 139–140° (12 mm.) and 111–112° (9 mm.), $n^{20}D$ 1.4270 and 1.4230, for the di-*n*-butyl- and diisobutylborinic anhydrides, respectively. [b] A. G. Davies and D. G. Hare [*J. Chem. Soc.*, 438 (1959)] reported b.p. 113° (4 mm.).

The ethanolamine esters of diaryl and alkylarylborinic acids are stable materials[14,15] which are useful for characterization purposes. The ethanolamine ester of diisobutylborinic acid was obtained by azeotropic distillation of the acid anhydride with ethanolamine in benzene. This derivative was only moderately stable in the presence of moist air. Attempts to prepare the ethanolamine esters of other dialkylborinic acids failed.

Experimental Section

Materials and Methods.—The trialkylboranes were prepared by the hydroboration of the corresponding olefins.[13] 2-Imino-4-pentanone was obtained as a gift from Mr. D. C. Young of the Union Oil Co. ^1H n.m.r. spectra were determined with a Varian A-60 spectrometer and infrared spectra with a Perkin-Elmer Model 137 spectrophotometer with sodium chloride optics. Ultraviolet spectra were obtained with a Beckman Model DB spectrophotometer employing a Sargent Model SRL recorder. Refractive indices were determined with a Zeiss refractometer. Reported melting points are uncorrected.

General Procedure for the Preparation of Dialkylboronium Acetylacetonates.—The general procedure for the preparation of the dialkylboronium acetylacetonates is described with diisobutylboronium acetylacetonate as a specific example. To 30.0 g. (0.30 mole) of acetylacetone in a 250-ml. round-bottom flask, supplied with a reflux condenser and magnetic stirrer, was added 36.4 g. (0.20 mole) of triisobutylborane. The mixture was kept under nitrogen at 75° for 24 hr. The excess acetylacetone and diisobutylboronium acetylacetonate were recovered by fractional distillation at reduced pressure, b.p. 75° (0.1 mm.), yield 66.1 g. (98.3%), $n^{20}D$ 1.4619.

Anal. Calcd. for $C_{13}H_{25}BO_2$: C, 69.64; H, 11.16. Found: C, 69.35; H, 10.99.

n-Butane was collected in a Dry Ice trap and identified by v.p.c., yield 15.7 g. (90.2%). Benzene was employed as solvent whenever one of the reactants was a solid such as tricyclohexylborane, 2-imino-4-pentanone, and dibenzoylmethane. The solid products (dicyclohexylboronium acetylacetonate and the diisobutyl derivative of dibenzoylmethane) were recrystallized from pentane at −80°. The diisobutyl derivative of dibenzoylmethane was extremely unstable in air owing to rapid hydrolysis by atmospheric moisture.

γ-Bromodi-*n*-butylboronium Acetylacetonate.—In a 1000-ml. three-neck, round-bottom flask supplied with a reflux condenser, gas dispersion tube, and a magnetic stirrer was placed 22.4 g. (0.1 mole) of di-*n*-butylboronium acetylacetonate dissolved in 250 ml. of carbon tetrachloride. Nitrogen was bubbled through the solution while 16.0 g. (0.1 mole) of bromine dissolved in 100 ml. of carbon tetrachloride was added during the course of 1 hr. Nitrogen was bubbled through the reaction mixture until all of the hydrogen bromide was removed. The solvent was removed under reduced pressure at room temperature. A small amount of calcium oxide was added to the product to neutralize any residual acid. The product was distilled at 1×10^{-3} mm. using a molecular still. Pure product was obtained after two distillations, yield 24.0 g. (79.2%), $n^{20}D$ 1.4911.

Anal. Calcd. for $C_{13}H_{24}BBrO_2$: C, 51.49; H, 7.92; Br, 26.40. Found: C, 51.43; H, 7.72; Br, 26.59.

General Procedure for the Synthesis of Dialkylborinic Anhydrides.—The general procedure is illustrated with the preparation of di-*n*-butylborinic anhydride. In a 1000-ml. round-bottom flask were placed 33.6 g. (0.15 mole) of di-*n*-butylboronium acetylacetonate, 28.0 g. (0.50 mole) of potassium hydroxide, and 250 ml. of water. The mixture was heated under nitrogen to the reflux temperature for 3 hr. After cooling to room temperature, the mixture was neutralized with 15% hydrochloric acid. The product was extracted with ethyl ether and dried over sodium sulfate. After removal of the solvent the product was distilled under reduced pressure, b.p. 82–84° (0.1 mm.), yield 15.9 g. (79.8%), $n^{20}D$ 1.4277 (lit.[9] $n^{20}D$ 1.4270).

Ethanolamine Ester of Diisobutylborinic Anhydride.—Diisobutylborinic anhydride (6.2 g., 23.3 mmoles) and 2.8 g. (46.6 mmoles) of ethanolamine were dissolved in 150 ml. of benzene. The mixture was heated under nitrogen to the reflux temperature in a small Soxhlet apparatus which contained calcium hydride in the thimble to remove water. After 1 hr. the solvent was removed under reduced pressure and the product was recrystallized by dissolving it in a minimum amount of ethyl ether and adding 50 vol. of pentane. After three recrystallizations, the ester was obtained as long white needles, m.p. 85–85.5°.

Anal. Calcd. for $C_{10}H_{24}BNO$: C, 64.86; H, 12.97. Found: C, 64.76; H, 13.27.

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