In one experiment in acetonitrile a rough rate of methanol formation was determined along with the rate of disappearance of the hydroperoxide. It was most significant that when 95% of the hydroperoxide content had disappeared, the methanol content was still 16% less than its final figure. This indicates an intermediate of some stability.

The products bear some similarity to those obtained from either triphenylsilyl hydroperoxide[13] or bis(triethyltin) peroxide.[8] The energy of activation (*ca.* 27 kcal./mole) for the first-order decomposition of the silyl hydroperoxides in most solvents is somewhat higher than that for the first-order decompositions of the tin hydroperoxide. This is reasonable in that as tin is more electropositive than silicon, it would confer a higher electron density on the attached oxygen and this generally promotes the thermal dissociation of a peroxide.[14]

$$\underset{1\text{ mole}}{Ph_3SiOOH} \longrightarrow \underset{0.45}{Ph_3SiOH} + \underset{0.29}{Ph_2Si(OH)_2} + \text{polymer}$$

$$\underset{1\text{ mole}}{(C_2H_5)_3SnOOSn(C_2H_5)_3} \longrightarrow \underset{1\text{ mole}}{(C_2H_5)_3SnOC_2H_5} + \underset{1\text{ mole}}{(C_2H_5)_2SnO}$$

Additional data are needed before mechanisms can be proposed which are not highly speculative.

Acknowledgment.—Grateful appreciation is expressed to Dr. G. E. Corbett for isolating the first sample of trimethyltin hydroperoxide.

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[13] R. L. Dannley and G. Jalics, *J. Org. Chem.*, **30**, 2417 (1965).

[14] C. G. Swain, W. H. Stockmayer, and J. T. Clark, *J. Am. Chem. Soc.*, **72**, 5426 (1950).

The Decomposition of Silyl Hydroperoxides[1]

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The thermal decomposition of triphenylsilyl hydroperoxide in anisole, methyl benzoate, nitrobenzene, and *o*-dichlorobenzene is first order and has an energy of activation of 22 to 27 kcal./mole. The reaction is complex; for example, in anisole it produces triphenylsilanol, diphenylsilanediol, phenol, and small quantities of *p*-hydroxyanisole. Triphenylsilyl, methyldiphenylsilyl, and tribenzylsilyl hydroperoxides all thermally decompose in *o*-dichlorobenzene with similar rates and almost identical energies of activation (26.7 ± 0.4 kcal./mole). The effect of the substituent group attached to silicon is therefore small. The decomposition of triphenylsilyl hydroperoxide is unaffected by acid but is accelerated by base. The base-catalyzed reaction is zero order with respect to the peroxide and has an energy of activation of 11.8 kcal./mole. Irradiation with ultraviolet light markedly accelerates the decomposition of triphenylsilyl hydroperoxide and the kinetics remain first order.

In a previous paper[2] the syntheses of several stable silyl hydroperoxides have been reported. The only other silyl hydroperoxide in the literature[3] (trimethylsilyl hydroperoxide) was described as an oil which decomposed at 0° to hydrogen peroxide and the bissilyl peroxide. No additional experiments have been performed with it.

Similarly, very little is known about the decomposition of bissilyl peroxides and the published papers[2–8] are almost exclusively preparative in nature. The only detailed study of the decomposition of a related compound concerns *t*-butyl trimethylsilyl peroxide. Hiatt[9] found that it produced acetone, *t*-butyl alcohol, and hexamethyldisiloxane by a first-order reaction sensitive to the nature of the solvent as well as to acid and base catalysis. The energy of activation was 41 kcal./mole.

The present work was undertaken to study the decomposition of silyl hydroperoxides with regard to the products formed and the kinetic behavior.

Experimental Section

Thermal Decomposition of Triphenylsilyl Hydroperoxide in Anisole.—A solution of triphenylsilyl hydroperoxide[2] (8 g., 0.0274 mole) in anisole (200 ml.) was refluxed for 12 hr. The anisole was distilled under reduced pressure (1 mm.) and the residue was dissolved in hot petroleum ether (b.p. 30–60°). Chilling the petroleum ether solution precipitated triphenylsilanol (2.3 g., 0.0083 mole), m.p. 148–152° (lit.[10] m.p. 150–152°), which was collected by filtration. The infrared spectrum was identical with that of an authentic sample. The petroleum ether filtrate was extracted with aqueous potassium hydroxide (40 ml., 1 *N*), and acidification of the aqueous extract deposited diphenylsilanediol (1.7 g., 0.0072 mole), m.p. 170–171°, which was identified by comparison of its infrared spectrum to that of an authentic sample. The acidified aqueous filtrate, after evaporation to dryness and high-vacuum distillation of the residue, gave *p*-hydroxyanisole (0.3 g., 0.0024 mole), identified as its aryloxyacetic acid derivative. From the remaining petroleum ether solution was isolated additional triphenylsilanol (1.1 g., 0.004 mole) and 2.3 g. of unidentified tar.

Thermal Decomposition of Triphenylsilyl Hydroperoxide in Dibutyl Phthalate.—A solution of triphenylsilyl hydroperoxide (4 g., 0.0137 mole) in dibutyl phthalate (100 ml.) was heated to 160° under a stream of nitrogen gas for 2 hr. in a distillation apparatus under vacuum (30 mm.). The distillate (30 ml.) was subjected to a vacuum (10^{-5} mm.) for 24 hr. at room temperature to sublime phenol (0.3 g., 0.0032 mole), m.p. 41–42°.

Base-Catalyzed Decomposition of Triphenylsilyl Hydroperoxide.—A solution of triphenylsilyl hydroperoxide (1 g., 0.0034 mole), triethylamine (1 ml., 0.01 mole), and ether (20 ml.) was heated on a steam bath while it was evaporated *in vacuo* to dryness, and the residue was dissolved in ether. The ether solution was washed with water and then cooled to precipitate triphenylsilanol (0.5 g., 0.0018 mole, 53%, m.p. 148–150°).

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[1] (a) Supported in part by the U. S. Army Research Office (Durham) through Grant No. DA-ARO(D)-31-124-G242 and in part by a Texaco Co. Fellowship. (b) Taken in part from the dissertation of G. Jalics, submitted in June 1964 to the Graduate School of Western Reserve University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. (c) Presented in part at the 145th National Meeting of the American Chemical Society, New York, N. Y. Sept. 1963.

[2] R. L. Dannley and G. Jalics, *J. Org. Chem.*, **30**, 2417 (1965).

[3] W. Hahn and L. Metzinger, *Makromol. Chem.*, **21**, 113 (1956).

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[8] A. Simon and H. Arnold, *J. prakt. Chem.*, **8**, 241 (1959).

[9] R. R. Hiatt, *Can. J. Chem.*, **42**, 985 (1964).

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Kinetic Studies of the Hydroperoxide Decompositions.—A weighed sample of the peroxide (0.8 to 1.5 g.) was placed in a 100-ml. volumetric flask to which was added the requisite amount of solvent preheated to the proposed decomposition temperature. After shaking to effect solution, the mixture was transferred to a thermostated vessel and at regular intervals samples were pipetted and titrated.[11]

The temperatures required for the hydroperoxide decompositions were too high for conventional laboratory thermostats. Therefore a flask was secured to the lid of a glass resin kettle equipped to contain a refluxing liquid. Liquids placed in the kettle were selected so that their refluxing would provide vapor baths of the chosen decomposition temperatures. Measurement of the temperatures of the reaction mixtures with a thermocouple showed a maximum variation of 0.3°. All the kinetic data here reported has a limitation of accuracy dependent on this possible variation of temperature.

Results

Identification of Products.—The decomposition of triphenylsilyl hydroperoxide in anisole gave 0.45 mole of triphenylsilanol and 0.29 mole of diphenylsilanediol per mole of hydroperoxide. The unidentified tar undoubtedly consisted largely of polymers derived from diphenylsilanediol. Some attack on solvent occurred, producing *p*-hydroxyanisole (0.09 mole).

Kinetics of Thermal Decompositions.—The hydroperoxides required heating to over 100° to obtain reasonable rates of reaction. Triphenylsilyl hydroperoxide decomposed with a good first-order dependence on hydroperoxide concentration in several solvents (Figure 1), but in mesitylene a shorter half-life and a deviation from the first-order kinetics were observed (Figure 2). A similar first-order behavior in *o*-dichlorobenzene was obtained for methyldiphenylsilyl, tribenzylsilyl, and tri-*n*-hexylsilyl hydroperoxides. Rates were determined at three temperatures and energies of activation were calculated as shown in Table I.

TABLE I

KINETIC DATA FOR THE THERMAL DECOMPOSITION OF 0.05 *M* SOLUTIONS OF TRIORGANOSILYL HYDROPEROXIDES IN VARIOUS SOLVENTS

Compd.	Solvent	Temp., °C.	Half-life, min.	*K*, min.$^{-1}$	E_a, kcal.
Ph_3SiOOH	Mesitylene[a]	128	38		
	Mesitylene[a]	141	23		
	Mesitylene[a]	154	11		
	Anisole	128	105	6.56×10^{-3}	22.63
	Anisole	141	37	1.93×10^{-2}	
	Anisole	154	21	3.7×10^{-2}	
	Methyl benzoate	128	168	7.4×10^{-3}	26.95
	Methyl benzoate	141	56	1.16×10^{-2}	
	Methyl benzoate	154	26	3.06×10^{-2}	
	Nitrobenzene	128	150	4.56×10^{-3}	27.63
	Nitrobenzene	141	60	1.15×10^{-2}	
	Nitrobenzene	154	23	3.79×10^{-2}	
	o-Dichlorobenzene	132	115	6.0×10^{-3}	27.10
	o-Dichlorobenzene	142	73	9.2×10^{-3}	
	o-Dichlorobenzene	154	25	3.5×10^{-2}	
$Ph_2MeSiOOH$[b]	*o*-Dichlorobenzene	118	800	8.48×10^{-4}	26.64
	o-Dichlorobenzene	137	140	4.92×10^{-3}	
	o-Dichlorobenzene	150	43	1.35×10^{-2}	
$Benzyl_3SiOOH$[b]	*o*-Dichlorobenzene	118	175	3.82×10^{-3}	26.40
	o-Dichlorobenzene	128	71	9.78×10^{-3}	
	o-Dichlorobenzene	138	23	2.01×10^{-2}	
$Hexyl_3SiOOH$	*o*-Dichlorobenzene	130	375	3.76×10^{-3}	

[a] In all solvents the hydroperoxide decomposition was first order except in mesitylene. [b] 0.03 *M* peroxide.

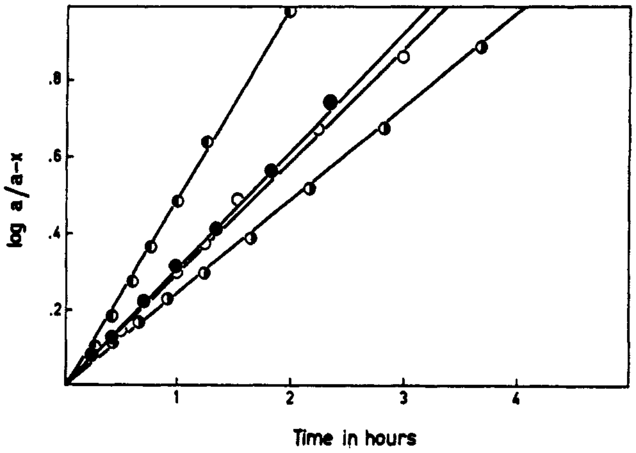

Figure 1.—First-order plots of the disappearance of 0.05 *M* triphenylsilyl hydroperoxide for its thermal decomposition at 142° in ◑, *o*-dichlorobenzene; ◐, anisole; ●, methyl benzoate; and ○, nitrobenzene.

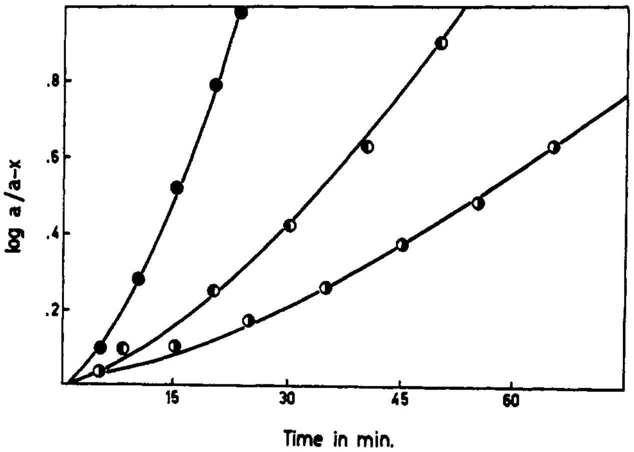

Figure 2.—First-order plots of the disappearance of 0.05 *M* triphenylsilyl hydroperoxide in mesitylene at ◑, 128°; ◐, 141°; and ●, 154°.

Base-Catalyzed Reactions.—The rate of disappearance of triphenylsilyl hydroperoxide is more rapid in the presence of base and is zero order with respect to hydroperoxide (Figure 3). The rates are more rapid with bases possessing the larger K_b values (Table II) unless sterically hindered (2,6-lutidine). The rate of the quinoline-catalyzed decomposition was measured at three temperatures (energy of activation, 11.8 kcal./mole) and three concentrations (Table II). A plot of the rates against concentration of quinoline gave a fractional-order rate dependence on base.

TABLE II

FIRST-ORDER RATE CONSTANTS FOR THE BASE-CATALYZED DECOMPOSITION OF TRIPHENYLSILYL HYDROPEROXIDE[a]

Catalyst	Concn., of amine, *M*	Temp., °C.	$k \times 10^6$, min.$^{-1}$	K_b of catalyst
γ-Picoline	0.0075	100	1.43	1.1×10^{-8}
Pyridine	0.0075	100	1.07	1.4×10^{-9}
2,6-Lutidine	0.0075	100	0.51	2.6×10^{-7}
Quinoline	0.0075	100	0.60	6.3×10^{-10}
Quinoline	0.0075	110	0.85	6.3×10^{-10}
Quinoline	0.0075	122	1.82	6.3×10^{-10}
Quinoline	0.00375	122	1.45	6.3×10^{-10}
Quinoline	0.00197	122	1.15	6.3×10^{-10}

[a] A 0.03 *M* solution in *o*-dichlorobenzene.

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[11] C. D. Wagner, R. H. Smith, and E. D. Peters, *Anal. Chem.*, **19**, 976 (1947).

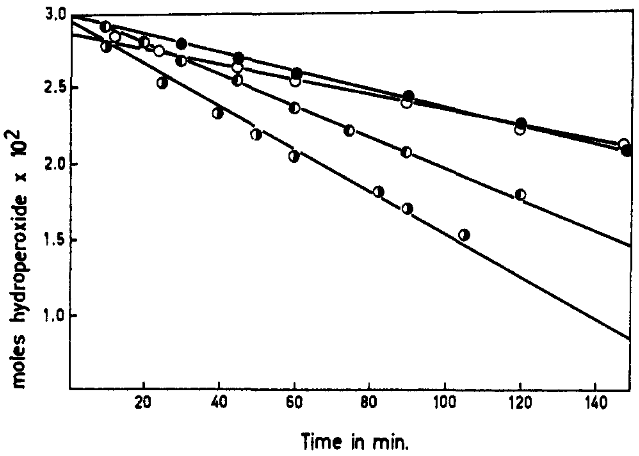


Figure 3.—Zero-order plots of the disappearance of triphenylsilyl hydroperoxide (0.03 M in *o*-dichlorobenzene) at 100° in the presence of 0.007 M concentrations of ◐, pyridine; ◑, γ-picoline; ○, 2,6-lutidine; and ●, quinoline.

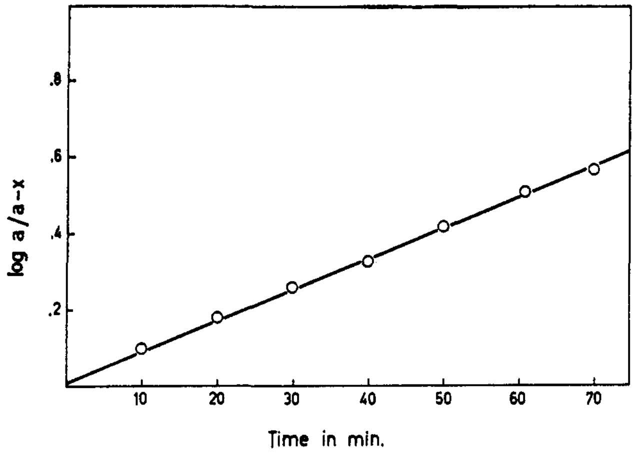


Figure 4.—First-order plot of the disappearance of triphenylsilyl hydroperoxide (0.03 M in chloroform) at 60° when irridiated with ultraviolet light.

Effect of Acid.—The addition of chloroacetic or trichloroacetic acids (0.0075 M) to triphenylsilyl hydroperoxide (0.03 M in *o*-dichlorobenzene) at 132° had no effect on the order of the reaction and a negligible effect on the rate.

Effect of Light.—Ultraviolet light (2537 Å.) greatly accelerated the rate (1.88×10^{-2} min.$^{-1}$, half-life 36 min. at 60°) of the decomposition of triphenylsilyl hydroperoxide (0.03 M in chloroform). The reaction was first-order with respect to hydroperoxide (Figure 4).

Discussion

Thermal Decomposition.—The great stability of the hydroperoxides used in the present work is in marked contrast to the extreme instability of trimethylsilyl hydroperoxide reported by Hahn and Metzinger.[3] The trimethylsilyl compound might similarly be quite stable at room temperature if prepared in a high state of purity.

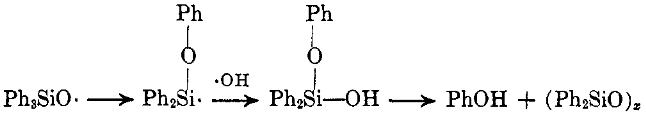
The classification of the thermal rearrangement as a free-radical process is supported by several observations. First, the rate in nitrobenzene is the same as in solvents of much lower dielectric constant (*e.g.*, methyl benzoate and *o*-dichlorobenzene). Second, this reaction exhibiting first-order kinetics is accelerated by light (Figure 4). Third, the reaction is not acid-catalyzed, in contrast to the marked influence of acids on reactions of carbon peroxides involving positively charged intermediates. Fourth, base catalysis (which should produce negatively charged intermediates) leads to an entirely different reaction path as evidenced by a change in kinetics (pseudo zero order, Figure 3).

For previously reported[5-7,9] rearrangements of organoperoxysilanes, ionic mechanisms have generally been proposed, primarily because of observed acid catalysis (in one instance[5] the relative migration aptitude of an aryl group also favored an ionic mechanism). Although the structural changes described were similar to those in the present work, the acid catalysis indicates a major mechanistic difference from the hydroperoxide rearrangements considered here.

In the thermal decompositions of the hydroperoxides both the rate and activation energy (Table I) are almost completely independent of the solvent and the groups attached to silicon. These data are consistent with the homolysis of the peroxide bond as a first and rate-determining step. The free radicals thus produced may then react in several ways.

$$Ph_3SiOOH \longrightarrow Ph_3SiO\cdot + \cdot OH$$

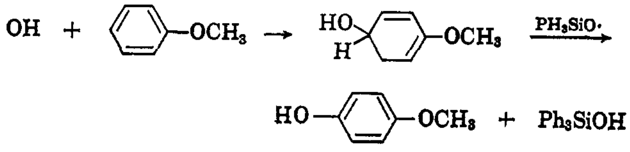
One reaction involves the rearrangement of the silyloxy radical to produce a phenoxysilanol which later is degraded[12] to phenol and a silanediol (or its polymer).



$$Ph_3SiO\cdot \longrightarrow Ph_2\overset{\overset{Ph}{|}\atop\overset{O}{|}}{Si}\cdot \xrightarrow{\cdot OH} Ph_2\overset{\overset{Ph}{|}\atop\overset{O}{|}}{Si}{-}OH \longrightarrow PhOH + (Ph_2SiO)_x$$

The production of the phenoxysilanol may be a cage reaction. The mechanism of the degradation of the phenoxysilanol is not known but a simple hydrolysis to the silanediol is possible if water (either present or produced) is available. The silanediol and polymeric products were obtained. The phenol was isolated in the present work from a thermal decomposition in dibutyl phthalate in which the phenol distilled as it was formed. If not removed in this manner, the phenol is oxidized by the free radicals to produce tar and triphenylsilanol.

A second reaction pathway of the free radicals is an aromatic substitution yielding *p*-hydroxyanisole. The



ortho and *meta* isomers are probably also produced but the analytical procedure was not precise enough to establish their presence. This reaction accounts for some of the triphenylsilanol which is found.

The energy of activation for the dissociation of a silylhydroperoxide is quite insensitive to the groups attached to silicon, varying between 26.40 and 27.10 kcal./mole for the three silyl hydroperoxides investigated (Table I). Any electronic effects must be transmitted too far through the molecule to appreciably affect the dissociation of the oxygen-to-oxygen bond. The

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[12] F. S. Kipping, *J. Chem. Soc.*, 2731 (1927).

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 $d\pi - p\pi$ 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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[15] R. L. Dannley, W. A. Aue, and G. Corbett, unpublished work.

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[17] A. Rieche and J. Dahlmann, *Ann.*, **675**, 19 (1964).

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[19] J. Murawski, J. S. Roberts, and M. Szwarc, *J. Chem. Phys.*, **19**, 698 (1951).

Dialklyboronium Acetylacetonates

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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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[6] W. Gerrard, M. F. Lappert, and R. Shafferman, *Chem. Ind.* (London), 722 (1958).

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