

## The Stereochemistry of Mercuri-deboronation of 1-Phenylethaneboronic Acid<sup>1</sup>

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(*R*)-(–)-Dibutyl 1-phenylethaneboronate reacts with mercuric chloride in water-glycerol-acetone containing sodium chloride and sodium acetate to yield (*R*)-(+)–1-phenylethylmercuric chloride. Synthesis of the boronic ester started from  $\alpha$ -chlorostyrene, which was converted via the Grignard reagent to dibutyl  $\alpha$ -styreneboronate. Catalytic hydrogenation yielded dibutyl 1-phenylethaneboronate. Resolution was carried out by crystallization of the bisdemethylbrucine derivative which yielded (–)-dibutyl 1-phenylethaneboronate on treatment with aqueous acid and extraction with butanol. The absolute configuration of (*R*)-(–)-dibutyl 1-phenylethaneboronate was proved by degradation with hydrogen peroxide to (*R*)-(+)–1-phenylethanol. The configuration of (*R*)-(+)–1-phenylethylmercuric chloride was proved by bromodemercuration to (*R*)-(+)–1-phenylethyl bromide. Because of optical instability of the mercury compound, the net retention measured was only 11–14%. The relation of mercuri-deboronation to other electrophilic displacements at saturated carbon is discussed.

### Introduction

Retention of configuration is the expected stereochemistry in concerted electrophilic (SE2) displacements at saturated carbon. However, we have observed preferential inversion in transannular displacement of boron from norborneneboronic acids,<sup>2</sup> and more recent work has shown that the bicyclo[2.2.2]-octene-5-boronic acids behave in analogous fashion.<sup>3</sup> We have suggested<sup>2</sup> that the normal preference for retention may result from cyclic transition states in which the attacking and leaving electrophiles are linked through an anionic ligand, not possible for steric reasons in the transannular displacements. Cram, *et al.*, have suggested analogous interpretations for electrophilic displacements involving carbanions, for which all possible stereochemical outcomes have been observed.<sup>4</sup> Accordingly, we do not regard the stereochemical outcome of concerted electrophilic displacements to be a foregone conclusion, even though all the small number of such (nontransannular) displacements studied so far proceed with retention.

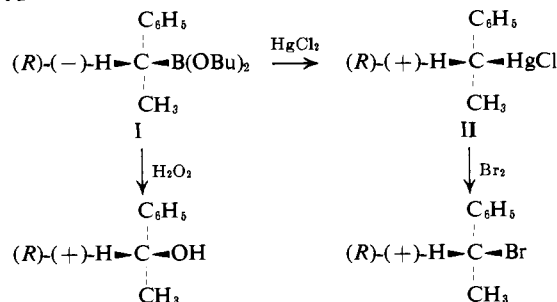
1-Phenylethaneboronic acid was chosen for the present study because benzylboronic acid reacts with

aqueous mercuric chloride<sup>5</sup> whereas ordinary aliphatic boronic acids do not.<sup>6</sup> An aqueous system was desired in order to minimize the energy to be gained by a cyclic transition state involving ion pairing.

### Results

Retention is favored in the reaction of 1-phenylethaneboronic acid (or ester) with mercuric chloride to yield 1-phenylethylmercuric chloride, but the optical instability of the product precludes proof of stereospecificity. Our evidence is based on reactions and products having known stereochemistry, namely, hydrogen peroxide deboronation with retention,<sup>7</sup> bromodemercuration with retention,<sup>8</sup> and the absolute configurations of 1-phenylethanol and 1-phenylethyl bromide.<sup>9</sup> These results are summarized in Chart I,

Chart I



and the difficulties and necessary innovations in obtaining them are described in the following paragraphs.

Dibutyl 1-phenylethaneboronate (I) was obtained only with much labor and in poor yield by the usual route to boronic esters, since extensive Wurtz coupling occurs in the reaction of 1-phenylethyl chloride or bromide with magnesium. This problem was circumvented by starting from  $\alpha$ -chlorostyrene, which readily yields the Grignard reagent in tetrahydrofuran, and preparing dibutyl  $\alpha$ -styreneboronate by the usual reaction with methyl borate and esterification with butanol. The unsaturated boronic ester was easily hydrogenated.

(5) E. Khotinsky and M. Melamed, *Ber.*, **42**, 3090 (1909).

(6) K. Torssell, *Acta Chem. Scand.*, **13**, 115 (1959).

(7) (a) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 2544 (1961); (b) D. S. Matteson and J. O. Waldbillig, *J. Org. Chem.*, **28**, 366 (1963).

(8) (a) F. R. Jensen and L. H. Gale, *J. Am. Chem. Soc.*, **82**, 148 (1960); (b) F. R. Jensen, L. D. Whipple, D. K. Wedegaertner, and J. A. Landgrebe, *ibid.*, **82**, 2466 (1960).

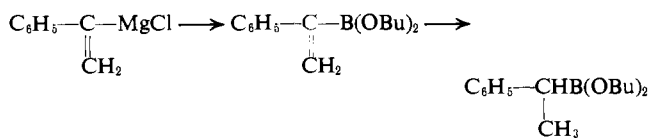
(9) (a) E. D. Hughes, C. K. Ingold, and A. D. Scott, *J. Chem. Soc.*, 1201 (1937); (b) critical literature survey: H. J. Dauben, Jr., and L. L. McCoy, *J. Am. Chem. Soc.*, **81**, 5404 (1959).

(1) We thank the National Science Foundation for financial support, NSF-G 19906 and GP 2953.

(2) D. S. Matteson and J. O. Waldbillig, *J. Am. Chem. Soc.*, **86**, 3778 (1964).

(3) D. S. Matteson and M. L. Talbot, to be published.

(4) D. J. Cram and A. S. Wingrove, *J. Am. Chem. Soc.*, **86**, 5490 (1964), and 23 preceding papers by Cram, *et al.*



Asymmetric syntheses of optically active boranes have been described,<sup>10</sup> but we could see no way to adapt these to our needs, nor are we aware of any previous resolution of a boronic acid. The weak acidity of boronic acids probably precludes salt formation with alkaloids. Amine-boronic anhydride complexes<sup>11</sup> provide a potential route to boronic acid resolution, but the brucine complex of 1-phenylethane-boronic anhydride appeared to be very soluble in polar solvents, and material crystallized from methylcyclohexane showed no optical activity on conversion to the butyl ester.

The desired resolution was accomplished by the use of a catechol, bisdemethylbrucine (bisapomethylbrucine),<sup>12</sup> which is presumably effective because it forms a stable chelate with boron.<sup>13</sup> The derivative crystallized from ethanol-water. Treatment of the solid with dilute hydrochloric acid and extraction with butanol yielded (–)-dibutyl 1-phenylethaneboronate (I) (about 50% resolved after six to eight recrystallizations, according to the rotation of the alcohol obtained on hydrogen peroxide deboronation<sup>7</sup>). The mother liquor from the first crystallization (carried out with a deficiency of bisdemethylbrucine) was similarly treated to yield the (+)-isomer. The acid presumably has little effect on the dissociation equilibrium of the chelate, but merely holds the bisdemethylbrucine in the aqueous phase while the boronic ester is extracted out.

Dibutyl 1-phenylethaneboronate (I) reacts readily with mercuric chloride in aqueous acetone or dimethyl sulfoxide buffered with sodium acetate. Crystalline 1-phenylethylmercuric chloride (II) begins to separate within a few minutes at room temperature. However, the product II is contaminated with mercurous chloride and apparently other by-products. Repeated recrystallization from acetone-water failed to purify it. The optical activity was completely lost except in one run, in which (–)-boronic ester I yielded mercury compound II with a barely detectable (+) rotation.

Addition of excess sodium chloride<sup>14</sup> drastically reduced the rate, no crystals appearing in 2 days under conditions where 5 min. would have sufficed in its absence. A useful rate was restored by adding glycerol or ethylene glycol to the reaction mixture, which apparently greatly activates the borono function as a leaving group. The reactants but not the product were soluble in 50% water, 31% glycerol, and 19% acetone. Under these conditions, (–)-dibutyl 1-phenylethaneboronate (I) yielded (+)-1-phenylethylmercuric chloride (II), and the product was easily purified. Consistent relation between the rotations of

Table I. Specific Rotations at 23°

Set no.	B compd. I (neat)	Hg compd. II (in pyridine)	PhCHBrCH <sub>3</sub> (in CHCl <sub>3</sub> )	PhCHOH-CH <sub>3</sub> (neat)
1	–7.40	+3.38	+4.04	+16.03
2	–8.42	+4.12		
3	–10.44	+5.12 <sup>a</sup>	+6.12	
4	+5.06	–2.47	–3.30	–10.50
5 <sup>b</sup>	+4.67	–2.14		
6 <sup>c</sup>	+3.67	–1.54		

<sup>a</sup> Isolated after 24 hr. (50% yield). Subsequent fractions had lower rotations: after 60 hr., +4.50 (14%); 120 hr., +3.79 (9%); and 300 hr., +3.16 (10%). Total yield, 83%. <sup>b</sup> *p*-Nitrophenoxide was substituted for acetate as the buffer. <sup>c</sup> Ethylene glycol was substituted for glycerol in the solvent mixture.

I and II (isolated after 12–24 hr.) was observed, as shown in Table I.

For optically pure (*R*)-1-phenylethanol,  $[\alpha]^{20}_D$  is +43.5° (neat).<sup>9b</sup> Assuming 100% retention in the deboronation with alkaline hydrogen peroxide,<sup>7</sup> the calculated rotation of optically pure (*R*)-dibutyl 1-phenylethaneboronate (I) is –20.1 to –20.9° (23°, neat) from Table I, sets 1 and 4. From the rotation of optically pure 1-phenylethyl bromide,  $[\alpha]^{20}_D$  96.4° (neat), the over-all net retention in the conversion of I to mercury compound II to 1-phenylethyl bromide is 11–14%.

Optically active 1-phenylethylmercuric chloride (II) in aqueous 90% acetone racemized slightly in a few minutes and completely in less than 3 hr. On recovery, II was shown by infrared to be otherwise unchanged. In the presence of 1.5 equiv. of sodium chloride, the specific rotation of a sample of II was –2.50° at 0 hr., –2.00 at 4 hr., –1.20 at 16 hr., –0.10 at 26 hr., and 0.00 at 44 hr. It is clear that no simple rate law is followed. Because of its insolubility, it is impossible to measure the rate of racemization of II in a system as aqueous as that used for the mercuri-deboronations. However, the decrease in optical activity of successive portions of II suggests racemization of II with increasing exposure to the reaction medium. Water decidedly increases the amount of mercurous chloride formed, which in our experience as well as that of others<sup>14</sup> is correlated with the amount of racemization. The reaction of I with mercuric chloride in water alone yielded mercurous chloride as the major product. The mercury compound II showed no change in rotation in a week in pyridine. However, the mercuri-deboronation did not proceed at an observable rate in the presence of enough pyridine to complex all the mercuric chloride.

## Discussion

The mercuri-deboronation is clearly a concerted electrophilic displacement, with the rate dependent on the mercuric species present as well as the boron compound. Thus, it is unlikely that racemization occurs as part of the mechanism of displacement of boron by mercury. Competing retention and inversion mechanisms are possible in principle, with retention being more than 1.25 times as fast as inversion. There is no evidence for any inversion at all. That the 1-phenylethylmercuric chloride (II) is 88% racemized is satisfactorily explained by its demonstrated optical instability. It is also possible that some of the racemization

(10) H. C. Brown, N. R. Ayyangar, and G. Zweifel, *J. Am. Chem. Soc.*, **86**, 397 (1964).

(11) H. R. Snyder, M. S. Konecky, and W. J. Lennarz, *ibid.*, **80**, 3611 (1958).

(12) H. Leuchs and R. Anderson, *Ber.*, **44**, 2136 (1911).

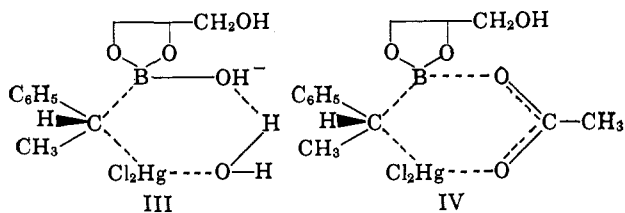
(13) M. J. S. Dewar, V. P. Kubba, and R. Pettit, *J. Chem. Soc.*, 3076 (1958).

(14) We thank Dr. T. G. Traylor for pointing out that racemization of organomercury compounds, generally accompanied by mercury(I) formation, often occurs and may be slowed by reagents such as chloride ion which complex with mercury(II).

occurs during the isolation of the 1-phenylethyl bromide, the compound on which the measurement of stereospecificity depends.

We are particularly interested in the role played by cyclic transition states as a factor governing the stereochemistry of electrophilic displacements. In the present system, the energy that might be gained by making the transition state cyclic appears to be small. While it is not possible to define the effective electrophilic mercury(II) species without much more data, a consideration of stability constants<sup>15</sup> of mercury(II) chloride complexes limits the possibilities. The chloride ion concentration in our solutions was 0.4 *M* (in excess of that complexed), which in water would leave about 4% (0.005 *M*) of the mercury(II) as  $\text{HgCl}_2$ , the rest  $\text{HgCl}_3^-$  and  $\text{HgCl}_4^{2-}$ . The calculated  $\text{HgCl}_3^-$  concentration is about  $5 \times 10^{-9}$  *M* if *K* for  $\text{HgCl}^+ + \text{Cl}^- \rightarrow \text{HgCl}_2$  is  $3 \times 10^6$ .<sup>15b</sup> The stability constant for  $\text{Hg}^{2+} + \text{OH}^- \rightarrow \text{HgOH}^+$  is about  $10^{11}$ .<sup>16a</sup> If it is assumed that  $\text{HgCl}^+$  has a similar constant, the concentration of  $\text{ClHgOH}$  at pH 5 is  $10^{-6}$  or  $10^{-7}$ . The stability constants for heavy metal ions with acetate appear to be generally about  $10^2$ ,<sup>16b</sup> which would make the  $\text{ClHgOAc}$  concentration about  $10^{-7}$  or  $10^{-8}$  *M* at 0.1 *M* acetate. These figures are very rough, but the probable 1000-fold or greater concentration advantage of  $\text{HgCl}_2$  over rival electrophiles suggests it is the active species.

Since chloride ion is essentially nonbasic toward boronic acids, a mercury-chloride-boron linkage would not assist the electrophilic displacement. However, in the transannular displacements of boron from the norborneneboronic acids, inversion was favored over retention by only about 3 kcal./mole.<sup>2</sup> If this figure truly represents the amount by which inversion is favored by the electronic structure around the central carbon atom, the energy of a single hydrogen bond linking the attacking and leaving electrophiles (possible only if retention occurs) would be sufficient to reverse the stereochemical preference completely. Aqueous mercuric chloride probably is coordinated with four water molecules<sup>16a</sup> and may also be "solvated" by acetate ions. (Mercuric chloride appears to assist the dissolving of sodium acetate in aqueous acetone.) There are several opportunities for fairly weak but significant interactions, for example, transition states III and IV. *p*-Nitrophenoxide ion, which would require



a four-membered ring if substituted for acetate in path IV, did not alter the stereochemistry and gave a rate of the same order of magnitude.

Similar considerations apply to previously studied electrophilic displacements. It has been argued<sup>17</sup>

(15) (a) P. K. Gallagher and E. L. King, *J. Am. Chem. Soc.*, **82**, 3510 (1960); (b) L. G. Sillén, *Acta Chem. Scand.*, **3**, 539 (1949); (c) Y. Marcus, *ibid.*, **11**, 599 (1957).

(16) J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, "Stability Constants," Metcalfe and Cooper, London, 1958: (a) Part II, pp. 18, 19; (b) Part I, p. 3.

(17) (a) H. B. Charman, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 2530 (1959); (b) H. B. Charman, E. D. Hughes, C. K. Ingold, and

that the cleavage of dialkylmercuries by mercury(II) in ethanol proceeds *via* an  $\text{SE}_2$  (acyclic, "apart from its solvation"<sup>17b</sup>) transition state, not an  $\text{SE}_i$  ( $\text{Hg}$ -anion- $\text{Hg}$  linkage) path, on the basis that the relative reactivities of attacking electrophiles are  $\text{Hg}(\text{NO}_3)_2 > \text{Hg}(\text{OAc})_2 > \text{HgBr}_2 > \text{HgBr}_3^-$ .<sup>17</sup> In contrast, the exchange of alkylmercuric bromide with mercuric bromide is catalyzed by bromide ion and is clearly  $\text{SE}_i$ .<sup>17</sup> In our view, these orders of reactivities prove that, in some cases, increasing the electrophilic character of the attacking species has more effect on the rate than does decreasing the electrophilic character of the leaving group, while in other cases the reverse is true, and nothing more. It is most unlikely under any circumstances that the leaving group is an unsolvated  $\text{RHg}^+$  cation, and it is probable that the attacking electrophile is an ion pair in ethanol. Cyclic transition states analogous to III and IV seem likely. There is a possible example of a true, noncyclic,  $\text{SE}_2$  reaction in the proto-demercuration of di-4-camphenylmercury,<sup>18</sup> but inversion is sterically prohibited in this system.

We conclude that there is a strong likelihood of cyclic ( $\text{SE}_i$ ) transition states in all electrophilic displacements that proceed with retention, that the energy advantage due to such interaction has been made small in our mercuri-deboronation and other<sup>17, 18</sup> displacements, but in view of the moderate preference for inversion in a transannular displacement,<sup>2</sup> that even this small energy advantage might be decisive.

As indicated for structures III and IV, it is probable that the cyclic glycerol (or ethylene glycol) ester coordinated with a basic anion is the active boron leaving group, the cyclic ester being significantly more acidic than the boronic acid or butyl ester. Base catalysis is generally required for mercuri-deboronation.<sup>19</sup>

The racemization of 1-phenylethylmercuric chloride (II) appears from the limited rate data to be a chain reaction. The fact that chloride ion or pyridine retards racemization and mercurous chloride formation while water accelerates mercurous chloride formation suggests that decomposition of 1-phenylmercuric ion initiates the racemization process, perhaps by solvolysis to mercury(0) and 1-phenylethyl cation, a reaction characteristic of activated alkylmercuric ions.<sup>20</sup> The nature of the chain-carrying species is not clear.

## Experimental

*α*-Chlorostyrene. Previous preparations<sup>21</sup> were improved by treating the crude 1-phenyl-1,1-dichloroethane from 240 g. of acetophenone and 453 g. of phosphorus pentachloride with 161 g. of *t*-butylamine in 250 ml. of ether during 1 hr. at 0°. The *t*-butylamine hydrochloride was filtered and washed with ether. The filtrate was concentrated, and the *α*-chlorostyrene was distilled through a 30-cm. packed column, b.p. 62° (7 mm.), yield 205 g. (74%).

*Dibutyl α*-Styreneboronate. The Grignard reagent was prepared from 192 g. of *α*-chlorostyrene and 35 g.

F. G. Thorpe, *ibid.*, 1121 (1961); (c) H. B. Charman, E. D. Hughes, C. K. Ingold, and H. C. Volger, *ibid.*, 1142 (1961); (d) E. D. Hughes and H. C. Volger, *ibid.*, 2359 (1961).

(18) S. Winstein and T. G. Traylor, *J. Am. Chem. Soc.*, **78**, 2597 (1956).

(19) H. G. Kuivila and T. C. Muller, *ibid.*, **84**, 377 (1962).

(20) F. R. Jensen and R. J. Ouellette, *ibid.*, **83**, 4477, 4478 (1961).

(21) F. K. Beilstein, "Handbuch der organischen Chemie," 4th Ed. 2nd Suppl., Springer-Verlag, Berlin, 1943, p. 367.

of magnesium in 300 ml. of tetrahydrofuran. This was added to 170 ml. of methyl borate in 640 ml. of ether with stirring below  $-65^{\circ}$ . The mixture was acidified with 550 ml. of 3 *M* hydrochloric acid, extracted with butanol and ether (1:1), and distilled to yield 270 g. (75%) of dibutyl  $\alpha$ -styreneboronate, b.p.  $98^{\circ}$  (0.4 mm.).

*Anal.* Calcd. for  $C_{16}H_{26}BO_2$ : C, 73.86; H, 9.68; B, 4.15. Found: C, 73.65; H, 9.80; B, 4.10.

*Dibutyl 1-Phenylethaneboronate.* Hydrogenation of 26 g. of dibutyl  $\alpha$ -styreneboronate in 100 ml. of butanol at 2–3 atm. over 0.05 g. of 10% palladium-on-charcoal catalyst yielded 23–25 g. of dibutyl 1-phenylethaneboronate, b.p.  $80$ – $83^{\circ}$  (0.1 mm.),  $d^{25}$  0.910,  $n^{25}_D$  1.4709.

*Anal.* Calcd. for  $C_{16}H_{27}BO_2$ : C, 73.29; H, 10.38; B, 4.12. Found: C, 73.09; H, 10.31; B, 4.12.

*Bisdemethylbrucine.* The nitric acid treatment<sup>12</sup> of pure brucine sulfate required a catalytic amount of sodium nitrite<sup>22</sup> to start the reaction. We used sodium bisulfite (instead of sulfur dioxide) for the reduction and found it necessary to keep the mixture below  $10$ – $15^{\circ}$  to avoid tar formation.

*Resolution of Dibutyl 1-Phenylethaneboronate.* The crude bisdemethylbrucine salt worked as well as the more elaborately prepared hydrochloride.<sup>12</sup> It was necessary to carry out all operations under nitrogen. A solution of 42 g. of bisdemethylbrucine sulfate in 420 ml. of near-boiling water was mixed with 37 g. of dibutyl 1-phenylethaneboronate in 840 ml. of cool 95% ethanol, then treated with 14 g. of sodium bicarbonate. Crystals separated on cooling. The filtrate was concentrated under vacuum to about half its volume, diluted with 2–3 volumes of water, and treated with 30 ml. of hydrochloric acid. Extraction with four  $\sim$ 300-ml. portions of 1:5 butanol–ether followed by distillation yielded 5.5–6 g. of dibutyl 1-phenyl-

ethaneboronate,  $[\alpha]^{25}_D +4$  to  $+5^{\circ}$ . The crystalline demethylbrucine derivative was recrystallized repeatedly from 65% ethanol–water, then treated with 0.5 *M* hydrochloric acid and extracted and distilled as described for the other enantiomer. After three recrystallizations, 4.7 g. of dibutyl 1-phenylethaneboronate was obtained,  $[\alpha]^{25}_D -7.4^{\circ}$ . Eight recrystallizations led to 1.9 g. of product,  $[\alpha]^{25}_D -10.4^{\circ}$ .

*1-Phenylethylmercuric Chloride.* A solution of 1.20 g. of sodium chloride, 1.00 g. of mercuric chloride, and 0.30 g. of sodium acetate in 8 ml. of water, 5 ml. of glycerol, and 3 ml. of acetone was mixed with a (slightly cloudy) solution of 0.65 g. of dibutyl 1-phenylethaneboronate in the same quantities of solvents. Crystallization began within 0.5 hr. at  $23^{\circ}$ . The yield of 1-phenylethylmercuric chloride after 24 hr. was 0.36 g. (53%), m.p.  $116$ – $118^{\circ}$ . In set 5, Table I, the sodium acetate was replaced by 0.13 g. of sodium hydroxide and 0.53 g. of *p*-nitrophenol and the product was isolated after 12 hr. The analytical sample was recrystallized from acetone, m.p.  $118$ – $119^{\circ}$ .

*Anal.* Calcd. for  $C_8H_9ClHg$ : C, 28.16; H, 2.66; Cl, 10.39; Hg, 58.79. Found: C, 28.25; H, 2.74; Cl, 10.12; Hg, 58.72.

*1-Phenylethyl Bromide.* Dropwise addition of 0.9 g. of bromine in 6 ml. of pyridine to 1.5 g. of 1-phenylethylmercuric chloride in 5 ml. of pyridine at  $\sim -60^{\circ}$  followed by addition of 20 ml. of hexane and 20 ml. of water, then further extraction with hexane below  $-5^{\circ}$ , yielded 0.45–0.5 g. (42–47%) of 1-phenylethyl bromide, b.p.  $46$ – $48^{\circ}$  (1 mm.), shown to be free of 1-phenylethyl chloride by n.m.r. comparison with authentic samples and by elemental analysis.

*Anal.* Calcd. for  $C_8H_9Br$ : C, 51.92; H, 4.90; Br, 43.18. Found: C, 52.18; H, 4.87; Br, 43.43.

*1-Phenylethanol* was prepared from optically active dibutyl 1-phenylethaneboronate by treatment with alkaline hydrogen peroxide<sup>7b</sup> and distilled, yield 64–77%.

(22) H. Leuchs, H. Seeger, and K. Jaegers, *Ber.*, 71, 2023 (1938).

## The Stereochemistry of 9-Decalyl Free Radicals

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*cis*- and *trans*-9-carbo-*t*-butylperoxydecalins undergo thermal decomposition in cumene at  $50^{\circ}$  at identical rates and with direct formation of decalyl radicals, carbon dioxide, and *t*-butoxy radicals. The products, *cis*- and *trans*-decalins, 1,9- and 9,10-octalins, formed from decalyl radicals in various degassed solvents, are the same from either perester. In the presence of oxygen at 1 atm. in cyclohexane or 1,2-dimethoxyethane, *cis*- and *trans*-9-decalyl hydroperoxides are formed (10% *cis*, 90% *trans* from either perester). This same ratio of hydroperoxides is also obtained from *trans* perester at 600 atm. of oxygen, while at high pressures from *cis* per-

ester more *cis* hydroperoxide is formed (e.g., at 545 atm. of oxygen in 1,2-dimethoxyethane, 70% *cis*, 30% *trans*). The results show that two different 9-decalyl radicals exist; one a short-lived (ca.  $10^{-8}$ – $10^{-9}$  sec.) radical from *cis* source which changes into the same radical obtained from *trans* source but yields *cis* product on reaction with oxygen, and the other a more stable radical from *trans* source which yields both *cis* and *trans* products on reaction with oxygen. The products obtained indicate a nonplanar arrangement of bonds at C-9 for the initial radical from *cis* source and a coplanar arrangement of bonds at C-9 for the more stable radical from both sources.