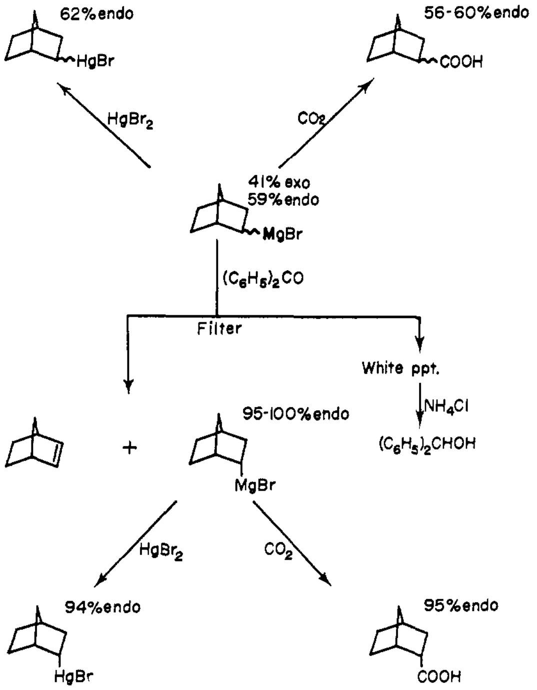
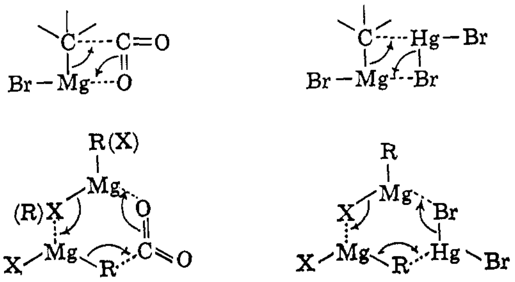


Figure 2. Reaction of carbon dioxide and mercuric bromide with the 2-norbornyl Grignard reagent with and without prior treatment with benzophenone.

substitution with retention of configuration. The results are summarized in Figure 2.

When a sample of the *endo* Grignard reagent was placed in the HA-100 probe at 37°, the multiplet due to the *exo* isomer slowly increased with time. Similarly, the equilibrium composition was obtained upon allowing a sample to stand at room temperature for 1 day. Whitesides and Roberts[10] have reported that typical secondary Grignard reagents interconvert slowly if at all on the nmr time scale. Thus, the norbornyl Grignard reagent appears to behave as a normal secondary aliphatic compound.

Reasonable SEi and SE2 type mechanisms can be written for these reactions. Because of the Lewis acid nature of magnesium(II), the SEi processes seem more likely. Plausible transition states are



Detailed kinetic, stereochemical, and interconversion rate studies are contemplated for these compounds.

Acknowledgment. Support of this work by the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

(10) G. M. Whitesides and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 4878 (1965).

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A Reinvestigation of the Purported SE1 Reaction of Di-*sec*-butylmercury

Sir:

Of importance to theoretical studies of electrophilic substitution would be the availability of a simple process for generating alkyl carbanions. Recently, Hart and Ingold[1] reported that carbanions are formed upon admixing di-*sec*-butylmercury and diethylthallium bromide, and they drew broad generalizations from their findings. This reaction has been reinvestigated and not only is the mechanism not of the type reported but the reaction which occurs is air oxidation of the mercurial.

These workers determined the kinetics of the reaction between di-*sec*-butylmercury (optically active) and diethylthallium bromide at 70° in dimethylformamide (DMF) solution in the presence of small amounts of water and cyclohexene which were thought to suppress kinetic disturbances. The atmosphere was not stated. First-order in mercurial and zero-order in thallium compound kinetics were observed, and an identical rate constant was obtained by following the rate of disappearance of titrable bromide, formation of base, or disappearance of optical activity in the solution. No products were isolated, but upon the kinetic results the following reaction scheme was proposed.

$$(sec\text{-Bu})_2\text{Hg} \xrightarrow{\text{slow}} sec\text{-BuHg}^+ + sec\text{-Bu}^- \qquad (1)$$

$$sec\text{-BuHg}^+ + \text{Br}^- \xrightarrow{\text{fast}} sec\text{-BuHgBr} \qquad (2)$$

$$sec\text{-Bu}^- + \text{Et}_2\text{Tl}^+ \xrightarrow{\text{fast}} sec\text{-BuEt}_2\text{Tl} \qquad (3)$$

$$sec\text{-BuEt}_2\text{Tl} + \text{H}_2\text{O} \xrightarrow{\text{fast}} \text{RH} + \text{R}_2\text{TlOH} \qquad (4)$$

The experimental work and conclusions appeared to be questionable on many grounds, but two particularly puzzling facets were that the carbanions were postulated to react faster with the thallium compound than with water and eq 1 is contrary to the established behavior of dialkylmercurials. A much more reasonable and simpler postulate appeared to be that the reaction which was observed was the well-known air oxidation of dialkylmercurials.[2]

The reaction was restudied in a thermostated gas buret under the exact specified conditions, except that both air and inert atmospheres were utilized. When the reagents were brought together in the gas buret under an air atmosphere a reaction occurred, but an uptake of gas (oxygen) resulted rather than the gas evolution expected from Hart and Ingold's conclusions. The products of this reaction were also inconsistent with the scheme proposed by the previous workers and included 1-butene, butane, *cis*- and *trans*-2-butene, 2-butanone, and 2-butanol. *sec*-Butylmercuric bromide and diethylthallium hydroxide were obtained in the work-up consistent with the postulate of Hart and Ingold. The rate of reaction, the total amount of oxygen uptake (0.5 to >2 molar amounts), and the distribution of products depends on the partial pressure

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(1) C. R. Hart and C. K. Ingold, *J. Chem. Soc.*, 4372 (1964); C. K. Ingold, *Helv. Chim. Acta*, **47**, 1191 (1964), *Record Chem. Progr.*, **25**, 145 (1964).

(2) Recent examples are Yu. A. Aleksandrov, O. N. Druzhkov, S. F. Zhil'tsou, and G. A. Razuvaev, *Dokl. Akad Nauk SSSR*, **157**, 1395 (1964); *Zh. Obshch. Khim.*, **35**, 1440 (1965).

of oxygen above the solution and the rate of stirring. The same products were obtained in the absence of the thallium compound, except that the alkylmercuric salt was formed as the hydroxide or alkoxide. *sec*-Butylmercuric bromide yields the same types of products when subjected to air or oxygen under these conditions, but the reaction is slower than with di-*sec*-butylmercury. We were unable to reproduce the kinetic data of Hart and Ingold, and the substantial agreement within their data was apparently fortuitous.

In marked contrast to this behavior under an air atmosphere, when the reagents were brought together in the absence of oxygen (nitrogen atmosphere) no reaction occurred. No gas was taken up or evolved, and after three half-lives (Hart and Ingold's half-lives) the diethylthallium bromide and di-*sec*-butylmercury were recovered in ~100 and >90% yields, respectively.

An important part of the discussion in Hart and Ingold's paper was in respect to the postulated alkyl group exchanges (eq 1–4). In order to ascertain the validity of these postulates, two samples were prepared in nmr tubes under Hart and Ingold's conditions but under an inert atmosphere; one sample contained diethylmercury and di-*sec*-butylthallium chloride and the other contained di-*sec*-butylmercury and diethylthallium bromide, along with the appropriate amounts of water, cyclohexene, and DMF as solvent. The tubes were placed in a bath at 70° and were removed from time to time to record the nmr spectrum of the contents. Since no interchange occurred after 1 week, as evidenced by the constancy of the peak positions, it is concluded that the postulated alkyl exchange does not occur.

Detailed studies of the reaction of diisopropylmercury with oxygen under conditions comparable to those of Hart and Ingold have been carried out by Aleksandrov, *et al.*[2] From their studies, they concluded that the reaction of diisopropylmercury and oxygen occurs by a free radical chain process and our results indicate the same for di-*sec*-butylmercury. In both reactions an induction period is observed, the reactions are subject to inhibition, the kinetics tend to be erratic, and the product distributions vary with the concentration of oxygen. Some possible chain propagating steps are shown in eq 5–8.

$$\mathrm{RHgO_2R} \longrightarrow \mathrm{RO\cdot} + \mathrm{RHgO\cdot} \tag{5}$$

$$\mathrm{RO\cdot} + \mathrm{R_2Hg} \longrightarrow \mathrm{RHgOR} + \mathrm{R\cdot} \tag{6}$$

$$\mathrm{R\cdot} + \mathrm{O_2} \longrightarrow \mathrm{RO_2\cdot} \tag{7}$$

$$\mathrm{RO_2\cdot} + \mathrm{R_2Hg} \longrightarrow \mathrm{RHgO_2R} + \mathrm{R\cdot} \tag{8}$$

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Rearrangement of 1,2- to 2,3-Dimethylpentaborane(9)

Sir:

The base-catalyzed rearrangement of 1,2-$(CH_3)_2B_5H_7$ (apex, basal) is shown here by X-ray diffraction methods to yield only one isomer, 2,3-$(CH_3)_2B_5H_7$, in which methyl groups are attached to adjacent B atoms. Absence of the 2,4 isomer is attributed to H(methyl)··· H(bridge) repulsions in a more detailed development of a probable nearly trigonal bipyramidal transition state of $(CH_3)_2B_5H_7$ (Figure 1), or of a possible closely related intermediate $(CH_3)_2B_5H_6^-$.

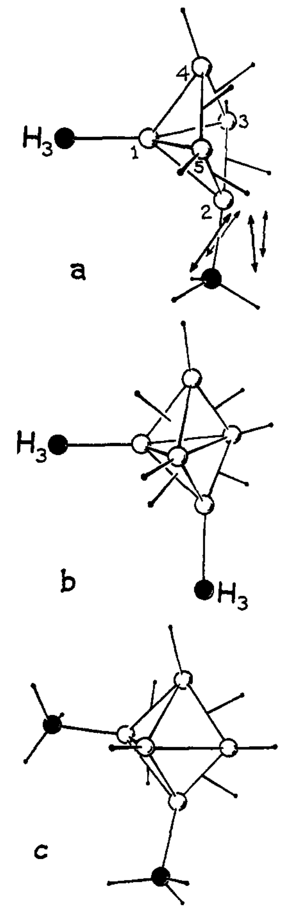

Figure 1. Proposed dimethylpentaborane rearrangement mechanism: a to b to c. Although H-atom positions are highly tentative, it seems likely that the H(methyl)···H(bridge) contacts indicated by double arrows in a may hinder B2···B4 approach. Hence, the transition state b formed by B3···B5 approach (and B2···B4 expansion) is favored.

Earlier studies have established that 1-$CH_3B_5H_8$ rearranges under base catalysis[1] (possibly with proton abstraction or complexing) and thermally[2] at 200° (possibly with intermolecular H exchange) to give 2-$CH_3B_5H_8$. In the present study, Friedel–Crafts methylation of 2-$CH_3B_5H_8$ yielded 1,2-$(CH_3)_2B_5H_7$. The dibasal substituted isomer was prepared by allowing a 4:1 mixture of 2,6-dimethylpyridine and 1,2-dimethylpentaborane to stand under ambient conditions for 5 days. Two vacuum fractionations through a trap cooled to −45° removed the catalyst, and glc gave the isomer of the dibasal substituted dimethylpentaborane. *Anal.* Calcd for $C_2H_{13}B_5$: C, 26.3; H, 14.3; mol wt, 91.2. Found: C, 26.0; H, 14.4; mol wt, 92.5 (gas density). The ^{11}B nuclear magnetic resonance spectrum exhibits a singlet [δ +1.2 ppm ($BF_3 \cdot C_2H_5O$ = 0)] and two doublets (δ +19.6 ppm, J = 160 cps; δ +50.4 ppm, J = 178 cps) with relative areas of

(1) T. P. Onak, *J. Am. Chem. Soc.*, **83**, 2584 (1961).

(2) T. P. Onak and F. J. Gerhart, *Inorg. Chem.*, **1**, 742 (1962).