

Concave-upward curves have been observed for the Hammett equation for the reactions of alkyl and acyl halides with nucleophilic reagents.<sup>22</sup> This type of relationship can best be explained by postulating a change in mechanism or a gradual change in the importance of the bond-making and bond-breaking steps in the transition state of a concerted type mechanism.<sup>22</sup>

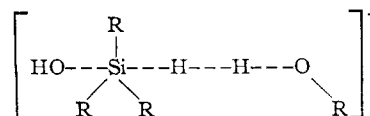
The significance of the concave-upward curve obtained from the Taft equation (Fig. 2) cannot readily be determined since the precision of the  $\sigma^*$ -values is not well known. However, if the concave-upward curve is significant, it could represent a gradual change from mechanism 1 to 2a or from mechanism 2b to 2a in the case of the base-catalyzed hydrolysis of the silicon-hydrogen bond. This can be demonstrated by using a qualitative free energy diagram (Fig. 3). Proceeding from A to B *via* the solid curve represents mechanism 1 and proceeding from B to A *via* the dashed curve represents mechanism 2b. As the groups attached to silicon are changed from electron-withdrawing groups to electron-releasing groups, the pentavalent silicon intermediate which possesses a negative charge on the silicon would be expected to become less stable. When the free energy minimum of the pentavalent silicon intermediate disappears, both mechanisms 1 and 2b would become identical to 2a.

In the light of the above discussion, the mechanism observed would depend on the structure of

(22) H. H. Jaffé, *Chem. Revs.*, **53**, 237 (1953).

the silane. If it can be assumed that silanes having strained rings and strongly electron-withdrawing groups proceed *via* mechanism 1 by analogy with the alkali-catalyzed hydrolysis of 1-methyl-1-silacyclobutane and from the large positive  $\rho^*$ -value, the curve obtained would represent a gradual change from mechanism 1 to 2a as electron-withdrawing groups are replaced by electron-releasing groups in the triorganosilanes.

Changing from mechanism 1 to 2a would be expected to reduce the  $\rho^*$ -value since a solvent molecule becomes involved in the transition state of the rate-determining step. The presence of a solvent molecule in the transition state would reduce the negative charge on the silicon by partially accepting the departing hydride ion. The transition state for mechanism 2a may be represented as<sup>23</sup>



**Acknowledgments.**—We wish to thank the Dow Computation Research Laboratory for the least squares analyses, G. Wayne Holbrook for the preparation of 5-bromo-1,1,1,2,2,3,3-heptafluoropentane, and the members of the Fluorine Research Laboratory for assistance in the rate measurements.

(23) C. Eaborn, "Organosilicon Compounds," Butterworths Scientific Publications, London, 1960, p. 200.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE UNIVERSITY, AMES, IOWA]

## Preparation and Characterization of Octaphenylcyclotetrasilane

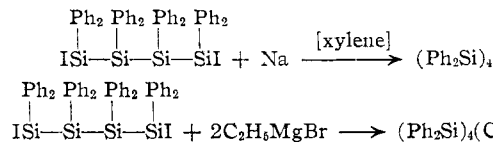
BY A. W. P. JARVIE, H. J. S. WINKLER, D. J. PETERSON AND H. GILMAN

RECEIVED DECEMBER 2, 1960

An improved method of preparation of Kipping's Compound (A) has been devised. The structure of this compound has been shown to be octaphenylcyclotetrasilane by the preparation of 1,4-dimethyloctaphenyltetrasilane from it. This latter compound was prepared by an independent route from methyldiphenylsilyllithium and *sym*-dichlorotetraphenyldisilane. In addition, 1,4-dichlorooctaphenyltetrasilane, which was prepared by the direct ring opening of octaphenylcyclotetrasilane, gave on reaction with phenyllithium the previously described decaphenyltetrasilane.

It was reported in a preliminary communication<sup>1a</sup> that the compound designated Compound (A) by Kipping,<sup>1b</sup> isolated from the reaction of dichlorodiphenylsilane with sodium, was octaphenylcyclotetrasilane. The structure assigned to Compound (A) by Kipping contained two "tervalent silicon atoms":  $-\text{SiPh}_2\text{SiPh}_2\text{SiPh}_2\text{SiPh}_2-$ .<sup>1b,2</sup> This structure provided a reasonable explanation for the high reactivity of the compound in free radical-type reactions. For example, Compound (A) reacted with one mole equivalent of iodine to give 1,4-di-iodooctaphenyltetrasilane,<sup>1b</sup> with atmospheric oxygen or nitrobenzene to give siloxanes,<sup>2a</sup>

and with certain halogenated solvents to give 1,4-dihalo-octaphenyltetrasilanes. The analytical results showed that the compound was composed of diphenylsilylene units and molecular weight determinations indicated that four such units were present. Two reactions of the di-iodo compound confirmed the presence of four diphenylsilylene units:



Analytical data and molecular weight determinations agreed with the structures shown for the 1,4-di-iodo- and the 1,4-diethyloctaphenyltetrasilane.

Paramagnetic resonance measurements on the solid Compound (A) as well as on its solution in tol-

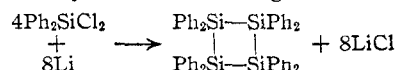
(1) (a) H. Gilman, D. J. Peterson, A. W. Jarvie and H. J. S. Winkler, *J. Am. Chem. Soc.*, **82**, 2076 (1960); (b) F. S. Kipping and J. E. Sands, *J. Chem. Soc.*, **119**, 830 and 848 (1921).

(2) (a) F. S. Kipping, *ibid.*, **123**, 2590 and 2598 (1923); (b) F. S. Kipping, *ibid.*, **119**, 848 (1921); (c) F. S. Kipping, *ibid.*, **125**, 2291 (1924); (d) F. S. Kipping, *ibid.*, 2978 (1927); (e) F. S. Kipping, "Bakerian Lecture," *Proc. Roy. Soc. (London)*, **159A**, 139 (1937).

uene failed to give free radical resonance.<sup>3</sup> The sensitivity for the detection of free radicals by this method is of the order of  $10^{15}$  unpaired electrons. It was hence concluded that the free radical-type behavior of Compound (A) could be attributed to the ready formation of such a biradical by a simple homolytic cleavage of the strained octaphenylcyclotetrasilane. It should be mentioned that the carbon analog, octaphenylcyclobutane, has not been prepared.

Ring strain and the accompanying homolytic cleavage to a biradical are probably contributing factors to the instability of a perphenylated cyclobutane. It will be recalled that hexaphenyldisilane in contrast to hexaphenylethane does not dissociate into free radicals.<sup>4</sup>

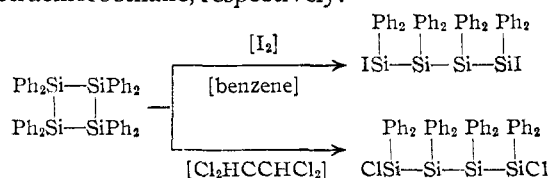
The preparation of Compound (A) was accomplished by the reaction of dichlorodiphenylsilane with sodium in toluene or xylene according to the procedure originally described by Kipping.<sup>1b</sup> The low yields obtained by this procedure promoted a search for an improved method of preparation. It was found that dichlorodiphenylsilane reacted with lithium in tetrahydrofuran to give improved yields of Compound (A) and various other products, currently under investigation. Improved



methods of isolation and purification of octaphenylcyclotetrasilane were devised since the physical data given in the original paper were insufficient.<sup>1b</sup> It was reported by Kipping that Compound (A) did not melt at  $300^\circ$ , and later it was stated to melt at  $335^\circ$ . We have found that a sample obtained by Soxhlet extraction with toluene melted at  $321\text{--}323^\circ$ , preshrinkage occurred at  $317^\circ$  and the melt was clear at  $325^\circ$ .<sup>5</sup>

A compound melting at  $313\text{--}317^\circ$  has been obtained in these laboratories from the reaction of dichlorodiphenylsilane with the stilbene-dilithium adduct. This compound was tentatively identified as Compound (A).<sup>6</sup>

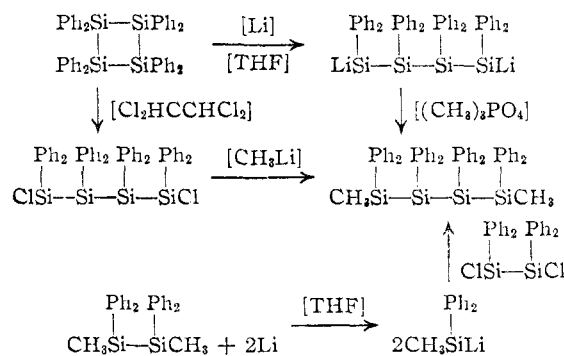
The linear di-iodo- and dichlorooctaphenyltetrasilanes were prepared by the reaction of iodine and tetrachloroethane, respectively.



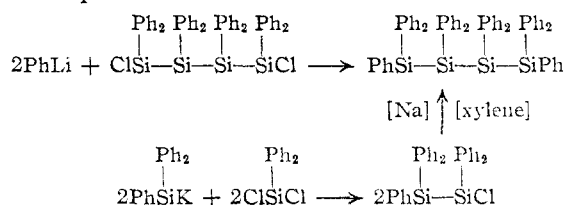
Methylolithium reacted with 1,4-dichlorooctaphenyltetrasilane to give the corresponding 1,4-dimethyl derivative. Another synthesis of this compound from octaphenylcyclotetrasilane was achieved by reaction of lithium to form 1,4-dilithiooctaphenyltetrasilane which was subsequently

treated with trimethyl phosphate. The silyllithium content of the tetrahydrofuran solution of the dilithio compound corresponded to the presence of two equivalents of the silyllithium group per mole of octaphenylcyclotetrasilane.

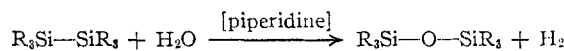
An independent synthesis of this 1,4-dimethyloctaphenyltetrasilane by the coupling of *sym*-dichlorotetraphenyldisilane<sup>7</sup> with methylphenylsilyllithium, using a 1:2 molar ratio, confirmed this structure.



Similarly, phenyllithium reacted with 1,4-dichlorooctaphenyltetrasilane to give the known decaphenyltetrasilane.<sup>8</sup> The reactions involved in the preparation of this compound<sup>8</sup> are shown in the equations



During the early studies of polysilanes a method was devised for the quantitative determination of silicon-silicon bonds.<sup>1b</sup> This method involves the measurement of the volume of hydrogen liberated on basic hydrolysis. We have found that wet



piperidine is the preferred medium in which to perform this hydrolysis. It is a base of sufficient strength to accomplish the quantitative cleavage of the silicon-silicon bond and has the added advantage of being a good solvent for most of the compounds studied. In the present study this method<sup>8</sup> was used extensively for the elucidation of the structures of the various polysilanes prepared herein. We shall report separately on the structure of Kipping's "Compound C," as well as on the reaction of phenyltrichlorosilane with various metals.

### Experimental<sup>9</sup>

**Octaphenylcyclotetrasilane.** A. From Dichlorodiphenylsilane and Sodium.—To a three-necked flask equipped with

(3) J. H. Chaudet and Dr. W. D. Kennedy, of the Tennessee Eastman Co., performed the electron spin resonance measurements.

(4) H. Gilman and T. C. Wu, *J. Am. Chem. Soc.*, **75**, 3762 (1953), and related papers from this Laboratory.

(5) The melting point determinations were made on a Mel-Temp capillary melting point apparatus set at 85 volts corresponding to a heating rate of  $2^\circ$  per minute at  $325^\circ$ .

(6) M. V. George, D. Wittenberg and H. Gilman, *J. Am. Chem. Soc.*, **81**, 361 (1959).

(7) H. J. S. Winkler and H. Gilman, *J. Org. Chem.*, **26**, in press (1961).

(8) H. Gilman, T. C. Wu, H. A. Hartzfeld, G. A. Guter, A. G. Smith, J. J. Goodman and S. H. Eidt, *J. Am. Chem. Soc.*, **74**, 560 (1952).

(9) All melting points are uncorrected and were taken as described in ref. 5. All reactions involving organometallic compounds were carried out in an atmosphere of dry, oxygen-free nitrogen.

a reflux condenser topped by a nitrogen inlet, a stirrer and an addition funnel was added 700 ml. of toluene and 35.6 g. (1.55 g. atoms) of finely cut sodium. Heat was applied until the sodium melted. After removing the heat, 180 g. (0.71 mole) of dichlorodiphenylsilane was added at a rate sufficient to maintain gentle reflux. Shortly after the start of the addition a blue insoluble solid formed and increased in concentration during the course of the reaction.

Subsequent to the complete addition, the reaction mixture was allowed to cool to room temperature. To destroy any excess sodium and to remove the inorganic materials the mixture was poured into ethanol, filtered and washed thoroughly with water. The finely divided solid was then dried by washing with ethanol.

Attempts to purify the insoluble solid with several hot solvents failed. Recrystallization from tetralin yielded 13.6 g. (10.6%) of octaphenylcyclotetrasilane, m.p. 313–316°.

The organic layer was separated from the original filtrate and dried over sodium sulfate. During a 24-hour period 7.5 g. (5.7%) of Compound (B), dodecaphenylcyclohexasilane, crystallized, m.p. 426–430° after a recrystallization from benzene–petroleum ether (b.p. 60–70°). Repeated attempts to obtain more Compound (A) or Compound (B) from the mother liquors were unsuccessful due to the presence of large amounts of diphenylsilylene polymers.

**B. From Dichlorodiphenylsilane and Lithium.**—A solution of 214 g. (0.85 mole) of dichlorodiphenylsilane in 325 ml. of tetrahydrofuran was added rapidly with stirring to 11.8 g. (1.70 g. atoms) of finely cut lithium wire. During the addition a white cloudiness appeared in the solution and the solvent refluxed mildly. As the reaction proceeded the white solid, octaphenylcyclotetrasilane, separated and the lithium was slowly consumed. After 24 hours the reaction was complete as evidenced by complete disappearance of the lithium. The reaction mixture was then a deep cream color, possibly due to the presence of small amounts of silyllithium compounds in the mixture. The insoluble octaphenylcyclotetrasilane was filtered from the tetrahydrofuran solution, washed with  $3 \times 150$  ml. of hot benzene,  $2 \times 100$  ml. of ethyl alcohol and  $3 \times 200$  ml. of hot water. The benzene extracts were kept separate for the isolation of Compound (B). After drying, the crude material weighed 40 g. (39%), m.p. 290–305°. The crude product was placed in a Soxhlet thimble and continuously extracted with toluene for 24 hours in an apparatus equipped with a heating tape at the section holding the thimble. There was obtained 16 g. of pure octaphenylcyclotetrasilane, m.p. 321–323°, preshrinkage at 317° and the melt was clear at 325°. After an additional 24 hours of extraction, another 14 g. of pure Compound (A) was collected. The total yield of Compound (A) was 30 g. (19.4%).

*Anal.* Calcd. for  $[(C_6H_5)_2Si]_4$ ,  $C_{48}H_{40}Si_4$ : C, 79.09; H, 5.53; Si, 15.37; mol. wt., 728; hydrogen value (1 Si–Si bond per  $(C_6H_5)_2Si$ ), 123 mg./g. Found: C, 79.13; H, 5.48; Si, 15.28, 15.27; mol. wt. (perylene method),<sup>10</sup> 707, 758; hydrogen value, 128, 126.

**Preparation of 1,4-Dichlorooctaphenyltetrasilane.**—To 5.3 g. (0.0073 mole) of octaphenylcyclotetrasilane was added 30 ml. of tetrachloroethane. On heating, the octaphenylcyclotetrasilane dissolved. The solution was heated at reflux temperature for 30 minutes. A yellow solid residue remained after removal of the solvent. This was washed twice with petroleum ether (b.p. 60–70°) and 4.5 g. (77%) of solid, m.p. 178–180°, was obtained. Recrystallization from benzene–petroleum ether (b.p. 60–70°) raised the melting point to 182–183°.

*Anal.* Calcd. for  $C_{48}H_{40}Si_4Cl_2$ : C, 72.25; H, 5.01; Si, 14.02; Cl, 8.94; hydrogen value, 84.15. Found: C, 72.26, 72.09; H, 4.81, 4.74; Si, 13.78, 13.94; Cl, 9.20, 9.41; hydrogen value (moist piperidine), 83.02, 83.20.

**Preparation of 1,4-Di-iodooctaphenyltetrasilane.**—To a stirred suspension of 4 g. (0.0055 mole) of octaphenylcyclotetrasilane in 30 ml. of benzene was added 1.4 g. (0.011 g. atom) of iodine. The temperature was maintained at approximately 60° throughout the addition. After addition was complete the mixture was stirred for 15 minutes until the brown color of the iodine had completely disappeared. Removal of the benzene left a white solid residue. This was dissolved in chloroform, and diethyl ether was added which caused the precipitation of a white crystalline

solid. The solid was filtered off and washed twice with ether. There was obtained 3 g. (55%) of a product melting at 274–276°. Recrystallization from benzene–diethyl ether did not improve the melting point. The di-iodo compound decomposed rapidly in solution and the solid material turned yellow after several hours, even in the absence of air and moisture.

*Anal.* Calcd. for  $C_{48}H_{40}Si_4I_2$ : C, 58.52; H, 4.08; Si, 11.42. Found: C, 59.80, 59.88; H, 4.33, 4.50; Si, 11.42, 11.50.

Both the carbon and the hydrogen analyses show that there was considerable loss of iodine before the compound was analyzed, whereas this was not the case for the silicon analysis which was performed immediately after the compound had been purified.

**Preparation of 1,4-Dimethyloctaphenyltetrasilane. A. From 1,4-Dichlorooctaphenyltetrasilane and Methylolithium.**—An ether solution containing 0.019 mole of methylolithium was added dropwise to a suspension of 5 g. (0.0063 mole) of 1,4-dichlorooctaphenyltetrasilane in 30 ml. of ether. After 3 hours stirring at room temperature the reaction mixture was hydrolyzed by addition to 250 ml. of 0.1 *N* hydrochloric acid. The aqueous layer was extracted with ether and the organic layers combined and dried. Removal of the ether left a white oil which solidified on treatment with petroleum ether (b.p. 60–70°). The solid was filtered from the petroleum ether and there was obtained 3 g. (63%) of a product, m.p. 196–202°. Several recrystallizations from benzene–petroleum ether (b.p. 60–70°) and from benzene–ethanol raised the melting point to 220–222°. A mixed melting point with an authentic sample of 1,4-dimethyloctaphenyltetrasilane (see B below) was not depressed.

**B. From 1,4-Dithiooctaphenyltetrasilane and Trimethyl Phosphate.**—To a three-necked flask, equipped with a stirrer, an addition funnel and a nitrogen inlet, was added 7.8 g. (0.0107 mole) of octaphenylcyclotetrasilane and an excess of finely cut lithium wire. Stirring was started and a small amount of tetrahydrofuran (*ca.* 5 ml.) was added.

Initiation of the cleavage was observed within 5 minutes as evidenced by the formation of a yellow color. When the color became deep yellow, the remaining portion (15 ml.) of tetrahydrofuran was added. As the cleavage progressed, the color changed from yellow to red and the insoluble Compound (A) disappeared. Subsequent to 3 hours of stirring, the solution of the silylmetallic compound was filtered through glass wool into an addition funnel. An aliquot of the solution was removed and was shown to contain two equivalents of silyllithium compound per mole of octaphenylcyclotetrasilane present at the beginning; the method of analysis used was a modification of the method used by Ziegler and co-workers for the estimation of organo-alkali metal compounds.<sup>11</sup>

The solution was then added slowly to an excess of trimethyl phosphate dissolved in tetrahydrofuran. Following an immediate reaction, the mixture was hydrolyzed with dilute acid. The organic layer was separated, dried over sodium sulfate and the solvent removed by distillation. The ensuing oil was chromatographed on alumina. Petroleum ether (b.p. 60–70°) eluted 2.85 g. (27%) of 1,4-dimethyloctaphenyltetrasilane. This compound melted at 217–219° following a recrystallization from a mixture of benzene and petroleum ether (b.p. 60–70°). A mixed melting point with the sample prepared by the procedure described immediately above was not depressed. Further elution of the column with various solvents produced oils which did not crystallize.

**C. From Methylidiphenylsilyllithium and *sym*-Dichlorotetraphenyldisilane.**—Methylidiphenylsilyllithium was prepared in tetrahydrofuran according to a published procedure.<sup>12</sup> The solution was analyzed for silyllithium content by the *n*-butyl bromide method.<sup>10</sup> The solution was found to be 0.40 *M* in silyllithium after it had been decanted through glass wool into an addition funnel. The funnel was placed in a three-necked flask equipped with a stirrer and a nitrogen inlet. In the flask was placed 3.0 g. of *sym*-dichlorotetraphenyldisilane<sup>7</sup> (0.0069 mole) and 40 ml. of

(11) K. Ziegler, F. Crössmann, H. Kleiner and O. Schafer, *Ann.*, **473**, 31 (1929); see, also, H. Gilman, R. A. Klein, and H. J. S. Vinkler, *J. Org. Chem.*, **26**, in press (1961).

(12) H. Gilman and G. D. Lichtenwalter, *J. Am. Chem. Soc.*, **80**, 608 (1958).

(10) G. Wittig and G. Lehmann, *Ber.*, **90**, 875 (1957).

tetrahydrofuran. The reaction flask was placed in ice-water and 37 ml. (containing 0.015 mole) of the methyl-diphenylsilyllithium solution was added dropwise within 10 minutes. The dark color of the silyllithium compound was discharged immediately on addition to the solution of the chlorosilane. A slight deepening in color of the reaction mixture was noticed during the addition of the last few milliliters of silyllithium reagent. This was evidence for the slight excess of silyllithium present. Color Test I<sup>13</sup> was positive immediately after addition, but stirring for 1 hour gave a negative Color Test. The solution was allowed to stand for 16 hours and then poured into 100 ml. of 1.0 *N* hydrochloric acid. The aqueous layer was extracted with ether and the organic layers were combined and dried over magnesium sulfate. The solvents were removed and 25 ml. of petroleum ether (b.p. 60–70°) was added. A precipitate separated which on recrystallization from cyclohexane–petroleum ether (b.p. 60–70°; 1:1) yielded 1.5 g. (29%) of a white solid melting at 216–217°. Further recrystallization from a 2:1 mixture of acetone–chloroform gave a product melting at 222–223°. This solid was shown to be identical with the samples prepared in A and B above. The identity was established by the method of mixed melting points and superimposability of their infrared spectra.

Anal. Calcd. for C<sub>50</sub>H<sub>48</sub>Si<sub>4</sub>: C, 79.09; H, 6.11; Si, 14.8; hydrogen value, 89.0 (ml. at S.T.P./g. of compd.).

(13) H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

Found: C, 79.16, 79.11; H, 6.41, 6.24; Si, 14.85, 14.72; hydrogen value, 89.8, 88.5 (the hydrogen values given in the preliminary communication<sup>1</sup> were not corrected to S.T.P.).

**Preparation of Decaphenyltetrasilane.**—A solution of 0.02 mole of phenyllithium in 20 ml. of diethyl ether was added dropwise to 5.7 g. (0.0072 mole) of 1,4-dichlorooctaphenyltetrasilane suspended in 30 ml. of diethyl ether. The reaction mixture was stirred for 24 hours then hydrolyzed by addition to 300 ml. of 0.1 *N* hydrochloric acid. Ether was added and the insoluble material was filtered off to yield 2.8 g. (44%) of a product, m.p. 280–315°. After recrystallization from benzene–ethanol, ethyl acetate–ethanol, and benzene–petroleum ether (b.p. 60–70°) the product melted at 358–360°. A mixed melting point with an authentic sample of decaphenyltetrasilane<sup>9</sup> was not depressed.

**Acknowledgment.**—The authors are grateful to J. H. Chaudet and Dr. W. D. Kennedy of the Tennessee Eastman Co., for the EPR studies. This research was supported in part by the United States Air Force under Contract AF 33(616)-6127 monitored by the Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright Patterson AFB, Ohio.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME, NOTRE DAME, IND.]

## Organoboron Compounds. XIII. Steric Inhibition of Disproportionation and Isomerization Mechanism Studies on Unsymmetrical Trialkylboranes<sup>1,2</sup>

BY PATRICK A. MCCUSKER, JOSEPH V. MARRA AND G. F. HENNION

RECEIVED NOVEMBER 25, 1960

Steric inhibition of disproportionation by *t*-butyl groups in unsymmetrical trialkylboranes is shown to be general while isobutyl groups do not inhibit disproportionation. Thermal isomerization of *t*-butyl to isobutyl groups is followed by rapid disproportionation. Isolation of isobutylene from the reaction of *t*-butylmagnesium chloride with boron fluoride and the effect of excess foreign olefin on the reaction indicate that isomerization occurs as an essential feature of the Grignard alkylation. Alkylation isomerization appears to proceed through reduction by the Grignard reagent and recombination of the olefin and alkyl boron hydride formed. Thermal isomerization may follow a different course. Two *t*-butyl groups survive alkylation isomerization when the third group is a normal alkyl group. When the third group is  $\beta$ -branched only one *t*-butyl group is retained, the second being isomerized to isobutyl. Excess olefin has no effect on the reaction of isobutylmagnesium bromide with boron fluoride. A trialkylborane with one *t*-butyl group exchanges alkyl groups with a Grignard reagent; when two *t*-butyl groups are present no exchange occurs.

The first reported attempt<sup>3</sup> to prepare an unsymmetrical triorganoborane resulted in the isolation of the symmetrical compounds only. In other more recent reports<sup>4–6</sup> the preparation of a number of unsymmetrical trialkylboranes has been described, but the compounds apparently were not subjected to efficient fractional distillation. When careful fractional distillation of the unsymmetrical trialkylboranes was attempted,<sup>7</sup> complete disproportionation to the symmetrical compounds took place.

In this Laboratory<sup>8</sup> it has been observed that *t*-butyldiisobutylborane could be obtained and purified by thorough fractional distillation with no disproportionation. This result suggested that a *t*-butyl group attached to boron could offer steric interference to the disproportionation mechanism involving a bridged dimer.<sup>9,10</sup> Further studies bearing on the generality of steric inhibition of the disproportionation reaction have now been carried out.

Reaction of *t*-butylmagnesium chloride with boron compounds results in partial or complete isomerization of the *t*-butyl groups to isobutyl groups at low temperature. Results of some studies bearing on the mechanism previously proposed for low temperature isomerization during the preparative reaction are reported herein. Pre-

(1) Previous paper, P. A. McCusker and S. M. L. Kilzer, *J. Am. Chem. Soc.*, **82**, 372 (1960).

(2) Contribution from the Radiation Laboratory operated by the University of Notre Dame and supported in part under Atomic Energy Commission Contract AT-(11-1)-38. From the doctoral dissertation of Joseph V. Marra, 1959.

(3) E. Krause and P. Nobbe, *Ber.*, **64B**, 2112 (1931).

(4) R. W. Auten and C. W. Kraus, *J. Am. Chem. Soc.*, **74**, 3398 (1952).

(5) J. C. Perrine and R. N. Keller, *ibid.*, **80**, 1823 (1958).

(6) S. L. Clark and J. R. Jones, Abstracts 133rd Meeting, American Chemical Society, April, 1958, p. 34L.

(7) B. M. Mikhailov and T. A. Shchegoleva, *Doklady Akad. Nauk S.S.S.R.*, **108**, 481 (1956).

(8) G. F. Hennion, P. A. McCusker and A. J. Rutkowski, *J. Am. Chem. Soc.*, **80**, 617 (1958).

(9) G. F. Hennion, P. A. McCusker, E. C. Ashby and A. J. Rutkowski, *ibid.*, **79**, 5190 (1957).

(10) T. D. Parsons, M. B. Silverman and D. M. Ritter, *ibid.*, **76**, 1714 (1954); **79**, 5091 (1957).