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

The Relative Reactivities of Triphenylsilyllithium and Organometallic Compounds in Coupling with Halosilanes

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Through the use of competitive reactions, triphenylsilyllithium was found to couple with monohalosilanes in tetrahydrofuran more readily than did *n*-butyllithium or phenyllithium in the same solvent. The difference was found to be still greater in a mixed ether–tetrahydrofuran solvent system. The relative reactivities of monohalosilanes in reaction with triphenylsilyllithium was found to be in the order: $(CH_3)_3SiCl$, $(C_2H_5)_3SiCl > (CH_3)_2(C_6H_5)SiCl > (CH_3)(C_6H_5)_2SiCl > (C_6H_5)_3SiCl$, $(C_6H_5)_3SiBr \gg (C_6H_5)_3SiOC_2H_5$. Steric factors appear to be of importance in determining the order. In a related reaction, evidence was obtained in support of the intermediate formation of triphenylsilylsodium in the coupling of chlorosilanes by sodium in xylene.

The first useful methods for the preparation of silylmetallic compounds were reported in 1951.[2,3] In 1958, a facile preparation of triphenylsilyllithium was reported.[4] In the following years, the chemistry of silylmetallic reagents has been studied extensively.[5]

Silylmetallic compounds have been recognized as highly reactive reagents and have been found to give reactions similar to those of organometallic reagents, although in some instances they show differences in their mode of reaction. For example, organolithium compounds react readily with tetrahydrofuran[6]; however, triphenylsilyllithium cleaved this solvent only after prolonged refluxing.[7] These reactions tend to indicate a higher degree of reactivity of organolithium reagents with tetrahydrofuran. However, when the two classes of reagents were tested in coupling reactions with halosilanes, rather surprising results were obtained.

Organometallic[8] and silylmetallic[5] reagents both couple readily with halosilanes to give tetrasubstituted-silanes and disilanes, respectively. The procedure employed for this study involved the

$$\mathrm{R'Li + R_3SiX \longrightarrow R_3SiR'}$$

$$\mathrm{R'_3SiLi + R_3SiX \longrightarrow R_3SiSiR'_3}$$

addition of one molar equivalent of a halosilane to a mixture of one molar equivalent each of an organometallic reagent and triphenylsilyllithium. In the majority of reactions, the halosilane used was chlorotriphenylsilane. Thus, the insoluble hexaphenyldisilane formed was easily separated from the tetrasubstituted silane, resulting in a satisfactory product analysis.

$$\mathrm{(C_6H_5)_3SiLi + RLi \xrightarrow{(C_6H_5)_3SiCl} (C_6H_5)_3SiSi(C_6H_5)_3 + (C_6H_5)_3SiR}$$

The reactions were run at a low temperature (−50°) to avoid secondary cleavages. Both tetrahydrofuran and tetrahydrofuran–ether mixed solvents were employed. The results of the study are given in Table I.

TABLE I

RELATIVE REACTIVITIES OF TRIPHENYLSILYLLITHIUM AND ORGANOMETALLIC COMPOUNDS WITH CHLOROSILANES

Organometallic	Solvent	Solvent ratio	Chlorosilane	Yield, % disilane	Yield, % Ph_3SiR
Phenyllithium	THF[a]	...	Triphenyl-	73.8	12.0
n-Butyllithium	THF	...	Triphenyl-	61.0	21.5
Benzyllithium	THF	...	Triphenyl-	54.0	23.0
Phenyllithium	THF–ether	~2:1	Triphenyl	81.7	7.72
n-Butyllithium	THF–ether	~2:1	Triphenyl-	77.2	13.9
Phenyllithium	THF	...	Trimethyl-	49.2	20.0

[a] THF is a symbol for tetrahydrofuran.

Aryl-, alkyl- and aralkyllithium reagents were investigated in the reaction. Phenyllithium, *n*-butyllithium and benzyllithium were brought into competition with triphenylsilyllithium for an insufficient amount of chlorotriphenylsilane. In every instance, the quantity of hexaphenyldisilane far outweighed that of the tetrasubstituted silane (73.8 *vs.* 12.0, 61.0 *vs.* 21.5 and 54.0 *vs.* 23.0%, respectively), indicating the much greater reactivity of triphenylsilyllithium in these coupling reactions. The difference was less with *n*-butyllithium than with phenyllithium as might have been expected on the basis of the generally observed greater reactivity of the former reagent.[9]

The reaction involving benzyllithium seems to be anomalous. On the basis of the yield of hexaphenyldisilane it appears to be more reactive than *n*-butyllithium, but on the basis of the tetrasubstituted silane it would be of about equal reactivity. The discrepancy may be due to side reactions involving the alkoxide ion produced in the preparation of benzyllithium.[10]

When the aforementioned reactions were carried out in a tetrahydrofuran–ether mixed solvent system, the yield of hexaphenyldisilane was increased significantly with a corresponding decrease in yield of tetrasubstituted silane. The results support previous observations made in this Laboratory,[11] *i.e.*, although the stabilities of organometallic reagents are increased in ether–tetrahydrofuran mixed solvent, there is a corresponding decrease in their reactivity in metalation reactions. At the lower temperatures employed in these reactions,

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(1) Shell Companies Fellow, 1959–1960.

(2) R. A. Benkeser and R. G. Severson, *J. Am. Chem. Soc.*, **73**, 1424 (1951).

(3) H. Gilman and T. C. Wu, *ibid.*, **73**, 4031 (1951).

(4) H. Gilman and G. D. Lichtenwalter, *ibid.*, **80**, 608 (1958).

(5) For a summarizing review, see D. Wittenberg and H. Gilman, *Quart. Revs.*, **13**, 116 (1959).

(6) H. Gilman and B. J. Gaj, *J. Org. Chem.*, **22**, 1165 (1957).

(7) D. Wittenberg and H. Gilman, *J. Am. Chem. Soc.*, **80**, 2677 (1958).

(8) For an excellent coverage of organosilicon chemistry, see C. Eaborn, "Organosilicon Compounds," Butterworths Scientific Publications, London, 1960.

(9) H. Gilman and R. H. Kirby, *J. Am. Chem. Soc.*, **55**, 1265 (1933).

(10) H. Gilman, H. A. McNinch and D. Wittenberg, *J. Org. Chem.*, **23**, 2044 (1958).

(11) W. J. Trepka, unpublished studies.

the decrease in reactivity may be amplified. However, the mixed solvent system did not appear to affect the reactivity of triphenylsilyllithium.

It was shown recently that organolithium reagents cleave hexaphenyldisilane in tetrahydrofuran under moderate conditions.[12] Such cleavages would affect the results of the coupling reactions. However, when *n*-butyllithium was allowed to react with hexaphenyldisilane under the low-temperature conditions of the competition reactions, hexaphenyldisilane was recovered almost quantitatively and *n*-butyltriphenylsilane was not isolated, indicating the absence of detectable cleavage.

The possibility of upsetting an equilibrium due to the presence of insoluble hexaphenyldisilane was considered at the start of the investigation. It did not seem likely that the reaction of an organometallic or a silylmetallic reagent with a chlorosilane is an equilibrium reaction since each goes to completion quite rapidly, Color Test I[13] being negative at the end of addition. The following reaction was carried out to give support to this belief. Phenyllithium and triphenylsilyllithium were brought into competition for chlorotrimethylsilane under the conditions used previously. All of the products were soluble; thus the system remained homogeneous throughout. Again, triphenylsilyllithium was more reactive than the organometallic compound as indicated by isolation of a larger quantity of disilane than tetrasubstituted silane (49.2 *vs.* 20.0%). The difference was not so large as encountered in reaction with chlorotriphenylsilane, but this was considered to be due to the greater reactivity of chlorotrimethylsilane as compared to chlorotriphenylsilane, resulting in a less selective reaction.

In order to obtain experimental proof for the latter hypothesis, a number of competitive reactions were run involving the addition of triphenylsilyllithium to a mixture of two halosilanes cooled to −50°. In every instance, one of the halosilanes involved contained the triphenylsilyl group. Thus, hexaphenyldisilane was again produced and isolated readily.

$$(C_6H_5)_3SiLi + (C_6H_5)_3SiX + R_3SiX \longrightarrow (C_6H_5)_3SiSi(C_6H_5)_3 + (C_6H_5)_3SiSiR_3$$

The results of the investigation are shown in Table II.

TABLE II

TRIPHENYLSILYLLITHIUM COUPLING WITH HALOSILANES

Mixture of halo-silanes	Yield, % $Ph_3SiSiPh_3$	Yield, % unsymm. disilane
Chlorotrimethyl- and chlorotriphenyl-	27.2	45.3
Chlorodimethylphenyl- and chlorotriphenyl-	30.0	40.5
Methyldiphenylchloro- and chlorotriphenyl-	34.4	35.9
Chlorotriethyl- and chlorotriphenyl-	26.1	44.8
Chlorotrimethyl- and bromotriphenyl-	26.1	48.5
Chlorotrimethyl- and ethoxytriphenyl-	0	60.3

On the basis of the amounts of hexaphenyldisilane and unsymmetrical disilane obtained, a distinction can be made involving the chlorosilanes: trimethyl, dimethylphenyl, methyldiphenyl and triphenyl. The decreasing order of coupling with triphenylsilyllithium appears to be dependent upon steric factors. This agrees with the work of Reid and Wilkins[14] who observed that small changes in the polarity of organic groups attached to silicon of monohalosilicon compounds had little effect on the reactivity of the halides toward methylmagnesium halides, but that steric effects were probably of major importance.

There seems to be little distinction between chlorotrimethylsilane and chlorotriethylsilane in their competition reactions with chlorotriphenylsilane for triphenylsilyllithium. The result was rather surprising since Sommer, *et al.*,[15] had shown that chlorotrimethylsilane reacts approximately twice as fast as chlorotriethylsilane in competitive reactions with ethylmagnesium bromide. Bromotriphenylsilane and chlorotriphenylsilane also gave similar results in their competitive reactions with chlorotrimethylsilane for triphenylsilyllithium. Upon closer inspection, the results become more meaningful. The reaction of triphenylsilyllithium is very rapid; in fact, Color Test I is negative immediately upon completion of addition. The reaction appears to be almost instantaneous. The steric differences between chlorotrimethyl- and chlorotriethylsilane and the electronic differences between chlorotriphenyl- and bromotriphenylsilane could become insignificant in a reaction occurring so rapidly.

The reaction of ethoxytriphenylsilane with triphenylsilylpotassium to give hexaphenyldisilane has been reported to proceed slowly.[16] Thus, it was not surprising that the only product observed from the competitive reaction of ethoxytriphenylsilane and chlorotrimethylsilane for triphenylsilyllithium arose through coupling of the silylmetallic with chlorotrimethylsilane.

The competitive reactions suggest the following order of reactivity of halosilanes in coupling reactions with triphenylsilyllithium: $(CH_3)_3SiCl$, $(C_2H_5)_3SiCl > (CH_3)_2(C_6H_5)SiCl > (CH_3)(C_6H_5)_2SiCl > (C_6H_5)_3SiCl$, $(C_6H_5)_3SiBr >> (C_6H_5)_3SiOC_2H_5$.

In a somewhat related reaction, a mixture of chlorotrimethylsilane and chlorotriphenylsilane was treated with sodium in an attempt to elucidate the mechanism of the coupling of chlorosilanes by sodium. It has been suggested that a silyl–sodium intermediate may be involved. A positive Color Test I has been reported[17] during the reaction of chlorotriphenylsilane with sodium in tetrahydrofuran; however, it is possible the color was due to ketyl formation through reaction of suspended sodium with Michler's ketone. Brown and Fowles[18] have reported that hexamethyldisilane cannot be prepared by reaction of chlorotrimethylsilane with sodium in refluxing xylene, a

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[12] B. J. Gaj and H. Gilman, *Chemistry & Industry*, 493 (1960).

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

[14] A. E. Reid and C. J. Wilkins, *J. Chem. Soc.*, 4029 (1955).

[15] L. H. Sommer, G. T. Kerr and F. C. Whitmore, *J. Am. Chem. Soc.*, **70**, 434 (1948).

[16] H. Gilman and T. C. Wu, *J. Org. Chem.*, **25**, 2251 (1960).

[17] M. V. George, D. J. Peterson and H. Gilman, *J. Am. Chem. Soc.*, **82**, 403 (1960).

[18] M. P. Brown and G. W. A. Fowles, *J. Chem. Soc.*, 2811 (1958).

fact which was later confirmed in this Laboratory. It should also be pointed out that sodium does not cleave hexaphenyldisilane under these conditions to produce a silylmetallic reagent. The isolation of 1,1,1-trimethyl-2,2,2-triphenyldisilane from a mixture of chlorotrimethylsilane and chlorotriphenylsilane with sodium and refluxing xylene would be proof of the intermediate formation of triphenylsilylsodium. Selin and West,[19] and others[20] have used a similar system involving the same chlorosilanes in tetrahydrofuran with magnesium to obtain support for an intermediate "silyl-Grignard reagent."

$$(C_6H_5)_3SiCl + Na \longrightarrow [(C_6H_5)_3SiNa] \xrightarrow[(C_6H_5)_3SiCl]{(CH_3)_3SiCl} (C_6H_5)_3SiSi(CH_3)_3 + (C_6H_5)_3SiSi(C_6H_5)_3$$

The coupling reaction involving a mixture of chlorotrimethyl- and chlorotriphenylsilane with sodium in refluxing xylene gave 12.7% of hexaphenyldisilane and 43.2% of 1,1,1-trimethyl-2,2,2-triphenyldisilane. Isolation of the unsymmetrical disilane offers strong support for the intermediate formation of triphenylsilylsodium. The larger amount of unsymmetrical compared to symmetrical disilane is in line with the greater reactivity of chlorotrimethylsilane in reactions with silylmetallic reagents.

Experimental[21]

Triphenylsilyllithium and Phenyllithium with Chlorotriphenylsilane.—The following reaction is illustrative of the procedure employed in competition reactions involving triphenylsilyllithium and an organometallic reagent with chlorotriphenylsilane. Tetrahydrofuran solutions of 0.05 mole of phenyllithium[6] and 0.05 mole of triphenylsilyllithium[4] were each cooled to −50° and mixed. While maintaining stirring, a solution containing 14.7 g. (0.05 mole) of chlorotriphenylsilane dissolved in 30 ml. of tetrahydrofuran was added over a period of 8 min. at the same temperature. The formation of a white solid was noted. Stirring was continued at −50° for 10 min. after the addition was complete. Water was added and the hydrolyzed reaction mixture allowed to warm to room temperature. Ether was added, and the solid was filtered, washed with ether, and dried to give 19.2 g. (73.8%) of hexaphenyldisilane, m.p. 360–366° (mixture melting point).

The organic layer was worked up in a conventional manner. Evaporation of the solvent left a yellow solid which was slurried with ethanol and filtered. The insoluble material was dried to give 3.00 g. (17.8%) of crude tetraphenylsilane melting over the range 218–229°. Several recrystallizations from ethyl acetate gave 2.02 g. (12.0%) of pure product, m.p. 231–234.5° (mixture melting point).

The competitive reactions of *n*-butyllithium[6] and of benzyllithium[10] in tetrahydrofuran with triphenylsilyllithium for chlorotriphenylsilane were carried out using identical molar ratios of reactants and reaction conditions, the only variation in procedure being the isolation of *n*-butyltriphenylsilane[22] and benzyltriphenylsilane[22] by the use of chromatography on alumina. For the mixed solvent system reactions, the organometallic reagent was prepared in ether and mixed with a tetrahydrofuran solution of triphenylsilyllithium. The chlorotriphenylsilane in tetrahydrofuran solution was added under the identical reaction conditions described above. The results of these competitive reactions are summarized in Table I.

***n*-Butyllithium in Tetrahydrofuran with Hexaphenyldisilane at −50°.**—A tetrahydrofuran solution of 0.05 mole of *n*-butyllithium, previously cooled to −50°, was added rapidly to a suspension of 26.0 g. (0.05 mole) of hexaphenyldisilane in 100 ml. of tetrahydrofuran at the same temperature. The reaction mixture was stirred at this temperature for 18 min. Hydrolysis was then effected with water and the suspension allowed to warm to room temperature. The suspended solid was filtered, washed with ether, and dried to give 25.2 g. (96.7%) of recovered hexaphenyldisilane, m.p. 365–368° (mixture melting point). The organic layer was worked up in the usual manner. However, *n*-butyltriphenylsilane could not be detected in the trace of white solid left upon evaporation of the solvent.

Triphenylsilyllithium and Phenyllithium with Chlorotrimethylsilane.—Tetrahydrofuran solutions of triphenylsilyllithium (0.05 mole) and phenyllithium (0.05 mole) were separately cooled to −50° and then mixed. A solution of 5.43 g. (0.05 mole) of chlorotrimethylsilane dissolved in 30 ml. of tetrahydrofuran was added dropwise at the same temperature over an 8-min. period. The resulting solution appeared homogeneous throughout the addition and for the subsequent 10-min. period of stirring. Hydrolysis was effected with water. After warming to room temperature, the solution was clear. Following the usual work-up, the solvent was removed by distillation and the resulting oil was distilled at reduced pressure to give 1.50 g. (20.0%) of trimethylphenylsilane,[23] b.p. 53–55° (10 mm.), n^{20}_{D} 1.4898. The infrared spectrum was superimposable with that of an authentic specimen. The distillation residue solidified upon cooling to give, subsequent to trituration with ethanol, 9.70 g. (58.3%) of crude 1,1,1-trimethyl-2,2,2-triphenyldisilane melting over the range 96–109°. Several recrystallizations from ethanol gave 8.20 g. (49.2%) of pure product, m.p. 107–109°[24] (mixture melting point, infrared spectrum). Evaporation of the ethanol extract gave only a yellow tarry residue which was not investigated further.

Chlorotriphenylsilane and Chlorotrimethylsilane with Triphenylsilyllithium.—The following reaction is illustrative of the competition reactions of monohalosilanes for triphenylsilyllithium. A solution of 14.7 g. (0.05 mole) of chlorotriphenylsilane, 5.43 g. (0.05 mole) of chlorotrimethylsilane and 75 ml. of tetrahydrofuran was cooled to −50°. To the solution was added 0.05 mole of triphenylsilyllithium in tetrahydrofuran, also cooled to −50°, over a 15-min. period. The reaction mixture was dark brown, and the formation of a white solid was noted. The mixture was stirred at −50° for 10 min., at which time Color Test I was negative. Hydrolysis was effected with water and the hydrolyzed mixture allowed to warm to room temperature. The solid was filtered, washed with ether, and dried to give 7.05 g. (27.2%) of hexaphenyldisilane, m.p. 363–366° (mixture melting point).

Work-up of the organic layer left a yellow solid which was chromatographed on alumina. The products isolated were 7.55 g. (45.3%) of 1,1,1-trimethyl-2,2,2-triphenyldisilane, m.p. 105–107.5° (mixture melting point); and 6.40 g. (46.2%) of triphenylsilanol, m.p. 150–151° (mixture melting point).

The competitive reactions involving mixtures of the monohalosilanes chlorodimethylphenyl and chlorotriphenyl, chlorodiphenylmethyl and chlorotriphenyl, chlorotriethyl and chlorotriphenyl, and chlorotrimethyl and bromotriphenyl[25] with triphenylsilyllithium were carried out using the same ratio of reactants and conditions described above. The results are summarized in Table II.

Ethoxytriphenylsilane and Chlorotrimethylsilane with Triphenylsilyllithium.—A solution of 15.3 g. (0.05 mole) of ethoxytriphenylsilane, 5.43 g. (0.05 mole) of chlorotrimethylsilane and 75 ml. of tetrahydrofuran was brought into reaction with a tetrahydrofuran solution of 0.05 mole of triphenylsilyllithium in the usual manner. There was no insoluble material. The usual chromatographic work-up was employed. The first fraction eluted with petroleum ether (b.p. 60–70°) was 21.4 g. of a white solid melting over the range 53–97°. The infrared spectrum indicated it to be a mixture of ethoxytriphenylsilane and 1,1,1-trimethyl-2,2,2-

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[19] T. G. Selin and R. West, *Tetrahedron*, **5**, 97 (1959).

[20] W. Steudel and H. Gilman, *J. Am. Chem. Soc.*, **82**, 6129 (1960).

[21] All melting points are uncorrected. Reactions were carried out under an atmosphere of dry, oxygen-free nitrogen. Tetrahydrofuran was freed from peroxides and moisture before use by refluxing over sodium, followed by distillation from lithium aluminum hydride.

[22] H. Gilman and H. Hartzfeld, *J. Am. Chem. Soc.*, **73**, 5878 (1951).

[23] H. Gilman, R. K. Ingham and A. G. Smith, *J. Org. Chem.*, **18**, 1743 (1953).

[24] A. G. Brook and H. Gilman, *J. Am. Chem. Soc.*, **76**, 278 (1954).

[25] A. G. Brook, H. Gilman and L. S. Miller, *ibid.*, **75**, 4759 (1953).

triphenyldisilane. The solid was mixed with 50 ml. of absolute ethanol and 50 ml. of 10% hydrochloric acid and stirred at room temperature for 1 hr. The suspension was extracted with ether. Evaporation of the solvent left a solid which was slurried with ethanol and filtered. The insoluble material was recrystallized from ethanol several times to give 10.1 g. (60.3%) of 1,1,1-trimethyl-2,2,2-triphenyldisilane, m.p. 107–110° (mixture melting point). The ethanol-soluble portion proved to be 5.20 g. (37.6%) of triphenylsilanol, m.p. 152–154° (mixture melting point). Further elution of the chromatographic column with ethyl acetate gave an additional 2.50 g. (18.1%) of triphenylsilanol.

Reaction of Chlorotriphenylsilane and Chlorotrimethylsilane with Sodium in Refluxing Xylene.—A mixture of 29.5 g. (0.10 mole) of chlorotriphenylsilane, 10.9 g. (0.10 mole) of chlorotrimethylsilane, 2.30 g. (0.10 g. atom) of sodium and 150 ml. of xylene was heated at reflux temperature for 5 hr. As refluxing started, the sodium melted and the solution became dark blue in color. After the solution had cooled, it was poured into ethanol. The suspended white solid was filtered, washed with water and ether, and dried to give 3.30 g. (12.7%) of hexaphenyldisilane, m.p. 360–365° (mixture melting point). The organic layer from the filtrate was subjected to the usual chromatographic work-up. From the petroleum ether (b.p. 60–70°) eluates was obtained 15.2 g. (45.4%) of crude 1,1,1-trimethyl-2,2,2-triphenyldisilane melting over the range 101.5–107°. Recrystallization from ethanol gave 14.4 g. (43.2%) of pure disilane, m.p. 106.5–109° (mixture melting point, infrared spectrum). Elution of the column with benzene, ethyl acetate and with ethanol gave a total of 8.15 g. (29.5%) of triphenylsilanol, m.p. 150–151.5° (mixture melting point).

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The Rate of the Chair–Chair Interconversion of Cyclohexane[1,2]

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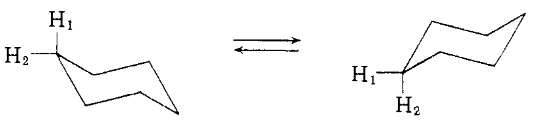
The low temperature proton magnetic resonance spectrum of cyclohexane shows separate axial and equatorial resonances as broad bands, each of which exists as a broad band with unresolved fine structure. The rate of the chair–chair interconversion at the temperature of half-peak separation (−66.7°) is $k = 52.5$ sec.$^{-1}$. Assuming the boat form as an unstable intermediate in this process, $\Delta F^{\ddagger}$ is 10.1 kcal./mole.

Introduction

One of the basic quantities of use in conformation analysis[3] is the facility with which one chair conformation may be converted to the other chair conformation. All chemical information suggests that this interconversion is rapid, and estimates based upon qualitative energetics[4] and upon spectroscopic assignments[5] have been made. Shoppee estimated the barrier to be 9–10 kcal./mole and Beckett, Pitzer and Spitzer estimated the barrier to be 14 kcal./mole.



Other investigators have been concerned with the chair–boat energy difference. Estimates have ranged from 2–10 kcal.,[3,4,6–8] with the boat being less stable.

Recently, a direct experimental method has given the value of 5.3 kcal. for this difference.[9]

Another type of measurement which appears useful for these constants is the ultrasonic relaxation method. Recent studies have demonstrated the utility of this method in determining the energy difference between conformers in 2-methylpentane and related compounds as well as the energy barrier between them.[10] Similar studies of cyclohexane derivatives[11,12] have not been carried out as a function of temperature, though these quantities would appear to be accessible for such compounds by this method. However, ultrasonic relaxation fails when two conformers are of equal energy.

A further method is extremely useful in cases of rapid interconversion of two (or more) isomers. This is nuclear magnetic resonance. Several situations have been investigated by this technique; inversion of ethylenimines,[13,14] *cis*- and *trans*-alkyl nitrites[15] and hindered rotation in amides.[16] At high temperatures, the spectrum obtained is the weighted time average of the two isomers; at low temperatures the spectrum is the summation for the individual isomers. The pertinent theoretical considerations are summarized by Pople, Schneider and Bernstein.[17]

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[1] Originally published in preliminary form; F. R. Jensen, D. S. Noyce, C. H. Sederholm and A. J. Berlin, *J. Am. Chem. Soc.*, **82**, 1256 (1960); presented, in part, at the 138th Meeting of the American Chemical Society, New York, N. Y., September, 1960.

[2] Supported, in part, by the National Science Foundation.

[3] For a recent review, see M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter I by W. G. Dauben and K. S. Pitzer.

[4] C. W. Shoppee, *J. Chem. Soc.*, 1138 (1946).

[5] C. S. Beckett, K. S. Pitzer and R. Spitzer, *J. Am. Chem. Soc.*, **69**, 2488 (1947).

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[13] A. T. Bottini and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 5126 (1956); **80**, 5203 (1958).

[14] A. Loewenstein, J. F. Neumer and J. D. Roberts, *ibid.*, **82**, 3599 (1960).

[15] L. H. Piette and W. A. Anderson, *J. Chem. Phys.*, **30**, 899 (1959); W. D. Phillips, *Ann. N. Y. Acad. Sci.*, **70**, 817 (1958).

[16] W. D. Phillips, *J. Chem. Phys.*, **23**, 1363 (1955); H. S. Gutowsky and C. H. Holm, *ibid.*, **25**, 1228 (1956).