precipitate (1.04 g.), obtained when the reaction mixture was cooled, was treated with 5 ml. of warm ethanol to dissolve the more soluble component. The filtrate was cooled and 0.70 g. (38%) of 3,4,5-triphenylpyrazoline (VII) was collected. The pyrazoline, m.p. 101–104° from ethanol, was unstable and turned brown when exposed to air.

Anal. Calcd. for $C_{21}H_{18}N_2$: C, 84.53; H, 6.08; N, 9.39. Found: C, 84.06; H, 6.01; N, 8.62.

The solid which did not dissolve when the original reaction product was treated with ethanol melted at 160–167°, solidified, and remelted at 250–260°. This material melted at 264–265° after one crystallization from ethanol and proved to be 3,4,5-triphenylpyrazole (m.p. and mixed m.p. 264–265°).

b. Conversion of VII to VI.—Bromine was added dropwise to 3,4,5-triphenylpyrazoline (0.101 g., 0.000339 mole) in carbon tetrachloride (3 ml.) until the color of bromine persisted. The mixture was heated on a steam-bath for several minutes and then the bromine and solvent were allowed to evaporate. The residue was recrystallized from ethanol to give 3,4,5-triphenylpyrazole (0.076 g., 76% yield, m.p. 265°). A mixed melting point of this product with a sample of VI obtained from IV was 265°.

Reaction of 1-Nitropropene with Diphenyldiazomethane.—A solution containing 1-nitropropene[12] (8.25 g., 0.0948 mole, b.p. 45–47° (15 mm.), $n^{25.5}\text{D}$ 1.4503), diphenyldiazomethane (18.4 g., 0.0948 mole) and petroleum ether (105 ml., b.p. 30–60°) was allowed to stand in a refrigerator. The precipitate that formed (7.2 g. after five days, 7.9 g. or 27% after five weeks) melted at 133–137° dec. 3-Nitro-4-methyl-5,5-diphenylpyrazoline (VIII) melted at 140–141° dec. (recrystallization from ethanol).

Anal. Calcd. for $C_{16}H_{15}O_2N_3$: C, 68.31; H, 5.38; N, 14.94. Found: C, 68.30; H, 5.31; N, 15.03.

Conversion of 3-Nitro-4-methyl-5,5-diphenylpyrazoline (VIII) into 3-Methyl-4,5-diphenylpyrazole (IX).—The procedure used was essentially that described for the conversion of IV to VI. A two-hour heating period was necessary for the elimination of oxides of nitrogen. From 3.22 g. (0.0114 mole) of VIII, 26 ml. of ethanol and 2 ml. of concentrated hydrochloric acid there was obtained 2.41 g. (90% yield) of product melting at 176–180°. The melting point of the product was raised to 183–184° by crystallization from ethanol; 185–186° by sublimation.

Anal. Calcd. for $C_{16}H_{14}N_2$: C, 82.02; H, 6.02; N, 11.96. Found: C, 81.75; H, 6.13; N, 12.02.

Oxidation of IX to 4,5-Diphenylpyrazole-3-carboxylic Acid.—A mixture of IX (0.37 g., 0.016 mole), potassium permanganate (0.50 g., 0.032 mole), water (5 ml.) and *t*-butyl alcohol[13] (6 ml.) was heated on a steam-bath until the permanganate was consumed (about three hours). The manganese dioxide was removed by filtration and most of the alcohol was removed by distillation. The mixture was cooled and unchanged starting material (0.14 g.) was removed by filtration. The filtrate was acidified and the crude acid (0.14 g., m.p. 267–268°, 54% based on pyrazole consumed) was collected. The acid melted at 271° after recrystallization from methanol–water. This acid caused no depression in melting point when admixed with a sample of 4,5-diphenylpyrazole-3-carboxylic acid (m.p. 269°) prepared by the method previously reported by Borsche and Hahn.[7]

4,5-Diphenylpyrazole.—Samples of 4,5-diphenylpyrazole-3-carboxylic acid (100 mg.), prepared either from IX or from desylglyoxylic ester[7] were heated at 280° for several minutes in an atmosphere of nitrogen. The product (100% yield) was then sublimed at 150° (1 mm.) to give 80 mg. (96% yield) of 4,5-diphenylpyrazole melting at 155° (reported[14] m.p. 155°).

Reaction of Dimethyldiazomethane with 1-Nitropropene.—Dimethyldiazomethane, contaminated with some xylene and water, was prepared by modifications of the procedures previously described by Staudinger and Gaule[15] and Guha and Sankaran.[16] The red oil containing dimethyldiazomethane was dissolved in 10 ml. of cold ether and 1-nitropropene was added dropwise to the solution. The color of the diazo compound was rapidly discharged, and when the solution changed from pale red to pale yellow, addition of nitroölefin was terminated. In one run a total of 1.22 g. (0.014 mole) of 1-nitropropene was required, indicating that there was 0.98 g. (0.014 mole) of dimethyldiazomethane present. The ether was removed by distillation and the residual oil was treated with 1.00 ml. of concentrated hydrochloric acid. An immediate evolution of oxides of nitrogen was observed. The solution was warmed on a steam-bath for one-half hour and then the cold reaction mixture was extracted with small portions of ether. The aqueous solution was made alkaline with sodium hydroxide and then allowed to stand at 0° for 12 hours. The long white needles that formed (0.16 g., 10.5% based on nitroölefin employed) melted at 133–137°, 137–138° after recrystallization from water. The picrate of this product melted at 237–239°. 3,4,5-Trimethylpyrazole is reported to melt at 137–138°.[17] The picrate of 3,4,5-trimethylpyrazole is reported to melt at 237–239°.[17]

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[12] E. Schmidt and G. Rutz, *Ber.*, **61**, 2142 (1928).

[13] When *t*-butyl alcohol was omitted the acid was not obtained even though all of the permanganate was consumed.

[14] W. Wislicenus and A. Ruthing, *Ann.*, **379**, 256 (1911).

[15] H. Staudinger and A. Gaule, *Ber.*, **49**, 1904 (1916).

[16] P. C. Guha and D. K. Sankaran, *ibid.*, **70**, 1689 (1937).

[17] L. Knorr and B. Oettinger, *Ann.*, **279**, 247 (1894).

MINNEAPOLIS, MINN.

[CONTRIBUTION FROM THE WHITMORE LABORATORY, THE PENNSYLVANIA STATE COLLEGE]

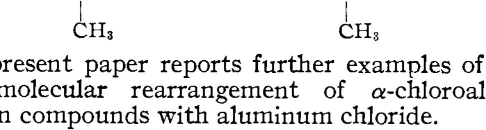
New Intramolecular Rearrangements of α-Chloroalkylsilicon Compounds[1,2]

BY LEO H. SOMMER, DONALD L. BAILEY, JACK R. GOULD AND FRANK C. WHITMORE[3]

RECEIVED APRIL 18, 1953

Three new examples of the intramolecular rearrangement of alkyl from silicon to carbon have been found, thereby demonstrating the generality of this phenomenon for organosilicon compounds.

In continuation of previous work which demonstrated, for the first time, the phenomenon of intramolecular rearrangement of alkyl from silicon to carbon in a change analogous to the Wagner–Meerwein rearrangements so common in organic chemistry[4]



$$CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-CH_2Cl \xrightarrow{AlCl_3} CH_3-\overset{Cl}{\underset{CH_3}{Si}}-CH_2CH_3 \quad (1)$$

the present paper reports further examples of the intramolecular rearrangement of α-chloroalkylsilicon compounds with aluminum chloride.

The products obtained from the reaction of aluminum chloride with α-chloroethyltrimethylsilane (R = Me) and α-chloroethyltriethylsilane (R = Et) are indicated by equation 2.

In 2a rearrangements entirely analogous to 1 have occurred. In 2b the presence of carbon and

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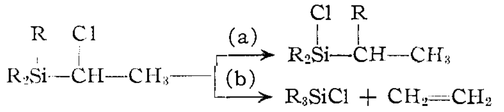
[1] Paper 37 in a series on organosilicon chemistry; for paper 36 see P. D. George, L. H. Sommer and F. C. Whitmore, THIS JOURNAL, **75**, 6308 (1953).

[2] Presented in part before the Division of Organic Chemistry at the 113th Meeting of the American Chemical Society in Chicago, April 22, 1948.

[3] Deceased.

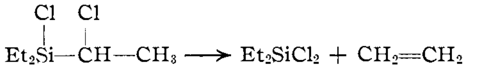
[4] F. C. Whitmore, L. H. Sommer and J. Gould, THIS JOURNAL, **69**, 1976 (1947).



$$R_2\overset{R}{\overset{|}{Si}}-\overset{Cl}{\overset{|}{C}}H-CH_3\begin{cases}\xrightarrow{(a)} R_2\overset{Cl}{\overset{|}{Si}}-\overset{R}{\overset{|}{C}}H-CH_3 \\ \xrightarrow{(b)} R_3SiCl + CH_2{=}CH_2\end{cases}\qquad (2)$$

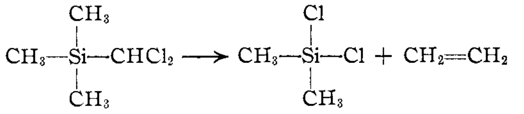
hydrogen in the beta relation to silicon (absent in chloromethyltrimethylsilane) has made possible a rearrangement of hydrogen from beta to alpha carbon followed by elimination of ethylene.

Treatment of α-chloroethyldiethylchlorosilane with aluminum chloride gave no rearrangement of alkyl from silicon to carbon. Instead, a reaction similar to 2b occurred exclusively with the formation of diethyldichlorosilane and ethylene.



$$Et_2\overset{Cl}{\overset{|}{Si}}-\overset{Cl}{\overset{|}{C}}H-CH_3 \longrightarrow Et_2SiCl_2 + CH_2{=}CH_2 \qquad (3)$$

In dichloromethyltrimethylsilane, the presence of two chlorine substituents at the alpha carbon introduces a new structural feature, thereby facilitating a reaction sequence of two consecutive processes which find precedent in reactions 1 and 3. Thus, rearrangement of methyl from silicon to carbon yields α-chloroethyldimethylchlorosilane and this substance then undergoes a change analogous to 3 giving dimethyldichlorosilane and ethylene.



$$CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{Si}}}}-CHCl_2 \longrightarrow CH_3-\underset{CH_3}{\underset{|}{\overset{Cl}{\overset{|}{Si}}}}-Cl + CH_2{=}CH_2 \qquad (4)$$

The presence of a single chlorine substituent on silicon in dichloromethyldimethylchlorosilane, Cl_2CHMe_2SiCl, and in chloromethyldimethylchlorosilane, $ClCH_2Me_2SiCl$, effectively prevents rearrangements of these substances with aluminum chloride.

While the new rearrangements reported in this paper may evidently be formulated in terms of current carbonium ion theory as applied to intramolecular rearrangements[5] and beta-eliminations involving silicon,[6] the data at hand are considered insufficient to justify a discussion of reaction mechanism details.

Experimental

Intramolecular Rearrangement of α-Chloroethyltrimethylsilane (Silicopinacolyl Chloride).—A 1-liter, three-necked flask was fitted with a dropping funnel, mercury-sealed stirrer and a reflux condenser leading to a Dry Ice–acetone trap and two bromine absorption tubes connected in series. Having first swept the apparatus with dry nitrogen, approximately 0.5 g. of anhydrous aluminum chloride was added to the reaction flask. α-Chloroethyltrimethylsilane, 92.0 g. (0.67 mole), prepared by the method of Sommer and Whitmore,[7] was placed in the dropping funnel and a few drops were cautiously introduced to the catalyst. A vigorous, exothermic reaction commenced and was accompanied by copious evolution of a gas which was readily absorbed by the bromine. Thereafter, addition of liquid was continued at such a rate (initially, one drop per minute; later, one drop per second) as to maintain reasonable reflux. The product which accumulated in the flask served the function of a diluent which reduced the vigor of the reaction. During the five hours required for the introduction of the α-chloroethyltrimethylsilane, it was necessary to add another 8.5 g. of catalyst, in portions of about 1.0 g. each, in order to maintain the reaction. As a further precaution against the hazard of inadvertent accumulation of unreacted α-chloroethyltrimethylsilane in the flask, the reaction mixture was heated occasionally with a Glas-Col mantle and was stirred vigorously.

The reaction was assumed to be complete when further addition of the catalyst caused no evolution of gas even when the mixture was refluxed. The contents of the reaction flask, 75 g., were combined with 6.0 g. of fuming liquid which had accumulated in the Dry Ice–acetone trap. Fractionation gave: I, trimethylchlorosilane, 42.1 g. (0.39 mole), 58% yield, b.p. 56.9° (738 mm.), $n^{20}D$ 1.3880, % Cl 33.2 (calcd. 32.7)[8]; II, isopropyldimethylchlorosilane, 12.2 g. (0.09 mole), 14% yield, b.p. 109.8–110.0° (738 mm.), $n^{20}D$ 1.4158, % Cl 27.5 (calcd. 26.0). Treatment of the slightly impure isopropyldimethylchlorosilane with excess methylmagnesium bromide gave isopropyltrimethylsilane[9] in 75% yield, b.p. 87° (737 mm.), $n^{20}D$ 1.3960, d^{20} 0.7083, MR_D 39.39 (calcd. 39.54), % Si 24.2 (calcd. 24.1).

The material from the bromine absorption tubes was washed with dilute sodium bisulfite and then with water. After drying the product, distillation gave 68 g. (0.36 mole) of ethylene bromide, b.p. 130° (738 mm.), $n^{20}D$ 1.5385, in 54% yield.

α-Chloroethyldiethylchlorosilane and α-Chloroethyltriethylsilane.—The preparation of α-chloroethyldiethylchlorosilane from triethylchlorosilane has been described in a previous paper.[10]

Using a similar procedure, chlorination of 400 g. (2.78 moles) of tetraethylsilane with 301 g. (2.23 moles) of sulfuryl chloride and 0.1 g. of benzoyl peroxide catalyst gave 139 g. (0.78 mole) of α-chloroethyltriethylsilane,[11] b.p. 112° (58 mm.), $n^{20}D$ 1.4540, d^{20} 0.9086, a yield of 64% based on unrecovered tetraethylsilane. The beta isomer was not obtained.

Intramolecular Rearrangement of α-Chloroethyltriethylsilane.—In a 200-cc. three-necked flask equipped with reflux condenser, dropping funnel, and mercury-sealed stirrer, there were placed 150 cc. of pentane and 2 g. of anhydrous aluminum chloride. The outlets to the dropping funnel and reflux condenser were connected to a Dry Ice trap leading to an absorption trap containing bromine. Through the dropping funnel there was then added with stirring 39 g. (0.22 mole) of α-chloroethyltriethylsilane over the course of one hour. The gas evolved during the addition was absorbed in the bromine trap and identified as ethylene by the formation of ethylene bromide, b.p. 128–219°, $n^{20}D$ 1.5379, in 22% yield. After stirring the reaction mixture for several hours the pentane solution was filtered from the aluminum chloride and the pentane distilled. Fractionation of the residual material gave 12.3 g. (0.081 mole) of triethylchlorosilane, b.p. 76–78° (78 mm.), $n^{20}D$ 1.4309, d^{20} 0.8970, % Cl 23.60 (calcd. 23.53), in 37% yield and 16.5 g. (0.092 mole) of s-butyldiethylchlorosilane, b.p. 90–91° (33 mm.), $n^{20}D$ 1.4451, d^{20} 0.9028, MR_D 52.70 (calcd. 53.06), % Cl 19.95 (calcd. 19.83), in 42% yield. The latter substance is a new compound which was further characterized by an unequivocal synthesis from s-butyllithium and diethyldichlorosilane in a pentane solvent which gave s-butyldiethylchlorosilane, b.p. 94–95° (41 mm.), $n^{20}D$ 1.4448, d^{20} 0.9017, in 68% yield. Further, treatment of the s-butyldiethylchlorosilane, obtained from rearrangement, with ethylmagnesium bromide gave s-butyltriethylsilane, b.p. 190° (718 mm.), $n^{20}D$ 1.4423, d^{20} 0.7927, MR_D 57.29 (calcd. 58.06), % Si 16.02 (calcd. 16.28), in 61% yield. Similar treatment of s-butyldiethylchlorosilane, prepared from s-butyllithium and diethyldichlorosilane, gave s-butyltriethyl silane, b.p. 190–190.5° (718 mm.), $n^{20}D$ 1.4420, d^{20} 0.7924, in 71% yield.

Intramolecular Rearrangement of α-Chloroethyldiethylchlorosilane.—Using a procedure similar to that described for the rearrangement of α-chloroethyltrimethylsilane, 30 g. (0.16 mole) of α-chloroethyldiethylchlorosilane was allowed

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[5] F. C. Whitmore, This Journal, **54**, 3274 (1932); J. D. Roberts, R. E. McMahon and J. S. Hine, *ibid.*, **72**, 4237 (1950).

[6] L. H. Sommer, D. L. Bailey and F. C. Whitmore, *ibid.*, **70**, 2869 (1948).

[7] L. H. Sommer and F. C. Whitmore, *ibid.*, **68**, 485 (1946).

[8] W. F. Gilliam and R. O. Sauer, *ibid.*, **66**, 1793 (1944).

[9] L. H. Sommer, G. T. Kerr and F. C. Whitmore, *ibid.*, **70**, 445 (1948).

[10] L. H. Sommer, D. L. Bailey, W. A. Strong and F. C. Whitmore, *ibid.*, **68**, 1881 (1946).

[11] S. N. Ushakov and A. M. Itenberg, *J. Gen. Chem., U.S.S.R.*, **7**, 2495 (1937).

to react with 6 g. of anhydrous aluminum chloride over a period of two hours. The gas evolved during the reaction was passed into bromine and identified as ethylene by the formation of ethylene bromide, b.p. 128–130°, $n^{20}D$ 1.5387, in 64% yield. Fractionation of the liquid reaction product gave 19 g. (0.12 mole) of diethyldichlorosilane, b.p. 127–128° (734 mm.), $n^{20}D$ 1.4311, d^{20} 1.0507, neut. equiv. 79.0 (calcd. 78.6), MR_D 38.72 (calcd. 38.8), a yield of 75%.

Chloromethyldimethylchlorosilane and Aluminum Chloride.—Chloromethyldimethylchlorosilane,[12] 35.0 g. (0.25 mole) was refluxed for three hours with 2.0 g. of anhydrous aluminum chloride. During this time the originally water-white liquid became almost black. Distillation, however, gave 34.0 g. (0.24 mole) of chloromethyldimethylchlorosilane, b.p. 112–115° at 735 mm., $n^{20}D$ 1.4360, a 96% recovery of the original compound.

Dichloromethyldimethylchlorosilane and Aluminum Chloride.—Dichloromethyldimethylchlorosilane, 62.0 g. (0.35 mole), was refluxed for two hours with 3.0 g. of anhydrous aluminum chloride. The same black coloration noted in the above experiment with chloromethyldimethylchlorosilane developed almost at once. After decanting the liquid product from the catalyst, distillation gave 43.5 g. (0.25 mole) of dichloromethyldimethylchlorosilane, b.p. 146–148°, 70% recovery of the starting material.

Intramolecular Rearrangement of Dichloromethyltrimethylsilane.—The violence and exothermal nature of the action of anhydrous aluminum chloride on dichloromethyltrimethylsilane is such as to necessitate a warning by the authors that unless care is exercised this reaction may lead to explosions. The procedure described above for the rearrangement of α-chloroethyltrimethylsilane was found to be satisfactory when adapted for dichloromethyltrimethylsilane. It is important (for reasons of safety) to note that the organosilicon compound is added *to* the aluminum chloride in both cases.

During six hours, 125.0 g. (0.80 mole) of dichloromethyltrimethylsilane[13] reacted exothermally with 4.5 g. of anhydrous aluminum chloride. Ethylene was evolved and was converted by liquid bromine into ethylene bromide, 115 g. (0.61 mole), b.p. 129–130° (735 mm.), $n^{20}D$ 1.5380, in 76% yield. The crude product in the reaction flask, 92 g., was combined with 10 g. of liquid which was collected in the Dry Ice–acetone trap and distilled to give 91 g. (0.71 mole) of dimethyldichlorosilane,[14] b.p. 69–70° (737 mm.), % Cl 54.4 (calcd. 54.9), in 88% yield.

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[12] R. H. Krieble and J. R. Elliott, THIS JOURNAL, **67**, 1810 (1945).

[13] J. L. Speier and B. F. Daubert, *ibid.*, **70**, 1400 (1948).

[14] W. F. Gilliam, H. A. Liebhafsky and A. F. Winslow, *ibid.*, **63**, 801 (1941).

[CONTRIBUTION FROM THE WHITMORE LABORATORY, THE PENNSYLVANIA STATE COLLEGE]

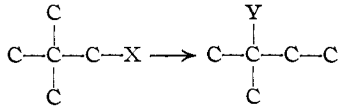
Non-rearrangement Reactions of the Neopentyl–Oxygen Bond. New Syntheses of Neopentyl Halides[1]

BY LEO H. SOMMER, HERBERT D. BLANKMAN AND PAUL C. MILLER

RECEIVED APRIL 18, 1953

New syntheses for neopentyl bromide and neopentyl chloride are reported which make these interesting aliphatic halides readily available in contrast to the previous methods used. These syntheses also provide unequivocal examples of reactions of the neopentyl–oxygen bond proceeding without rearrangement.

Anionoid substitution reactions of neopentyl compounds have long been known to proceed with rearrangement of the carbon skeleton.[2]



Indeed, these changes are often cited in textbooks as classical simple examples of the Wagner–Meerwein rearrangement.

While these changes are of considerable interest for the theory of intramolecular rearrangements, neopentyl compounds, especially the neopentyl halides, were previously rather difficult to prepare, since the chloride was available only from vapor-phase chlorination of neopentane,[3] and the bromide was made from the chloride by a multi-step procedure involving conversion to the Grignard reagent, treatment of the latter with mercuric chloride and, finally, reaction of neopentylmercuric chloride with bromine.[2c]

In a recent elegant series of papers, however, Dostrovsky, Hughes and Ingold[4] have demonstrated rearrangement for neopentyl bromide in S_N1 reactions and non-rearrangement in S_N2 reactions. This suggested that similar non-rearrangement reactions of the neopentyl–oxygen bond might be isolated by appropriate structural variations in neopentyl alcohol (which left intact the neopentyl–oxygen configuration) or by reaction conditions unfavorable to reaction of the alcohol by an S_N1 mechanism.

In this article we report unequivocal examples of reactions of the neopentyl–oxygen bond proceeding without rearrangement,[5] which provide new and convenient syntheses of neopentyl bromide and neopentyl chloride.

$$\mathrm{Me_3CCH_2OSiEt_3 + PBr_3 \xrightarrow{C_9H_7N\cdot HX} Me_3CCH_2Br + Et_3SiBr} \quad (1)$$

$$\mathrm{Me_3CCH_2OSiEt_3 + SOCl_2 \xrightarrow{C_9H_7N\cdot HX} Me_3CCH_2Cl + Et_3SiCl} \quad (2)$$

$$\mathrm{Me_3CCH_2OH + PBr_3 + C_9H_7N \longrightarrow Me_3CCH_2Br + C_9H_7N\cdot HBr} \quad (3)$$

An important feature of the above reactions is the choice of reactants which will not give hydrogen chloride or hydrogen bromide as reaction products

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[1] For a preliminary Communication see L. H. Sommer, H. D. Blankman and P. C. Miller, THIS JOURNAL, **73**, 3542 (1951).

[2] (a) F. C. Whitmore, *ibid.*, **54**, 3274 (1932); (b) F. C. Whitmore and H. S. Rothrock, *ibid.*, **54**, 3431 (1932); (c) F. C. Whitmore, E. L. Wittle and B. R. Harriman, *ibid.*, **61**, 1586 (1939).

[3] Whitmore and Fleming, *ibid.*, **55**, 4161 (1933).

[4] I. Dostrovsky, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 157 (1946).

[5] Subsequent to the completion of this work, F. G. Bordwell, B. M. Pitt and M. Knell, THIS JOURNAL, **73**, 5004 (1951), reported non-rearrangement reactions of neopentyl *p*-toluenesulfonate. Evidence for non-rearrangement of *d*-pinacolyl hydrogen sulfate in sulfuric acid during racemization has been presented by N. C. Deno and M. S. Newman, *ibid.*, **73**, 1920 (1951).