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.

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

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.

(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).

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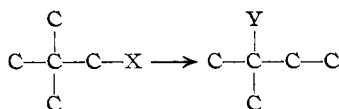[CONTRIBUTION FROM THE WHITMORE LABORATORY, THE PENNSYLVANIA STATE COLLEGE]

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

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]
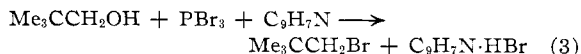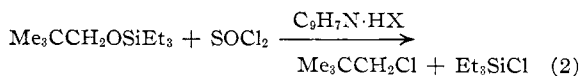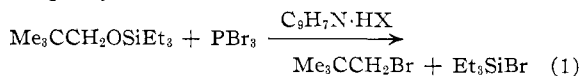
$$\begin{array}{ccc} & \text{C} & & \text{Y} \\ & | & & | \\ \text{C}-\text{C}-\text{C}-\text{X} & \longrightarrow & \text{C}-\text{C}-\text{C}-\text{C} \\ & | & & | \\ & \text{C} & & \text{C} \end{array}$$

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.

$$\text{Me}_3\text{CCH}_2\text{OSiEt}_3 + \text{PBr}_3 \xrightarrow{\text{C}_9\text{H}_7\text{N}\cdot\text{HX}} \text{Me}_3\text{CCH}_2\text{Br} + \text{Et}_3\text{SiBr} \quad (1)$$

$$\text{Me}_3\text{CCH}_2\text{OSiEt}_3 + \text{SOCl}_2 \xrightarrow{\text{C}_9\text{H}_7\text{N}\cdot\text{HX}} \text{Me}_3\text{CCH}_2\text{Cl} + \text{Et}_3\text{SiCl} \quad (2)$$

$$\text{Me}_3\text{CCH}_2\text{OH} + \text{PBr}_3 + \text{C}_9\text{H}_7\text{N} \longrightarrow \text{Me}_3\text{CCH}_2\text{Br} + \text{C}_9\text{H}_7\text{N}\cdot\text{HBr} \quad (3)$$

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

(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).

(in 3 an excess of quinoline is available for immediate combination with hydrogen bromide). Hydrogen bromide gives extensive rearrangement with neopentyl alcohol.[2b]

Experimental

Neopentyl Alcohol.—To 27 moles of *t*-butylmagnesium chloride in 10 liters of ether contained in a copper-lined stirred Grignard reactor there was added (12 hours) 13.5 moles of methyl formate. After stirring the reactants for an additional 12 hours, the product was hydrolyzed in the usual way. Fractionation gave 9.75 moles (72% yield) of neopentyl alcohol, b.p. 111° (730 mm.), m.p. 51–52°. This convenient preparation of neopentyl alcohol is made possible by Grignard reduction of the intermediate trimethylacetaldehyde.

Triethylneopentoxysilane.—In a 12-liter, three-necked, round-bottomed flask equipped with a condenser, mercury-sealed anchor-type glass stirrer, and protected from moisture by a sulfuric acid trap were mixed 514 g. (5.84 moles), of neopentyl alcohol, 770 g. (5.95 moles) of quinoline and 2700 cc. of dry benzene. To this mixture there was added, with rapid stirring, over a period of 2.5 hours, 981 g. (6.50 moles) of triethylchlorosilane.[6] After the addition, the reactants were heated on the steam-bath with stirring for an additional 20 hours. Fractionation followed by treatment of the triethylneopentoxysilane with silica gel to remove quinoline and quinoline hydrochloride gave 4.97 moles (85% yield), b.p. 63°(7 mm.), n^{20}D 1.4189.

Anal. Calcd. for $C_{11}H_{26}OSi$: Si, 13.84. Found: Si, 13.78.

Neopentyl Bromide from Triethylneopentoxysilane.—In a two-bottom glass-jointed, round-bottomed flask were placed 411 g. (2.03 moles), of triethylneopentoxysilane, 1078 g. (3.97 moles) of phosphorus tribromide, and 3.0 g. of quinoline hydrochloride. The flask was attached to an efficient multiple-bulb condenser, which was open to the atmosphere through a Dry Ice-ethanol trap and a concd. sulfuric acid trap. Mixing of the reactants was accompanied by a temperature rise of 45°. The reaction mixture was then heated at reflux temperature for 16 hours. During that period the reaction temperature dropped from 173 to 148°. After cooling, fractional distillation gave 264 g. (1.75 moles) of pure neopentyl bromide, b.p. 104° (733 mm.), n^{20}D 1.4371, d^{20} 1.199; lit.[2c] b.p. 105°, n^{20}D 1.4370, d^{20} 1.199; anilide, m.p. and mixed 130°; less than 0.5% reaction with NaOEt in EtOH at reflux for four hours; (calcd. for C_5H_{11}-Br: Br, 52.9. Found: Br, 52.9). The yield of pure neopentyl bromide was 86%.

Hydrolysis of the higher-boiling material gave hexaethyldisiloxane, from hydrolysis of Et_3SiBr, in 94% yield.

Neopentyl Chloride from Triethylneopentoxysilane.—The apparatus used here was the same as that used above in the neopentyl bromide preparation. In the reaction flask were placed 413 g. (2.05 moles) of triethylneopentoxysilane, 3.73 moles of thionyl chloride and 2.9 g. of quinoline hydrochloride. When the contents of the flask were well mixed,

a temperature rise of 40° was noted, causing the contents to start to boil. The flask was quickly charged to the condenser and heated; the time of heating was 23 hours; the temperature of the reactants in the flask during heating at reflux dropped from 115 to 103°.

After cooling to room temperature, the reaction products were added to cracked ice to remove excess thionyl chloride. The organic layer was separated, washed with water five times, and then dried over Drierite. Fractional distillation gave 132 g. (1.24 moles, 60% yield) of pure neopentyl chloride, b.p. 83.5° (725 mm.), n^{20}D 1.4043, d^{20} 0.8659, lit.[3] b.p. 83.5 (740 mm.), n^{20}D 1.4043, d^{20} 0.865; completely inert to NaOEt in EtOH; anilide, m.p. and mixed 130° (calcd. for $C_5H_{11}Cl$: Cl, 33.27. Found: Cl, 32.58).

Neopentyl Bromide from Neopentyl Alcohol.—In a two-liter, three-necked, round-bottomed flask containing a thermometer well and fitted with a dropping funnel and mercury-sealed stirrer and protected from moisture by a sulfuric acid trap, were placed the following: 176 g. (2.0 moles) of neopentyl alcohol, 313 g. (2.43 moles) of quinoline and 740 cc. of dry bromobenzene.

The flask was placed in an ice–salt-bath and the contents cooled to −5°. Then, over a period of six hours, 402 g. (1.48 moles) of phosphorus tribromide was added with stirring. During the addition the temperature was allowed to rise gradually until it reached 15°. The material in the flask was transferred, with the aid of an additional 150 cc. of bromobenzene, to a 2-liter glass-jointed flask which was attached to an efficient multiple-bulb condenser; heat was applied to the flask. The time of heating was 24 hours, the temperature of the mixture dropping from 181 to 162° during this period.

The reaction mixture was then allowed to cool, giving a clear reddish liquid over a red, viscous residue. The liquid was decanted and the residue broken up and extracted with three 65-cc. portions of bromobenzene. The combined bromobenzene solution was poured onto ice to remove excess phosphorus tribromide; the resulting organic layer was washed with water and dried, first over calcium chloride and then over Drierite. Fractional distillation gave 143 g. (0.93 mole) of pure neopentyl bromide, b.p. 105°, n^{20}D 1.4370, inert to NaOEt in EtOH, anilide m.p. and mixed m.p. 130°, a yield of 47%.

Neopentyl Alcohol and Phosphorus Tribromide.—Reaction of 38 g. (0.433 mole) of neopentyl alcohol with 134 g. (1.49 moles) of phosphorus tribromide in 180 cc. of dry bromobenzene was carried out by a procedure similar to that used above. After heating for 19 hours at 131–136° the product was poured onto ice, separated and dried. Fractional distillation gave a mixture of amyl bromides, b.p. 104–114°, n^{20}D 1.4380–1.4433; reaction to the extent of 48–58% with NaOEt in EtOH; 28.6 g., 44% yield.

The Uncatalyzed Reaction of Triethylneopentoxysilane and Phosphorus Tribromide.—In the absence of quinoline hydrochloride, reaction of 52.1 g. (0.257 mole) of triethylneopentoxysilane with 107 g. (0.395 mole) of phosphorus tribromide, under conditions identical with those used in the quinoline hydrochloride-catalyzed reaction, gave a mixture of amyl bromides, b.p. 106–112°, n^{20}D 1.4376–1.4407, reaction with alcoholic potassium hydroxide to the extent of 20–40%; a yield of only 26%.

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(6) For a convenient preparation see P. A. Di Giorgio, W. A. Strong, L. H. Sommer and F. C. Whitmore, This Journal, **68**, 1380 (1946).