

benzene which gave a yellow color (faint) with propyl tetrabromophthalate was hemimellitene.

2. Dimethylaniline. On mixing with dimethylaniline, dibutyl and dipropyl tetrachlorophthalates were orange-red and brown-red respectively, while the bromophthalate and methyl propyl tetrachlorophthalate were yellow-green and yellow, respectively.

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Preparation of 1-Alkylated 2-Haloethers by the Grignard Method. 2-Bromo-1,1-dimethylethyl Ethyl Ether¹

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In the course of an investigation of the properties of 2-haloethers the authors have had occasion to prepare 2-bromo-1,1-dimethylethyl ethyl ether, which has not previously been reported. This compound is of special interest because it cannot lose hydrogen bromide in a simple way or rearrange to a 1-haloether, two possibilities in the thermal decomposition³ of 2-bromoethers, without the breaking of a carbon-carbon bond.

The desired 2-bromoether was synthesized following the general procedure of Sherrill and Walter^{3c} for a similar 2-bromo-1,1-dialkylated ether, modified to employ ethyl vinyl ether as a starting material,⁴ from which 1,2-dibromoethyl ethyl ether was made. The over-all yield (25%, based on starting vinyl ether) was considerably better than those previously given^{5,3c} for such compounds.

During the work reported here it was found that 2-chloro-1-methylethyl ethyl ether could not be made from 1,2-dichloroethyl ethyl ether and the Grignard reagent prepared from methyl iodide. Reaction was violent and by either mode of addition, Grignard reagent to halogenated ether or halogenated ether to Grignard reagent only tars

and small quantities of impure products resulted.⁶ This compound could, however, be synthesized in good yield (48%, based on the dichloro ether)⁷ when methyl chloride was used instead of methyl iodide.

EXPERIMENTAL⁸

2-Bromo-1-methylethyl ethyl ether (I). To 144 g. (2.00 moles) of redistilled (fraction boiling at 34.4°) ethyl vinyl ether (General Aniline and Film Corp.) and 700 ml. of sodium-dried diethyl ether in a 3-necked, 2-liter flask fitted with a dropping funnel, mercury-sealed stirrer, and reflux condenser, immersed in a Dry Ice-acetone bath at -70°, bromine was added at the rate of one drop per second. All openings to the system were fitted with drying tubes. The bromine color was lost rapidly after the addition of each drop. Addition was stopped when the bromine color persisted (320 g., 2.00 moles, of bromine), and a few drops of the vinyl ether were added to decolorize the solution. This solution of 1,2-dibromoethyl ethyl ether was then removed from the bath and added at 0°, in an assembly like that just described, to a Grignard solution, in excess, made from methyl bromide (65.2 g., 2.68 g.-atoms, magnesium and 840 ml. ether, with about 10% excess methyl bromide). Addition required about 5 hr. whereupon the mixture was refluxed with stirring for 8 hr. Then the product was poured onto ice and dilute hydrochloric acid, the ether layer separated, washed with 10% sodium bicarbonate and then with water until the washings were neutral. After drying over calcium chloride, the bulk of the solvent ether was removed by fractionation at atmospheric pressure. The remaining 2-bromoether was distilled (Vigreux column) at reduced pressure over a few sodium hydroxide pellets. The main fraction boiled at 39°/18 mm. and weighed 275 g. (82%). Redistillation gave 252 g. (75%) of a product of constant boiling point and refractive index, b.p. 36.5°/16.5 mm., n_D^{25} 1.4396, d_4^{25} 1.2689.

Ethyl isopropenyl ether (II). Dehydrohalogenation was effected with solid potassium hydroxide in a copper flask, according to the procedure of Sherrill and Walter.^{3c} Careful control of the temperature was necessary to moderate the vigorous reaction that ensued. From 208 g. (1.24 moles) of I, 81.2 g. (76%) of II was obtained upon redistillation, b.p. 59.2-61.2/733 mm., n_D^{27} 1.3882.

2-Bromo-1,1-dimethylethyl ethyl ether (III). Bromine was added to 74.5 g. (0.865 mole) of II in 435 ml. of diethyl ether as in the preparation of I except that the temperature of the bath was kept at -30°, since the bromination was slower and at lower temperatures an increasing amount of frozen bromine collected at the bottom of the flask. An almost theoretical amount of bromine (138.5 g., 0.867 mole) was used, with the solution pale yellow at the end of the addition. This solution was then added dropwise with stirring to the Grignard reagent (made from 30.2 g., 1.24 g.-atoms, magnesium, 390 ml. ether and a slight excess of

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(3) (a) F. B. Tutwiler and R. L. McKee, *J. Am. Chem. Soc.*, **76**, 6342 (1954); (b) M. H. Palomaa and A. Kenetti, *Ber.*, **64B**, 797 (1931); (c) M. L. Sherrill and G. F. Walter, *J. Am. Chem. Soc.*, **58**, 742 (1936).

(4) D. C. Rowlands, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Org. Chem.*, **17**, 807 (1952). See also D. Gagnaire, *Compt. rend.*, **245**, 1732 (1957).

(5) C. G. Schmitt and C. E. Boord, *J. Am. Chem. Soc.*, **54**, 751 (1932).

(6) See V. S. Abramov and A. P. Pakhomova, *Zhur. Obshchei Khim.*, **24**, 1198 (1954), for a similar observation in the reaction of methyl magnesium iodide with 1,2-dibromoethyl ether.

(7) The authors are indebted to Mr. W. A. Dickens of this laboratory for help in this preparation. The physical constants of the product obtained, which was distilled to constant boiling point and refractive index, differ from those previously recorded and give a better value for the molar refraction; b.p. 30.3°/25 mm., n_D^{25} 1.4103, d_4^{25} 0.9582, M_R Calcd. 31.80 (Ref. 10), M_R found 31.72. See L. C. Swallen and C. E. Boord, *J. Am. Chem. Soc.*, **52**, 651 (1930); A. Dewael, *Bull. soc. chim. Belg.*, **39**, 395 (1930); V. A. Sklyarov, *J. Gen. Chem. U.S.S.R.*, **9**, 2121 (1939); A. K. Seleznev and A. Balakirev, *Zhur. Priklad Khim.*, **27**, 650 (1954).

(8) Boiling points of pure compounds are corrected.

methyl bromide) held in an ice bath at 0°. After addition was complete the reaction mixture was stirred at room temperature for 10 hr. and then allowed to stand for 8 hr. The product was worked up as in the preparation of I except for the addition of a few pellets of sodium hydroxide (the solution was pale yellow before the solvent ether was removed). After distilling a forerun of about 4 ml. a main fraction of 90 g. (49%) of very slightly yellow product was obtained, b.p. 34.1–34.5°/8.0 mm. A small quantity of dark brown, lachrymatory residue was left. Careful refractionation⁹ gave 80 g. (44%) of product of constant boiling point and refractive index, b.p. 37.5°/8.0 mm., n_D^{25} 1.4453, d_4^{25} 1.2315, M_R Calcd.¹⁰ 39.32, M_R found 39.16.

Anal. Calcd. for C_6H_5OBr : C, 39.80; H, 7.24; Br, 44.13. Found:¹¹ C, 39.91; H, 7.10; Br, 43.96.

This compound, in contrast to I and those previously studied,^{3a} was found neither to lose HBr nor to commence to fume in moist air at temperatures up to its normal boiling point (about 162°). It was found, however, to undergo peroxidation quite easily upon standing.

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(9) We continued to distill over sodium hydroxide pellets though they seemed not to be necessary.

(10) Using Eisenlohr's atomic refractions. See K. Fajans in A. Weissberger, *Physical Methods of Organic Chemistry*, 2nd ed., Part Two, Interscience Publishers, Inc., New York, New York, 1949, p. 1163.

(11) Analysis by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

Some Reactions of RX Compounds with Triphenylsilyllithium in Tetrahydrofuran

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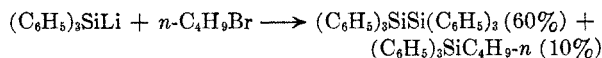
Incidental to a study of some silyllithium compounds with epoxides,¹ a significant difference was noted in the behavior of epichlorohydrin and epibromohydrin toward triphenylsilyllithium in tetrahydrofuran. The particular difference that concerns us here involves the formation of hexaphenyldisilane. The yield of this product from the epibromohydrin reaction was 68.6%; and essentially none of it was obtained from the reaction with epichlorohydrin. The formation of this coupling product may be due, at least in part, to a halogen-metal interconversion reaction.²

This unusual secondary coupling reaction suggested an examination of other related types.

(1) H. Gilman, D. Aoki, and D. Wittenberg, *J. Am. Chem. Soc.*, in press.

(2) H. Gilman and D. H. Miles, *J. Am. Chem. Soc.*, **80**, 611 (1958); A. G. Brook, H. Gilman, and L. S. Miller, *J. Am. Chem. Soc.*, **75**, 4759 (1953); A. G. Brook and S. Wolfe, *J. Am. Chem. Soc.*, **79**, 1431 (1957); D. Seyferth, *J. Am. Chem. Soc.*, **79**, 2738 (1957); R. A. Benkeser and R. G. Severson, *J. Am. Chem. Soc.*, **73**, 1424 (1951); A. G. Brook and H. Gilman, *J. Am. Chem. Soc.*, **76**, 278 (1954); O. H. Johnson and D. M. Harris, *J. Am. Chem. Soc.*, **72**, 5566 (1950); and H. Gilman and C. W. Gerow, *J. Am. Chem. Soc.*, **78**, 5823 (1956).

Reactions are now reported of triphenylsilyllithium with *n*-butyl chloride, *n*-butyl bromide, *n*-dodecyl chloride, allyl chloride, cyclopentyl chloride, 1,3-dichloropropane, and 1,3-dibromopropane. The pronounced effect of the nature of the halogen is reflected in the reactions with *n*-butyl chloride and *n*-butyl bromide.



Under corresponding conditions, *n*-butyl chloride gave a 75% yield of the "primary" coupling product, *n*-butyltriphenylsilane. Related variations occur with mono and polyhalogenated aromatic compounds,³ in which the secondary coupling product (hexaphenyldisilane) is formed in some cases in yields close to 90%.

EXPERIMENTAL

Reaction of triphenylsilyllithium with n-butyl chloride. A solution of triphenylsilyllithium (0.05 mole) in tetrahydrofuran was added dropwise to 4.63 g. (0.05 mole) of *n*-butyl chloride. The reaction was exothermic and Color Test I was negative immediately after the addition. Work-up of the reaction mixture gave a solid residue which was crystallized from methanol, yielding 11.8 g. (75%) of *n*-butyltriphenylsilane, m.p. 89–90°; identified by a mixed melting point determination with an authentic sample, and by comparison of infrared spectra.

Reaction of triphenylsilyllithium with n-butyl bromide. A solution of triphenylsilyllithium (0.025 mole) in tetrahydrofuran was added dropwise to 3.42 g. (0.025 mole) of *n*-butyl bromide. The reaction was exothermic and Color Test I was negative immediately after addition. Subsequent to hydrolysis by dilute sulfuric acid, 3.90 g. (60%) of hexaphenyldisilane was isolated, m.p. 349–350°. Work-up of the organic layer gave an oily residue which was chromatographed on alumina. Using petroleum ether (b.p. 60–70°) as an eluant, there was obtained 0.8 g. (10%) of *n*-butyltriphenylsilane, m.p. 90–91°, after recrystallization from methanol. A mixed melting point determination with the compound obtained from the reaction of triphenylsilyllithium with *n*-butyl chloride was not depressed, and their infrared spectra were superimposable.

Reaction of triphenylsilyllithium with n-dodecyl chloride. A solution of triphenylsilyllithium (0.026 mole) in tetrahydrofuran was added dropwise to 5.30 g. (0.026 mole) of *n*-dodecyl chloride. The reaction was exothermic and Color Test I was negative immediately after addition. Work-up gave a solid which was recrystallized twice from methanol to yield 3.20 g. (28.7%) of *n*-dodecyltriphenylsilane, m.p. 65–67°; identified by mixed melting point determination with an authentic sample and by infrared spectra.

Reaction of triphenylsilyllithium with allyl chloride. A solution of triphenylsilyllithium (0.025 mole) in tetrahydrofuran was added dropwise to 1.91 g. (0.025 mole) of allyl chloride. The reaction was exothermic and Color Test I was negative immediately after the addition. The work-up gave a solid residue which was chromatographed on alumina. Using petroleum ether (b.p. 60–70°) and carbon tetrachloride as the eluants there was isolated 4.20 g. (56%) of allyltriphenylsilane, m.p. 90–91°, after recrystallization from petroleum ether (b.p. 60–70°); identified by a mixed melting point determination with an authentic sample. In addition

(3) Studies by Glen Dappen. Details of reactions of silylmetallic compounds with a wide variety of halogenated compounds will be reported later.