[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

Derivatives of the Methylchlorosilanes. III. *n*-Butyl Ethers

BY ROBERT O. SAUER

In the course of an investigation of the polymeric hydrolysis products of the methylalkoxysilanes,[1] $(CH_3)_NSi(OR)_{4-N}$, several new *n*-butyl ethers have been prepared. Treatment of dimethyldichlorosilane and methyltrichlorosilane with excess *n*-butanol give the expected dimethyldi-*n*-butoxy- and methyltri-*n*-butoxy-silanes.[2] With one mole of *n*-butanol per mole of dimethyldichlorosilane the principal product was dimethyl-*n*-butoxychlorosilane.

In addition to the normal alcoholysis product of dimethyldichlorosilane with excess *n*-butanol, tetramethyl-1,3-di-*n*-butoxydisiloxane and hexamethyl-1,5-di-*n*-butoxytrisiloxane were isolated. These two polysiloxanes were also present in the product of homogeneous neutral hydrolysis of dimethyldi-*n*-butoxysilane.

Experimental

Reaction of *n*-Butanol with $(CH_3)_2SiCl_2$ and CH_3SiCl_3.—A 12-liter flask was fitted with (1) a 1-liter addition funnel, the stem of which was drawn to a 1-mm. capillary and which reached to the bottom of the flask, and (2) a condensing system comprising a 24-in. bulb condenser and an acetone–Dry Ice condenser. The flask was charged with a mixture of 3.82 kg. (29.5 moles) of dimethyldichlorosilane and 0.33 kg. (2.2 moles) of methyltrichlorosilane. Over a period of eight hours 5.8 kg. (20% excess) of *n*-butanol was added, the reaction mixture being heated meanwhile to distill most of the hydrogen chloride. At the end of the addition the temperature had reached 90°. Fractional distillation of the reaction mixture at atmospheric pressure yielded, after removal of the excess butanol: Fraction A, b. p. 184–190°, 4.05 kg.; Fraction B, b. p. 190–217°, 0.17 kg.; Fraction C, b. p. 217–240°, 0.53 kg.; Fraction D, b. p. 240–325°, 0.61 kg. A residue amounting to 0.22 kg. remained.

The yield of **dimethyldi-*n*-butoxysilane** (Fraction A) was but 67% based on the starting dimethyldichlorosilane. The properties of the purified ether are: b. p. 186–188° (760 mm.), 75° (10 mm.); $n^{25}D$ 1.4035, $n^{20}D$ 1.4058; d^{20}_4 (vac.) 0.8434.

Anal. Calcd. for $C_{10}H_{24}SiO_2$: C, 58.77; H, 11.84; Si, 13.73; mol. wt., 204.4. Found: C, 58.4; H, 11.4; Si, 13.9, 13.4; mol. wt. (in cyclohexane), 207.

A portion of dimethyldi-*n*-butoxysilane (0.5 mole) was treated with benzoyl chloride[3] (1.0 mole) in the presence of quinoline phosphate. From the boiling mixture there was distilled 51.5 g. (80%) of dimethyldichlorosilane over a period of ten hours. Upon distillation the higher boiling residue yielded 142 g. (80%) of *n*-butyl benzoate, b. p. 243–250°, $n^{20}D$ 1.5000.

After standing in a stoppered bottle for a period of nine months, 300 g. of Fraction C was fractionally distilled yielding about 15 g. of *n*-butanol (apparently produced by slow hydrolysis during the storage period), 128.7 g. of **tetramethyl-1,3-di-*n*-butoxydisiloxane,** b. p. 224.5–225.5° (741 mm.), 99–100° (10 mm.), $n^{20}D$ 1.4051, d^{20}_4 (vac.) 0.8733 [*Anal.* Calcd. for $C_{12}H_{30}Si_2O_3$: C, 51.75; H, 10.86; Si, 20.15. Found (two samples): C, 51.3, 51.2; H, 10.5, 10.8; Si, 19.9, 20.0] and 25.0 g. of **methyltri-*n*-butoxysilane,** b. p. 115° (10 mm.), $n^{20}D$ 1.4106, d^{20}_4 (vac.) 0.8775. *Anal.* Calcd. for $C_{13}H_{30}SiO_3$: C, 59.49; H, 11.52; Si, 10.69. Found: C, 59.5; H, 11.1; Si, 10.9.

There was also obtained 6.3 g. of a material, b. p. 125° (10 mm.), $n^{20}D$ 1.4053, which when later obtained in larger amounts, was identified as hexamethyl-1,5-di-*n*-butoxytrisiloxane (see below).

Dimethyl-*n*-butoxychlorosilane.—In the above experiment it was noted that the refluxing of the methylchlorosilanes virtually ceased after 3 liters (2.4 kg.) of *n*-butanol had been added. This indicated the preferential reaction of one chlorine atom on each chlorosilane molecule with the alcohol and the formation of $(CH_3)_2Si(Cl)OC_4H_9$.[4]

A 300-ml. flask bearing a reflux condenser and an addition funnel was charged with 129 g. (1.0 mole) of dimethyldichlorosilane. While gentle reflux was maintained 74 g. (1.0 mole) of anhydrous *n*-butanol was added dropwise over a period of two hours. The reaction mixture was refluxed for an additional one and one-half hours (final reflux temperature, 136°) and then fractionally distilled giving 101.5 g. (61%) of dimethyl-*n*-butoxychlorosilane, b. p. 142° (769 mm.). The residue yielded 15 g. of dimethyldi-*n*-butoxysilane. *Anal.* Calcd. for $C_6H_{15}SiOCl$: Cl, 21.27. Found: Cl, 21.1, 21.3.

Homogeneous Neutral Hydrolysis of Dimethyldi-*n*-butoxysilane.—A 12-liter flask fitted with an addition funnel and a propeller type stirrer was charged with 1.0 liter of distilled water, 1.25 liter of dioxane, and 7.75 liter of *n*-butanol. While this hydrolytic mixture was vigorously stirred, 830 g. (4.06 moles) of dimethyldi-*n*-butoxysilane was added evenly over a period of one hour. The homogeneous reaction mixture was allowed to stand in the dark for two days without agitation and then gently warmed at atmospheric pressure until distillation began. The first few drops of distillate, b. p. 89–92°, were burned; a cold watch glass held in the flame showed a small grayish deposit, presumably silica. None of the subsequent distillates collected over the boiling point range 92–117° (total volume, 10.23 liters) gave silica by this test. The residue (740 ml.), upon further fractionation in a low hold-up column of twenty theoretical plates, gave an additional 370 ml. of *n*-butanol, b. p. 116°; this was collected in three fractions each of which gave a trace of silica on burning. It was concluded, however, on the basis of the very small amounts of silica detected and the absence of any material distilling below 85° that an extremely small amount—if any—of dimethyloxosilane had been formed under these conditions.

The higher boiling material contained 76.7 g. (9.2%) of the starting dimethyldi-*n*-butoxysilane, 55.8 g. (4.9%) of tetramethyl-1,3-di-*n*-butoxydisiloxane (calcd., mol. wt. 278.5; found, cryoscopic in cyclohexane, 280), and 36.8 g. (2.6%) of **hexamethyl-1,5-di-*n*-butoxytrisiloxane,** b. p. 124–125° (10 mm.), $n^{20}D$ 1.4053, d^{20}_4 (vac.) 0.8932. The distillation was then discontinued leaving a residue (104 g.) of undetermined composition.

Anal. Calcd. for $C_{14}H_{36}Si_3O_4$: Si, 23.87; mol. wt., 352.6. Found: Si, 23.5, 23.9; mol. wt. (cryoscopic in cyclohexane), 352, 354, 345.

In the purification by distillation at reduced pressure of the combined four fractions of hexamethyl-1,5-di-*n*-butoxytrisiloxane after storing for one month it was noted that a few droplets of *n*-butanol were obtained and that crystals of a white solid, presumably hexamethylcyclo-

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[1] The nomenclature used has been discussed [Sauer, *J. Chem. Ed.*, **21**, 303 (1944)].

[2] Trimethyl-*n*-butoxysilane was described earlier [Sauer, THIS JOURNAL, **66**, 1707 (1944)].

[3] *Cf.* Ladenburg, *Ann.*, **164**, 306 (1872).

[4] Ladenburg (ref. 3) prepared diethylethoxychlorosilane, b. p. 146–148°, by the cleavage of diethyldiethoxysilane with acetyl chloride at 200°.

trisiloxane,[5] simultaneously appeared in the water-cooled condenser. However, no other cyclopolysiloxanes were noted in the course of these distillations.

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Summary

The following *n*-butoxy silicon compounds have been prepared: dimethyl-*n*-butoxychlorosilane, dimethyldi-*n*-butoxysilane, methyltri-*n*-butoxysilane, tetramethyl-1,3-di-*n*-butoxydisiloxane and hexamethyl-1,5-di-*n*-butoxytrisiloxane.

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(5) Hyde and DeLong, THIS JOURNAL, **63**, 1194 (1941).

NOTES

Preparation of Salts of 2-Phenylethene-1-sulfonic Acid[1]

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In connection with some other work it became necessary to prepare salts of 2-phenylethene-1-sulfonic acid in appreciable quantity. Salts of this acid have previously been obtained by the reaction of ammonium sulfamate with styrene[3] and by the reaction of sodium bisulfite with styrene in the presence of oxygen.[4] The yields are not good by either of these procedures. It has now been found that the reaction of dioxane sulfotrioxide[5] with styrene can be used to obtain good yields of 2-phenylethene-1-sulfonic acid.

The sodium, calcium and barium salts of the acid were isolated on addition of water and the appropriate metallic carbonate or hydroxide to the original sulfonation mixture. The salts were identified by conversion to 2-phenylethene-1-sulfonyl chloride,[3,4] 2-phenylethene-1-sulfonamide[3,4] and to the *p*-chlorobenzylthiouronium salt.[6] In addition the anilide, S-benzylthiouronium salt and *p*-toluidine salt were prepared.

A water-insoluble compound, $C_{16}H_{16}O_3S$, was obtained as a by-product in this sulfonation. Preliminary observations indicate that this material is a sultone.

Experimental

Sodium 2-Phenylethene-1-sulfonate.—To a stirred suspension of dioxane sulfotrioxide[5] prepared by distillation of 160 g. (2 moles) of sulfur trioxide into a cooled mixture of 175 ml. of dry dioxane and 175 ml. of dry ethylene chloride, was added dropwise 257 ml. (2.2 moles) of styrene. The addition required two hours, the flask being cooled by an ice-bath during that time. The mixture was allowed to stand overnight, heated on the steam-bath for thirty minutes, and then poured into 700 ml. of water. After standing, the layers were separated. Evaporation of the ethylene chloride layer yielded 52 g. of colorless water-insoluble material, m. p. 142–145°. After several crystallizations from acetone–water and from alcohol the substance melted at 152–153°. The yield of crude material was 9% based on sulfur trioxide. A qualitative analysis for the elements showed the presence of sulfur.

Anal. Calcd. for $C_{16}H_{16}O_3S$: C, 66.66; H, 5.55; mol. wt., 288. Found: C, 66.52, 66.47; H, 5.70, 5.70; mol. wt., 278 (Rast method[7]).

The aqueous layer was neutralized with sodium hydroxide, and the following crops of crystals collected: (1) from 1350 ml., 40 g.; (2) from 500 ml., 158 g.; (3) from 350 ml., 46 g.; (4) residue, 125 g. The calcium and barium salts are much less soluble. Crops 1, 2 and 3 were practically pure sodium 2-phenylethene-1-sulfonate since they gave S-benzylthiouronium 2-phenylethene-1-sulfonate in yields and purity comparable to that from an authentic sample of this compound. The yield from these crops was 244 g. (60% based on sulfur trioxide). The residue contained sodium 2-phenylethene-1-sulfonate, sodium sulfate and probably sodium 2-hydroxy-2-phenylethane-1-sulfonate.

The *p*-chlorobenzylthiouronium salt of 2-phenylethene-1-sulfonic acid after several crystallizations from dilute alcohol melted at 203–204° (Suter and Milne[6] report 199°).

Anal. Calcd. for $C_{16}H_{17}O_3N_2ClS_2$: N, 7.28. Found: N, 6.94.

The S-benzylthiouronium salt was crystallized from dilute alcohol to a constant m. p., 166–167°.

Anal. Calcd. for $C_{16}H_{17}O_3N_2S_2$: N, 8.00. Found: N, 7.50.

The *p*-toluidine salt was crystallized from water containing a drop of acetic acid to a constant m. p., 208–209°.

Anal. Calcd. for $C_{15}H_{17}O_3NS$: neut. equiv., 291. Found: neut. equiv., 289.

2-Phenylethene-1-sulfonanilide was prepared and crystallized to a constant m. p., 114–114.5°.

Anal. Calcd. for $C_{14}H_{13}O_2SN$: N, 5.40. Found: N, 5.22.

2-Phenylethene-1-sulfonyl chloride[4] was readily prepared from crops 1, 2 and 3 (but not from the residue) by heating the dried salt on the steam-bath with an equimolar quantity of phosphorus pentachloride for six hours, and after removal of the phosphorus oxychloride under vacuum, pulverizing the resultant mass under ice-water. The yield of crude material, m. p. 86–89°, was practically

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(3) Qinlico and Fleischner, *Atti accad. Lincei*, **1**, 1050 (1938).

(4) Kharasch, May and Mayo, *J. Org. Chem.*, **3**, 175 (1938); Kharasch, Schenk and Mayo, THIS JOURNAL, **61**, 3092 (1939).

(5) Bordwell, Suter and Webber, *ibid.*, **67**, 827 (1945), and ref. cited therein.

(6) Suter and Milne, *ibid.*, **65**, 582 (1943).

(7) Fuson and Shriner, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1940, pp. 122.