at 10 mm., and then boiled sharply at 139–140°. The purified material had n^{20}_D 1.4350 and d^{20}_4 0.954, whence *MR* 87.0. The literature values therefore are believed somewhat inaccurate.

Fraction c when redistilled comprised 40 g. (14%). It boiled at 198° at 10 mm. and had n^{29}_D 1.4315 and d^{29}_4 0.957; Fiesselmann and Hörndler[3] give the boiling point of 2,3,5,6-tetra-*n*-butoxy-1,4-dioxane as 195–202° at 10 mm.

Anal. Calcd. for $C_{20}H_{40}O_6$: C, 63.8; H, 10.70; mol. wt., 376; *MR*, 101.9. Found: C, 64.3; H, 11.07; mol. wt., 355; *MR*, 102.2.

The compound gave little or no osazone upon standing with an acid solution of 2,4-dinitrophenylhydrazine.

The preparation of 1,1,2,2-tetramethoxyethane by the same method[3] failed, the removal of water by entrainment with methanol being very unsatisfactory, as would be expected.

To obtain 1,2-dichloro-1,2-di-*n*-propoxyethane, 150 ml. of commercial glyoxal was evaporated to half-volume, diluted with 250 ml. of 1-propanol, stirred, and saturated with hydrogen chloride at 0–10° (about 4 hours required). Pouring the mixture into ice-water gave about 200 ml. of a lower layer which was roughly dried over calcium chloride, freed of hydrogen chloride *in vacuo*, further dried at 0–10° (it darkened and evolved hydrogen chloride in 12 hours at room temperature), and fractionally distilled. The portion boiling at 106–107° at 15 mm., n^{29}_D 1.4420, d^{29}_4 1.083 (literature 98–99° at 10 mm.[5] or 97° at 17 mm.,[4] n^{23}_D 1.4448,[4] d^{23}_4 1.0825,[4] *MR* thence 52.88[4]) proved upon analysis to be slightly impure.

Anal. Calcd. for $C_8H_{10}O_2Cl_2$: Cl, 32.6; mol. wt., 215; *MR*, 52.1. Found: Cl, 30.9; mol. wt., 201; *MR*, 52.6.

Redistillation at higher pressures caused even more departure from the theoretical value for chlorine, evidently by loss of hydrogen chloride.

When either 1,1,2,2-tetra-*n*-butoxyethane or *p*-dioxano-[b]-*p*-dioxane was heated with excess trioxane or paraformaldehyde and sulfuric acid catalyst, no definite evidence of the formation of either the desired 1,3-dioxolano[4,5-*d*]-1,3-dioxolane, or the by-products (di-*n*-butoxymethane and 1,3-dioxolane, respectively) could be obtained.

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Preparation of 4-Chlorobutyl *p*-Toluenesulfonate from Tetrahydrofuran and *p*-Toluenesulfonyl Chloride[1]

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ω-Haloalkyl sulfonates containing alkyl groups of two or three carbon atoms have been used for alkylation of a variety of substances, and are of interest because the alkyl group introduced is terminated by a halogen atom, which is available for subsequent reaction. The alkylation of a Grignard reagent,[2] which illustrates one such use of these esters and which is referred to in a number of textbooks, is shown by the equation

$$\begin{aligned}&\mathrm{RMgX} + 2p\text{-}\mathrm{CH_3C_6H_4SO_3(CH_2)_3Cl} \longrightarrow \\ &\qquad \mathrm{R(CH_2)_3Cl + Cl(CH_2)_3X} + (p\text{-}\mathrm{CH_3C_6H_4SO_3})_2\mathrm{Mg}\end{aligned}$$

The synthesis of 4-chlorobutyl benzoate from tetrahydrofuran and benzoyl chloride[3] suggested that 4-chlorobutyl *p*-toluenesulfonate (I), a previously unknown homolog in the series of ω-haloalkyl sulfonates, might be obtained conveniently from *p*-toluenesulfonyl chloride.

When *p*-toluenesulfonyl chloride was heated with tetrahydrofuran and a little zinc chloride, compound I was isolated in 46% yield. 4,4′-Dichlorodibutyl ether (II, 18%) and 1,4-dichlorobutane (III, 12%), the formation of which have been noted previously in related cleavages with inorganic acid halides,[4] were obtained as by-products.

$$\begin{aligned}&p\text{-}\mathrm{CH_3C_6H_4SO_2Cl + (CH_2)_4O} \xrightarrow{\mathrm{ZnCl_2}} \\ &\qquad \underset{\mathrm{I}}{p\text{-}\mathrm{CH_3C_6H_4SO_3(CH_2)_4Cl}} + \underset{\mathrm{II}}{\mathrm{[Cl(CH_2)_4]_2O}} + \underset{\mathrm{III}}{\mathrm{Cl(CH_2)_4Cl}}\end{aligned}$$

Variation of the scale of the reaction had little effect, and as much as two moles of the sulfonyl chloride was used successfully and with only minor modifications. Iodine was moderately effective as a catalyst, but aluminum chloride, boron trifluoride etherate and cadmium chloride were unpromising.

The structure I for the product was supported by saponification (which was accompanied by dehydrohalogenation) and by the reactions with inorganic halides discussed below, as well as by physical and chemical evidence of customary character.

In order to ascertain the extent to which the sulfonoxy group of I might react in preference to the chlorine atom in selective alkylation reactions, the reaction of I and sodium iodide was examined. Reaction in acetone at room temperature gave pure 1-chloro-4-iodobutane in 60% yield.

In certain instances, a desired alkylation product may be difficultly separable from unchanged I because of close similarity in physical properties. A method for circumventing this difficulty is suggested by the observation that lithium chloride, which should have no effect on most reaction products, effects virtually quantitative cleavage of the I, with the formation of easily separable III.

The reaction of I with phenylmagnesium bromide yielded 1-bromo-4-chlorobutane (IV, 52%) and 4-chlorobutylbenzene (V, 27%). Although IV and V had physical properties approximating reported values, contamination by difficultly separable impurities resulted in unsatisfactory analyses.

Experimental[5]

4-Chlorobutyl *p*-Toluenesulfonate (I). (a) Preparation.—A mixture of 93.5 g. of tetrahydrofuran, 190.6 g. of *p*-toluenesulfonyl chloride and 12.3 g. of freshly fused zinc chloride was stirred and submerged in an oil-bath preheated to 95°. When the temperature of the mixture reached 80°, a brief but vigorous exothermic reaction began, which resulted in a rise of temperature within about 4 minutes to 168°. The temperature then began to decrease almost immediately, and a viscous oil containing a small amount of solid resulted. The heating bath was removed while the temperature exceeded 100°. When the mixture had cooled again to 100°, it was heated at 85–100° for six hours. The oil, which no longer contained solid, was cooled, and poured into ice-water. Combined ether extracts were washed with saturated aqueous sodium bicarbonate and water until neutral and were dried over anhydrous sodium sulfate–potassium carbonate (1:1). After filtration, the filtrate was distilled through a 25-cm. Vigreux column under reduced pressure until ether had been removed. Anhydrous potassium carbonate (5 g.) was then added, after which distillation with

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[2] (a) H. Gilman and N. J. Beaber, THIS JOURNAL, **45**, 839 (1923); (b) S. S. Rossander and C. S. Marvel, *ibid.*, **50**, 1491 (1928).

[3] M. E. Synerholm, *Org. Syntheses*, **29**, 30 (1949).

[4] K. Alexander and L. E. Schniepp, THIS JOURNAL, **70**, 1839 (1948).

[5] Melting points are corrected and boiling points uncorrected. Analyses, except for sulfur, were by Micro-Tech Laboratories, Skokie, Ill.

only a short distilling head yielded fractions as follows: (A) 30.2 g., b.p. up to 166° (0.25 mm.), n^{25}_D 1.4660; (B) 122.1 g. (46%) of I, b.p. 164–165° (0.1 mm.), n^{25}_D 1.5140–1.5189; (C) 28.6 g. of material in the Dry Ice trap which protected the pump.

Fraction B, upon redistillation from 5 g. of anhydrous potassium carbonate through a 20-cm. modified Claisen head, yielded 89.6 g. (34%) of clear, colorless I, b.p. 167–170° (0.06 mm.), n^{25}_D 1.5182–1.5187, n^{25}_D 1.5183, d^{25}_4 1.2284; M_D calcd.[6] 65.25, found 64.85. The saponification equivalent[7] of I (n^{29}_D) was 137 (calcd. for saponification and dehydrohalogenation of I, 131).

Anal. Calcd. for $C_{11}H_{15}ClO_3S$: C, 50.28; H, 5.76; Cl, 13.49; S, 12.20. Found: C, 50.25; H, 5.80; Cl, 13.89; S, 12.26.

When I was distilled without potassium carbonate, small amounts of flocculent white solid appeared in the distillate. Solid of similar properties also resulted upon heating I alone at 215° for 45 minutes, and was identified as *p*-toluenesulfonic acid; S-benzylthiuronium salt, m.p. 182–183°, reported[8] m.p. 181–182°. Distillation from carbonate helps prevent this decomposition, apparently autocatalytic.

(b) **By-products.**—Redistillation of fraction A through an 18-cm. modified Claisen head yielded 1.4 g. (fraction D, presumably III), b.p. up to 42° (8 mm.), n^{25}_D 1.4526, together with 18.1 g. (18%, based on *p*-toluenesulfonyl chloride) of 4,4′-dichlorodibutyl ether (II), b.p. 122.5–123° (8.0 mm.), n^{25}_D 1.4565–1.4585. Further distillation of a portion of the II gave material having b.p. 116° (6 mm.), n^{25}_D 1.4565; reported[4] for II, 84–86° (0.5 mm.), n^{25}_D 1.4567.

Anal. Calcd. for $C_8H_{16}Cl_2O$: C, 48.25; H, 8.10; mol. wt., 199. Found: C, 48.51; H, 8.39; mol. wt. (Rast), 190.

Fraction C, dried and redistilled through a semi-micro column,[9] gave 6.5 g. of 1,4-dichlorobutane (III), b.p. 43.5° (10 mm.), 154–156°, n^{25}_D 1.4517; reported[10] b.p. 155°, n^{20}_D 1.4542. The total yield of III, including fraction D, was 7.9 g. (12%, based on *p*-toluenesulfonyl chloride).

Anal. Calcd. for $C_4H_8Cl_2$: C, 37.82; H, 6.35. Found: C, 38.04; H, 6.53.

(c) **Variations in Reaction Conditions.**—Portionwise addition of the zinc chloride, or reduction of its amount to one-half, had no significant effect. The use of iodine as a catalyst gave I in 32% crude yield, but cadmium chloride gave I in only about 3% yield, and anhydrous aluminum chloride or boron trifluoride etherate gave even less.

Doubling the scale of (a) or reduction to one-fifth scale was without apparent effect. On a doubled scale, however, two condensers are desirable, owing to the large volume of refluxing tetrahydrofuran during the exothermic phase; the larger amount of product was best distilled in two or more portions, to minimize exposure to heat and the decomposition referred to above.

Moderate variations in the time of heating (after the exothermic phase of the reaction) seemed to have little effect. Thus a 10-hour period at 125–130° gave I in 35% yield, n^{29}_D 1.5160, and a period of 4.5 hours at 95–100° reduced the yield only slightly (28%, n^{25}_D 1.5185–1.5193); a heating period of only 0.3 hour (including the exothermic phase), however, resulted in negligible I. Cooling during the exothermic phase of the reaction, so that the temperature was maintained at 90–100°, proved to be undesirable; compound I was then isolated in only 10% yield (n^{25}_D 1.5168–1.5182).

Larger excesses of tetrahydrofuran, or protection of the reaction from moisture by calcium chloride tubes and a sealed stirrer, conferred no advantages.

Reaction of I with Inorganic Halides. (a) **Sodium Iodide.**—For the preparation of 1-chloro-4-iodobutane, I (12.5 g.) and 22 ml. of acetone were added to 7.2 g. of anhydrous sodium iodide in 50 ml. of acetone. Precipitation began within a few seconds, and after 48 hours resulted in 91% of the expected sodium *p*-toluenesulfonate. The solid was collected, the acetone was removed using a 25-cm. Vigreux column, and the residue was distilled using a 7-cm. modified Claisen flask. After redistillation through a semi-micro column,[9] the yield of 1-chloro-4-iodobutane was 6.3 g. (60%), b.p. 90–93° (17 mm.), n^{25}_D 1.5382–1.5387. A portion having n^{25}_D 1.5385 was analyzed[11]; d^{25}_4 1.7853; M_D calcd. 38.34, found 38.31.

Anal. Calcd. for C_4H_8ClI: C, 21.99; H, 3.69; Cl, 16.23; I, 58.09. Found: C, 21.98; H, 3.70; Cl, 16.13; I, 57.71.

(b) **Lithium Chloride.**—In order to determine the feasibility of destroying I with anhydrous lithium chloride, 2.02 g. was heated with 10.5 g. of I in 50 ml. of acetone, with stirring at the reflux temperature for 48 hours. The mixture was then concentrated to 30 ml. and poured into water. Ether extracts were dried, the ether removed, and the residue distilled; yield of 1,4-dichlorobutane (III), 2.74 g. (54%), b.p. 154°, n^{20}_D 1.4514–1.4542. The tarry residue from the distillation amounted to only 0.21 g. (2% recovery, if assumed to be I).

Reaction of I with Phenylmagnesium Bromide.—Compound I (88.6 g., 0.34 mole) was added during 2 hours, together with ether as necessary to permit efficient stirring, to 75 ml. of 2.25 *N* phenylmagnesium bromide. The mixture was stirred and heated under moderate reflux for 16 hours, and was then hydrolyzed with cold dilute hydrochloric acid. Ether extracts were washed with saturated sodium bicarbonate solution and water until neutral, and were dried over anhydrous sodium sulfate. Two fractionations, the last through a 15-cm. helix-packed column, gave 15.2 g. (52%) of 1-bromo-4-chlorobutane (IV), b.p. 58–58.5° (10 mm.), n^{25}_D 1.4835–1.4843 (reported[12] b.p. 63–64° (10 mm.), n^{20}_D 1.4865); IV (n^{25}_D 1.4843) contained 29.56% C and 5.04% H (calcd. for IV: C, 28.01; H, 4.70). Some improvement in the purity of the IV was effected by washing with concentrated sulfuric acid, drying and refractionation (C, 28.70; H, 4.90).

Two fractionations, the last through a 15-cm. column, also were used to separate the 4-chlorobutylbenzene (V), which then amounted to 7.61 g. (27%), b.p. 108.5–111.5° (13 mm.), n^{25}_D 1.5177–1.5195; reported[2b] b.p. 98–102° (6 mm.), n^{25}_D 1.5183. V of n^{25}_D 1.5185 contained 71.85% C and 7.82% H (calcd. for V: C, 71.21; H, 7.77). Washing the V with concentrated sulfuric acid and refractionating it resulted in no improvement in its analysis.

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(6) The M_D used for the $-SO_2O-$ group was 10.99, as given by R. H. Wiley and R. P. Davis for $-SO_2O-$ in *n*-butyl *p*-toluenesulfonate (THIS JOURNAL, **74**, 6142 (1952).

(7) Heating was effected at 150° for 5 minutes. Otherwise the procedure was that involving diethylene glycol. R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1940, p. 118.

(8) E. Chambers and G. W. Watt, *J. Org. Chem.*, **6**, 376 (1941).

(9) C. W. Gould, Jr., G. Holzman and C. Niemann, *Anal. Chem.*, **20**, 361 (1948).

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(11) 1-Chloro-4-iodobutane was obtained by K. Ahmad and F. M. Strong, but in an estimated purity of only 94%, b.p. 93–94.5° (17 mm.); THIS JOURNAL, **70**, 1699 (1948).

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The Piperidine-catalyzed Reaction of Triphenylsilane with Some Hydroxy Compounds

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In some studies on the kinetics of hydrolysis of triarylsilanes in methyl cellosolve containing water and piperidine it was found that at low water concentrations the reaction became principally one of alcoholysis. Therefore it appeared that this method might be generally applicable to the preparation of alkoxysilanes. Table I shows that the reaction has been used successfully for the preparation of five triphenylalkoxysilanes, one triphenylaryloxysilane and two hexaaryldisiloxanes. At-

$$Ar_3SiH + HOCH_2CH_2OCH_3 \xrightarrow{C_5H_{10}NH} Ar_3SiOCH_2CH_2OCH_3 + H_2$$

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[1] E. I. du Pont de Nemours and Co. Fellow, Iowa State College, 1950–1951.