boiling in an equal mixture of ethanol and concentrated hydrochloric acid for eighteen hours. (The methyl and ethyl homologs required only three hours under the same conditions.) After saturation with hydrogen chloride, the crystalline platelets of amine hydrochloride were separated and converted to amine by shaking with 20% sodium hydroxide solution and ether. The ether extract on distillation gave 37% of **2-*t*-butyl-4-bromoaniline,** a colorless oil, b. p. 146–147° (9 mm.), $n^{23}\mathrm{D}$ 1.5811.

Anal. Calcd. for $C_{10}H_{14}BrN$: C, 52.64; H, 6.19; Br, 35.03; N, 6.14. Found: C, 53.03; H, 6.20; Br, 34.40; N, 6.23.

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Aryl Esters of Substituted Benzenesulfonic Acids

The esters of benzenesulfonic acid listed in the table were prepared by the Hinsberg[1] method with slight variations. One mole of the arylsulfonyl chloride and one mole of the phenol were heated together with stirring at 60–70°. One mole of dilute sodium hydroxide solution (0.7 *N*) was added during a half-hour period, keeping the temperature at 60–80°. The reaction mass was heated for an additional hour at 60–80°. As the reaction proceeded, the ester precipitated and crystallized. The slurry was cooled, filtered, and washed with water. The dried crystals were purified by repeated crystallizations from ethyl alcohol containing a little benzene.

TABLE I

Compound	Crude yield, %	Chlorine, % Found	Chlorine, % Calcd.	Sulfur, % Found	Sulfur, % Calcd.	M. p., °C.[a]
p-Chlorophenyl *m*-nitrobenzenesulfonate	87.0	11.24	11.30	10.27	10.22	104–105
p-Bromophenyl *p*-bromobenzenesulfonate	93.0	40.53 Br	40.76 Br	8.04	8.18	121–122
p-Chlorophenyl *p*-bromobenzenesulfonate[b]	96.5	10.23 Cl	10.11 Cl	9.47	9.22	109–110
p-Bromophenyl *p*-chlorobenzenesulfonate[c]	88.5	10.17 Cl	10.11 Cl	8.94	9.22	95.5–97.5
2,4-Dichlorophenyl *p*-chlorobenzenesulfonate	94.5	31.79	31.51	9.58	9.50	118–119
2,4,5-Trichlorophenyl *p*-chlorobenzenesulfonate	92.0	37.56	38.12	8.80	8.62	130–131
2,4,6-Trichlorophenyl *p*-chlorobenzenesulfonate	96.4	38.14	38.12	8.72	8.62	97–98
2,3,4,6-Tetrachlorophenyl *p*-chlorobenzenesulfonate	83.0	44.37	43.61	7.72	7.88	123–124
Pentachlorophenyl *p*-chlorobenzenesulfonate	93.0	48.80	48.25	7.34	7.27	146.5–147.5
p-Tolyl *p*-chlorobenzenesulfonate	97.5	12.80	12.54	11.56	11.34	76–77
o-*s*-Butylphenyl *p*-chlorobenzenesulfonate	88.2	10.87	10.91	9.79	9.87	60–61.5
p-*t*-Butylphenyl *p*-chlorobenzenesulfonate	93.7	11.04	10.92	9.82	9.87	92–93
o-Allylphenyl *p*-chlorobenzenesulfonate	89.0	11.58	11.48	10.29	10.38	58–59
2-Biphenylyl *p*-chlorobenzenesulfonate	92.5	10.31	10.28	9.32	9.30	85.5–86.5
p-Methoxyphenyl *p*-chlorobenzenesulfonate	95.3	12.11	11.87	10.73	10.73	90–91

[a] Uncorrected. [b] Br calcd. 22.99; found 22.95. [c] Br calcd. 22.99; found 22.92.

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[1] Hinsberg, *Ber.*, **23**, 2962 (1890).

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Some New Glycol Trichloroacetates

We have prepared several new glycol trichloroacetates which may serve as model substances for carbohydrate trichloroacetates. Two methods were used. The first method consisted of the direct reaction of the glycol with trichloroacetic acid in the absence of a catalyst and either with or without the presence of a water entrainer. The second method employed trichloroacetyl chloride in the presence of pyridine. This method was suitable for the preparation of mixed esters.

An attempt was made to determine whether the trichloroacetyl group acts as a neighboring group in the displacement of the *p*-toluenesulfonoxy group from a position *trans* to it on the cyclohexane ring, under conditions similar to those employed by Winstein and co-workers.[1] Although a first order reaction was observed, the products were not isolated.

All melting points are corrected and the micro-analyses were performed by Mrs. C. F. Spencer.

Ethylene Glycol Bis-trichloroacetate.—Ethylene glycol (5.6 ml., 0.1 mole) and trichloroacetic acid (32.7 g., 0.2 mole, Dow Chemical Co.) were distilled slowly at atmospheric pressure until the temperature had reached 125° and about 3.5 ml. of distillate (largely water) had collected. The residue, which crystallized on cooling, was mixed with some cold water, and the solid (17.6 g., m. p. 40–41°) removed by filtration. After recrystallization from an ethanol-water mixture, 50% recovery of a product melting at 41–42° was obtained. The substance was very soluble in most organic solvents including alcohols, hydrocarbons, ethers, and chlorinated hydrocarbons. It was difficultly soluble in hot water. The compound was also prepared by the reaction of trichloroacetyl chloride and ethylene glycol in pyridine. It is probable that the ester undergoes hydrolysis with some ease.

Anal. Calcd. for $C_6H_4O_4Cl_6$: C, 20.40; H, 1.13; Cl, 60.34; sapon. equiv., 353. Found: C, 20.34; H, 1.18; Cl, 60.60; sapon. equiv., 324.

***trans*-1,2-Cyclohexanediol Bis-trichloroacetate.**—*trans*-1,2-Cyclohexanediol[2] (11.6 g., 0.1 mole) and pyridine (32 ml., 0.4 mole) were mixed and trichloroacetyl chloride[3] (36.4 g., 0.2 mole) was slowly added with sufficient cooling to keep the temperature in the range of 60–70°. The mixture was then allowed to stand overnight at room temperature. It was then shaken with 200 ml. of water, and the yellow oil which separated crystallized on refrigeration, yield 37.2 g., 91%. The crude product (m. p. 59–61°) was recrystallized from an alcohol-water mixture to a constant melting point of 60–61°.

Anal. Calcd. for $C_{10}H_{10}O_4Cl_6$: C, 29.48; H, 2.46; Cl, 52.33; sapon. equiv., 407. Found: C, 29.40; H, 2.55; Cl, 52.09; sapon. equiv., 402.

***trans*-1,2-Cyclohexanediol Monotrichloracetate.**—*trans*-1,2-Cyclohexanediol[2] (11.5 g., 0.1 mole) and trichloroacetic acid (16.4 g., 0.1 mole, Dow Chemical Co.) and benzene (100 ml.) were heated under reflux in an all-glass

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[1] Winstein, Hanson and Grunwald, THIS JOURNAL, **70**, 812 (1948).

[2] "Org. Syn.," **28**, 35 (1948).

[3] Prepared from trichloroacetic acid and benzoyl chloride according to the method of Brown, THIS JOURNAL, **60**, 1352 (1938).