[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

IDENTIFICATION OF AMINES

BY C. S. MARVEL AND F. E. SMITH

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Many crystalline products are available for the identification of primary and secondary amines since most of their acetyl, benzoyl and benzenesulfonyl derivatives are known solids. However, certain of these derivatives are not entirely satisfactory because their melting points lie too close to one another.

Benzenesulfonyl chloride has been shown[1] to be a particularly desirable reagent in the examination of amines and is almost always used in routine qualitative organic analysis of nitrogen compounds. However, some of the benzenesulfonyl derivatives of the commoner amines are oils or low-melting solids, and after application of the Hinsberg test, another solid derivative must be prepared for complete identification.

Ssolonina[2] has prepared the *p*-bromobenzenesulfonyl derivatives of a few amines and has found that as a rule these melt higher than the unbrominated compound. It was thought that *p*-bromobenzenesulfonyl chloride would be useful to replace benzenesulfonyl chloride in the Hinsberg test, as better melting substances could be expected.

The *p*-bromobenzenesulfonyl amides of most of the common amines have now been prepared and characterized. As a general rule they are easily crystallizable compounds with sharp melting points. They make especially good derivatives for ethyl aniline, *n*-propylaniline, *n*-butylaniline and piperidine. However, *p*-bromobenzenesulfonyl chloride cannot be used in place of benzenesulfonyl chloride in the Hinsberg test because it gives alkali insoluble derivatives with many primary amines. This insolubility may be explained by the theory developed by Adams[3] to explain the alkali insolubility of certain phenols.

Experimental Part

***p*-Bromobenzenesulfonyl Chloride.**[4]—This reagent is readily obtained by heating a mixture of 100 g. of sodium *p*-bromobenzenesulfonate and 70 g. of phosphorus pentachloride on the water-bath for about 16 hours. After the mixture has cooled, water is added to destroy the phosphorus oxychloride and the *p*-bromobenzenesulfonyl chloride which separates is filtered and washed with water. After the product is carefully washed it is dried. The yield is 85 to 90 g. (86–90%) of a product melting at 75°. The reagent may be recrystallized from petroleum ether if a very pure product is desired.

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[1] Hinsberg, *Ber.*, **23**, 2963 (1890).

[2] Ssolonina, *Chem. Zentr.*, [2] **1899**, 867.

[3] Adams, THIS JOURNAL, **41**, 247 (1919).

[4] *Ann.*, **180**, 98 (1876).

Preparation of the *p*-Bromobenzenesulfonamides.—*p*-Bromobenzenesulfonyl chloride is treated with a slight excess of the amine and warmed if necessary to start the reaction. The reaction takes place smoothly with the evolution of heat and after a few minutes is complete. The excess amine is removed by washing the product with dil. hydrochloric acid. The crude product is then recrystallized from alcohol of the proper strength, depending on the particular compound used (see Table I).

The derivatives of methylamine, dimethylamine and piperidine are prepared by treating a water solution of the amine hydrochloride with *p*-bromobenzenesulfonyl chloride and aqueous alkali in the usual manner.

The new compounds that have been prepared are given in Table I, together with their physical properties and analyses.

Diethylamine gives an oily product which solidifies in an ice-bath. Since it is not of use as a derivative it was not analyzed.

TABLE I

PARA-BROMOBENZENESULFONAMIDES

Amine	M. p. of crude product °C.	No. of recryst. to give constant m. p.	Strength of alcohol used in cryst. %	M. p. of pure product °C.	Analysis		Solubility in 10% NaOH solution
					Br calc. %	Br found %	
Methylamine	75–77	2	92	77	32.0	31.9	+
Benzylamine	115	1	60	117	24.5	..	+
Dimethylamine	93	1	60	94	30.3	29.7	–
Piperidine	88	1	92	91	26.3	26.1	–
o-Toluidine	92–104	3	80	116	24.5	24.9	–
p-Toluidine	96–97	2	92	98	24.5	24.6	–
o-Chloro-aniline	103	1	60	105[d]	28.8[a]	28.8[a]	
p-Chloro-aniline	130–132	1	60	134[e]	29.2[b]	29.2[b]	
p-Bromo-aniline	121–126	3	92	145[e]	40.9	40.7	
p-Anisidine	120–125	2	92	142	23.4	23.3	+
p-Phenetidine	135–140	2	92	143	22.7	23.8	+
α-Naphthylamine	158–167	2	92	183.5	22.1	22.2	–
β-Naphthylamine	125–128	2	80	129	22.1	22.4	–
Monomethylaniline	88	2	80	92	24.5	23.6	–
Mono-ethylaniline	82–85	2	92	91	23.5	23.6	–
Monopropylaniline	95–102	3	60	109	22.6	22.4	–
Monobutylaniline	81–86	2	60	87	21.7	21.8	–
p-Bromo-ethylaniline[c]	117	1	60	118.5	38.2	38.0	–

[a] Cc. of 0.1001 *N* $AgNO_3$ required for the halogen and not % of Br.

[b] Cc. of 0.0981 *N* $AgNO_3$ required for the halogen and not % of Br.

[c] *p*-Bromo-ethylaniline was prepared in connection with another problem by brominating ethylaniline in glacial acetic acid. The compound boils at 143–147° at 20 mm. Calc. for $C_8H_{10}NBr$: Br, 40.0 Found: 39.61.

[d] Slightly soluble in hot NaOH; insoluble in cold.

[e] Soluble in hot NaOH; slightly soluble in cold.

Summary

The *p*-bromobenzenesulfonyl derivatives of several common amines have been characterized. These compounds are useful for the identification of amines.

URBANA, ILLINOIS

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THE ALLYL ETHERS OF VARIOUS CARBOHYDRATES

BY C. G. TOMECKO[1] WITH ROGER ADAMS

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Some of the most important developments in the chemistry of carbohydrates during the past fifteen years have been through the use of the alkyl ether derivatives. The original method of alkylation, as developed by Irvine[2] and his co-workers, was by means of silver oxide and alkyl iodides. More recently, an improvement has been made upon this procedure by Haworth[3] who has used methyl and ethyl sulfates in place of the alkyl iodides; with these reagents aqueous alkaline solutions or suspensions are employed and the preparation of the ethers is thus rendered very simple. Of especial interest may be mentioned that the ethers of the disaccharides have been used in the determination of the structure of the disaccharides; the ethers of cellulose apparently are of commercial importance and consequently their preparation by this same process has engaged the attention of many investigators. In spite of the general interest and importance of the ethers of the carbohydrates, no other ethers than the methyl and ethyl derivatives have been prepared until very recently. Gomberg and Buchler[4] made the benzyl derivatives of a variety of carbohydrates, following the same procedure as with the alkyl sulfates; this was possible due to the great reactivity of the chlorine in the benzyl chloride. In that paper a review of the previous articles discussing alkylation was given. Since that time many patents[5] have appeared on the

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[1] This communication is an abstract of a portion of a thesis submitted by C. G. Tomecko in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Purdie and Irvine, *J. Chem. Soc.*, **83**, 1021 (1903).

[3] Haworth, *ibid.*, **107**, 8 (1915).

[4] Gomberg and Buchler, THIS JOURNAL, **43**, 1904 (1921). See also U. S. pat., 1,451,331; *C. A.*, **17**, 2505 (1923).

[5] Lilienfeld, Brit. pat. 163,016, 163,017, 163,018 [*C. A.*, **15**, 3207 (1921)]; Can. pat. 220,831 [*C. A.*, **16**, 2989 (1922)]; Brit. pat. 177,810 [*C. A.*, **16**, 3206 (1922)]; Brit. pat. 181,392, 181,393, 181,395 [*C. A.*, **16**, 3758 (1922)]; Can. pat. 222,377 [*C. A.*, **16**, 4087 (1922)]; U. S. pat. 1,441,889 [*C. A.*, **17**, 1141 (1923)]. Young, Brit. pat. 184,825 [*C. A.*, **17**, 878 (1923)]. Clancy, U. S. pat. 1,439,293 [*C. A.*, **17**, 879 (1923)]. Seel, U. S. pat. 1,437,820, 1,437,821 [*C. A.*, **17**, 879 (1923)]. Dreyfuss, Brit. pat. 187,639 [*C. A.*, **17**, 1141 (1923)].