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

IDENTIFICATION OF AMINES. III. BENZYLSULFONAMIDES

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RECEIVED AUGUST 16, 1926 PUBLISHED NOVEMBER 5, 1926

Benzenesulfonyl chloride and various derivatives are often used in the separation and identification of amines. One difficulty with all of these reagents in actual practice is that once the sulfonamide is obtained, it is hydrolyzed to give the original amine only with great difficulty.

Johnson and Ambler[1] have studied a few benzylsulfonamides and report that they are hydrolyzed somewhat more readily than the amides of aromatic sulfonic acids. This fact suggested a study of the benzylsulfonyl derivatives of various common amines in the hope that they would be useful, not only as derivatives for identification, but also for the separation of mixtures of primary, secondary and tertiary amines in preparative work.

The benzylsulfonamides are easily prepared in fair yields. The derivatives of primary amines are all soluble in dilute alkali as would be expected. Most of the compounds prepared are easily obtained pure by crystallization from dil. alcohol (50–75%) and the melting points are well distributed so that they are of value in identification. However, experiments with benzylsulfonanilide and benzylsulfon-*p*-toluidide show that these derivatives are not readily hydrolyzed by hot, concd. hydrochloric or hydrobromic acid. Johnson and Ambler[1] were able to hydrolyze the benzylsulfonbenzylamide with hydrochloric acid by heating it to 130–150° in a sealed tube.

Experimental Part

In the preparation of the benzylsulfonamides it was found that the best results were obtained by treating a benzene solution of two molecular proportions of amine with a benzene solution of one of benzylsulfonyl

TABLE I

BENZYLSULFONAMIDES

Amine	M. p. of amide, °C.	Amine	M. p. of amide, °C.
Allylamine	79	*m*-Bromo-aniline	99.5
Diethylamine	oil	*p*-Bromo-aniline	133.5
Piperidine	131.5	Methylaniline	101
n-Heptylamine	76	Ethylaniline	118.5
Di-*n*-butylamine	oil	*n*-Propylaniline	135
o-Toluidine	83	*n*-Butylaniline	108
m-Toluidine	75	*o*-Anisidine	72
o-Chloro-aniline	91	*p*-Anisidine	103
p-Chloro-aniline	110	*p*-Phenetidine	117.5

[1] Johnson and Ambler, THIS JOURNAL, **36**, 385 (1914).

chloride. The amine hydrochloride that formed was removed by filtration and the pure amide was obtained by evaporating the filtrate and crystallizing the residue from dilute alcohol twice or thrice until the melting point was constant. Unless the amine is in excess, some of the disulfonyl derivative may be obtained from a primary amine. The new benzylsulfonamides that have been characterized are recorded in Table I.

The compounds were analyzed for nitrogen in nearly every case and the analyses were satisfactory. The melting points of the derivatives from aniline,[2] *p*-toluidine,[3] methylamine,[4] dimethylamine[4] and benzylamine,[5] which are already in the literature, were checked. The melting point of the *o*-phenetidine derivative is given in the literature[3] as 85°. Our sample melted at 74°.

Dibenzylsulfonanilide was obtained when aniline was treated with an excess of benzylsulfonyl chloride. After several crystallizations from 50% alcohol it melted at 71.5°.

Anal. Calcd. for $(C_6H_5CH_2SO_2)_2NC_6H_5$: N, 3.50; S, 15.95. Found: N, 3.55; S, 15.57.

Dibenzylsulfon-*p*-toluidide was obtained in an analogous manner and melted at 74.5°.

Anal. Calcd. for $(C_6H_5CH_2SO_2)_2NC_6H_4CH_3$: N, 3.37; S, 15.31. Found: N, 3.03; S, 15.39.

Attempts to Hydrolyze Benzylsulfonamides.—A mixture of 5 g. of benzylsulfonanilide and 20 cc. of concd. hydrochloric acid (d., 1.19) was placed in a flask under a reflux condenser and heated in an oil-bath at 130–140° for five hours. No trace of aniline was obtained by making alkaline and distilling the mixture. About 90% of the amide was recovered unchanged. The same experiment was carried out with 48% hydrobromic acid with similar results. Benzylsulfon-*p*-toluidide was substituted for the anilide and was not hydrolyzed under these conditions.

Summary

The benzylsulfonyl derivatives of several common amines have been characterized and found to be suitable derivatives for identification.

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[2] Fromm and Palma, *Ber.*, **39**, 3313 (1906).

[3] Ref. 2, p. 3314.

[4] Ref. 1, p. 382.

[5] Ref. 1, p. 385.