water was added and the ester extracted with ether. The ether solution was dried over sodium sulfate and the product distilled.

Bis-(β-acetoxy-ethyl)ether was hydrolyzed to the corresponding dihydroxy compound by heating with a methyl alcoholic solution of hydrogen chloride.[5] The yield of dihydroxy ether was 51%. This compound was previously made by Lourenco.[6]

Summary

Several new compounds have been prepared from β,β'-dichloro-diethyl ether by reaction with sodium alcoholates, aromatic primary amines and sodium salts of organic acids.

The study of this ether will be continued.

PITTSBURGH, PENNSYLVANIA

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

IDENTIFICATION OF AMINES. II. META-NITROBENZENE-SULFONAMIDES

BY C. S. MARVEL, F. L. KINGSBURY AND F. E. SMITH

RECEIVED JUNE 30, 1924 PUBLISHED JANUARY 8, 1925

The general use of benzenesulfonyl chloride for the separation and identification of primary and secondary amines has suggested the use of substituted benzenesulfonyl chlorides in order to obtain more easily crystallizable compounds. The *p*-bromobenzene-sulfonamides[1] were found to be of considerable use for identification purposes, although they could not be used for the separation of primary and secondary amines on account of the alkali insolubility of the primary amine derivatives.

The *m*-nitrobenzene-sulfonamides have now been studied. They are all easily prepared and purified and are therefore suitable for use in identification. In addition almost all of the common primary amines give derivatives that are soluble in alkalies, so that separations of primary and secondary amines may be made through the amides. The only primary amine derivative that has been found to be but slightly soluble in alkalies is that of *p*-bromo-aniline.

The nitrobenzenesulfonyl derivatives of diethylamine, di-*n*-butylamine and the mono-alkyl anilines are particularly useful as derivatives for identification, since the common reagents give oils or low-melting solids that crystallize only with considerable difficulty.

Experimental Part

Two procedures were used to prepare the sulfonamides. They worked equally well. *m*-Nitrobenzenesulfonyl chloride was treated with a slight

---

[5] Gattermann's "Methods of Organic Chemistry;" Schober and Babasinian's translation, MacMillan Co., third ed., **1914**, p. 198.

[6] Lourenco, *Ann. chim.*, [3] **67**, 257 (1863).

[1] Marvel and Smith, THIS JOURNAL, **45**, 2696 (1923).

excess of the amine and if necessary heat was applied to start the reaction. Once started, the reaction proceeded rapidly with the evolution of heat. The excess of amine was washed out with acid and the product was filtered off and recrystallized from alcohol of the proper strength (Table I). The alternate procedure was to warm a mixture of the sulfonyl chloride, the amine and dil. sodium hydroxide solution until the reaction was complete. When a primary amine was used the solution was acidified and filtered and the product recrystallized. With secondary amines no acid was used.

The amides which have been characterized are given in Table I.

TABLE I

m-NITROBENZENE-SULFONAMIDES

Amine	M. p. of pure product °C.	Strength of alcohol for cryst. %		Analysis Calcd. %	Found %
Diethylamine	66	90	C,	46.15	46.13
Di-*n*-butylamine	61	90	N,	8.9	8.9
Methylaniline	100	60	N,	9.6	9.45
Ethylaniline	100.5	60	N,	9.15	9.10
n-Propylaniline	111.5	60	N,	8.75	8.63
n-Butylaniline	78.5	60	N,	8.38	8.31
α-Naphthylamine	166.5	90	N,	8.54	8.44
β-Naphthylamine	165.5	90	N,	8.54	8.50
o-Chloro-aniline	153	60	Cl,	11.34	11.0
p-Chloro-aniline	119.5	60	Cl,	11.34	10.93
p-Bromo-aniline	120.5	75	Br,	22.36	22.32

Summary

The *m*-nitrobenzenesulfonyl derivatives of several common amines have been characterized. The secondary amine derivatives are especially useful for identification purposes.

URBANA, ILLINOIS

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

THE REDUCTION OF PHENYLHYDRAZONES

BY R. C. GOODWIN AND J. R. BAILEY

RECEIVED JULY 28, 1924 PUBLISHED JANUARY 8, 1925

Foster and Bailey,[1] employing the catalytic method of reduction with colloidal platinum as catalyst, succeeded in converting acetaldehyde phenylhydrazone to phenyl-hydrazo-ethyl, $C_6H_5NHNHC_2H_5$, a method of preparation of mixed aliphatic-aromatic hydrazo compounds which is a decided improvement over the processes described by earlier investigators.[2]

As shown in the present paper, acetone-phenylhydrazone can be reduced

---

[1] Foster and Bailey, THIS JOURNAL, **44**, 1562 (1922).

[2] Fischer, *Ann.*, **190**, 102 (1877); **199**, 325 (1879). Tafel, *Ber.*, **18**, 1741 (1885). Knorr, *Ber.*, **39**, 3265 (1906). Knorr and Weidel, *Ber.*, **42**, 3523 (1909).