

peroxide solution added slowly to the cold mixture. The solution was allowed to come to room temperature as the ice-bath melted and stand at room temperature overnight.²² Manganese dioxide²³ was added, the solution transferred to a Claisen flask and the solvent removed under reduced pressure. The solid residue was dissolved in a mixture of ether and acetone, dried over sodium sulfate and the solvent removed on the water-bath. The yield of crude product was 88 g. (77%), m. p. 59–62°. Recrystallization from toluene gave the pure acid, m. p. 67.5–68.5° (corr.).

Anal. Calcd. for $C_8H_{12}O_4S$: S, 17.79. Found: S, 17.76, 17.91.

α -*n*-Butylsulfonyl-*N*-ethylacetamide (III).—Crude α -*n*-butylsulfonylacetic acid (40.5 g., 0.225 mole) was placed in an Erlenmeyer flask which was connected by a wide rubber tube to the neck of a three-necked, round-bottomed flask. The acid chloride was prepared by adding the solid acid slowly to thionyl chloride and treating according to the method described for *n*-butyryl chloride.²⁴ Ethylamine, generated from the hydrochloride by the addition of concentrated alkali and heating, was passed through a tube of soda-lime and bubbled into 250 ml. of dry ether in a 1-liter, three-necked, round-bottomed flask surrounded by an ice-salt bath. When the increase in weight of the ethereal solution was 26 g. (0.58 mole of ethylamine) the flask was fitted with a reflux condenser, a mercury-sealed stirrer and a dropping funnel, kept in the cooling bath, and the acid chloride added dropwise. The reaction mixture stood overnight and the ether then distilled on the steam-bath and replaced by dry benzene during the distillation. The resulting benzene solution was filtered while hot through a fluted filter, concentrated, and the product precipitated by the addition of ligroin and chilling. The product weighed 37.6 g. (81%), m. p. 60–65°, but was contaminated with *n*-

(22) A longer oxidation period would probably give better results.

(23) Manganese dioxide was used in small amounts, since it formed a manganese salt of the product. Nevertheless, it appeared to assist in the decomposition of the excess peroxide and was always used.

(24) Gilman, "Organic Syntheses," John Wiley and Sons, New York, N. Y., 1932, Coll. Vol. I, p. 142.

butylsulfonylacetic acid. It was dissolved in cold benzene, washed with a saturated solution of sodium bicarbonate, dried over sodium sulfate and recrystallized from a benzene–ligroin mixture. The pure product so obtained weighed 17.4 g., m. p. 73–73.5° (corr.). Concentration of the mother liquor gave an additional 7.4 g., m. p. 70–71°, making the total yield of product 24.8 g. (53%).

Anal. Calcd. for $C_8H_{17}O_3NS$: N, 6.76; S, 15.47. Found: N, 6.69, 6.71; S, 15.36, 15.55.

Summary

The alkylation of α -alkylsulfonylamides ($RSO_2CH_2CONH_2$) was complicated by the fact that the compounds were not acidic enough to form sodium derivatives satisfactorily in the presence of a considerable amount of alcohol. In inert solvents alkyl halides were not very reactive but ethyl sulfate reacted readily with the sodium derivative of α -*n*-butylsulfonylacetic acid (I). The products of this reaction were, in addition to unchanged starting material, α -*n*-butylsulfonyl-*n*-butyramide (II), α -*n*-butylsulfonyl-*N*-ethylacetamide (III) and α -*n*-butylsulfonyl-*N*-ethyl-*n*-butyramide (IV). Under similar conditions both II and III gave IV. The results may be interpreted as evidence that in the system $-CH_2-CO-NH_2$ of this series, two types of sodium derivatives are formed and that the $-CH_2-$ and $-NH_2$ are activated to about the same extent. Introduction of an alkyl substituent on either $-CH_2-$ or $-NH_2$ decreases the relative reactivity of the group to which the alkyl substituent is attached and subsequent alkylation occurs on the other active group.

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

The Reductive Alkylation of Aromatic Primary Amines. II¹

BY WILLIAM S. EMERSON AND W. D. ROBB

In view of earlier success with the reductive alkylation of aniline¹ it seemed advisable to test the generality of this reaction with other aromatic primary amines. For this purpose we selected *p*-toluidine, *p*-anisidine and α - and β -naphthylamines.

Using the procedure previously described¹ ethyl- α -naphthylamine was prepared in 88% yield, ethyl-, *n*-butyl- and benzyl- β -naphthylamine, and ethyl- and *n*-butyl-*p*-toluidine in 50 to

64% yields. These amines were identified by the formation of known salt or amide derivatives.

The new substances, *N*-*n*-butyl- α -naphthylamine and *N*-ethyl- and *N*-*n*-butyl-*p*-anisidine, were also prepared by this method. Their properties, as well as those of the new benzamide of benzyl- α -naphthylamine, are given in Table I.

***N,N*-Dialkylarylamines.**—In the alkylation of *p*-toluidine and *p*-anisidine with *n*-butyraldehyde, a high boiling fraction was obtained. Three grams of this material was boiled with 20 cc. of acetic

(1) For paper I. see Emerson and Walters, *THIS JOURNAL*, 60, 2023 (1938).

TABLE I
 PROPERTIES OF AMINES

Amine	N- <i>n</i> -Butyl- α -naphthylamine	N-Ethyl- <i>p</i> -anisidine	N- <i>n</i> -Butyl- <i>p</i> -anisidine	Benzyl- α -naphthylamine		
Yield, %	80	51	65	24		
B. p. { °C.	155-167	135-140	142-145	..		
{ Mm.	8	20	6	..		
d_{20}^{20}	1.004	1.017	0.963	..		
n_D^{20}	1.5963	1.5444	1.5207	..		
Derivative	HCl	<i>p</i> -Br-Bz-sulfonamide	HCl	Benzamide		
Deriv. m. p., °C.	151-152	113-114	187.5-188	103-104		
Anal. {	Calcd. {	C, %	71.4	48.7	61.3	N, 4.16
		H, %	7.64	4.32	8.36	
	Found {	C, %	71.4	49.3	61.5	N, 4.21
		H, %	8.07	4.50	8.60	

anhydride for one-half hour and then diluted with water. After neutralization with sodium carbonate the mixture was boiled until all the tertiary amine had distilled. Upon extraction of the oil from the filtrate with ether and evaporation of the ether the alkylations were found to have produced a 19% yield of N,N-di-*n*-butyl-*p*-toluidine and a 25% yield of N,N-di-*n*-butyl-*p*-anisidine.

Summary

The method for preparing N-alkylanilines by reducing an alcoholic solution of aniline and an aldehyde with hydrogen in the presence of Raney nickel and sodium acetate has been extended to four other aromatic primary amines from which ten N-alkylarylamines have been obtained in 24 to 88% yield.

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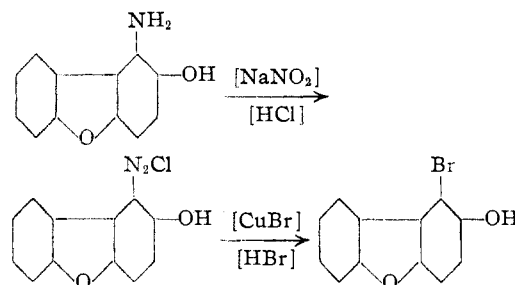
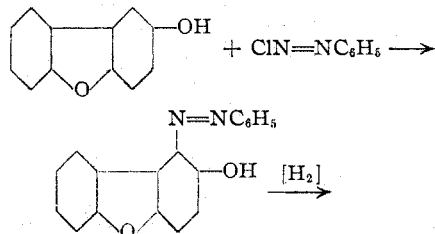
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Dibenzofuran. XIV. Diazo Coupling of 2-, 3-, and 4-Hydroxy Compounds¹

BY HENRY GILMAN AND MARIAN WESTON VAN ESS

Introduction

The recent availability of authentic specimens of some bromohydroxydibenzofurans² has made possible the determination of structure of the benzeneazo-hydroxydibenzofurans formed by diazo coupling with the 2-, 3-, and 4-hydroxydibenzofurans. The following transformations illustrate the general procedure used for proof of structure of the coupling products.



The 3-hydroxydibenzofuran also coupled in an ortho position to give 2-benzeneazo-3-hydroxydibenzofuran; but the 4-hydroxydibenzofuran coupled in a para position to give 1-benzeneazo-4-hydroxydibenzofuran. These general directions of coupling are consistent with early observations on phenols.³ However, there are two available ortho positions for diazo coupling of the 2- and the 3-hydroxydibenzofurans. On general grounds, it might have been predicted that 3-hy-

(1) Paper XIII, Gilman, Parker, Bailie and Brown, *THIS JOURNAL*, **61**, 2836 (1939).

(2) Gilman and P. R. Van Ess, *ibid.*, **61**, 1365 (1939).

(3) Chattaway and Hill, *J. Chem. Soc.*, **121**, 2756 (1922).