

0.2106 g. subst.; 8.70 cc. N, 757 mm., 26.5°.

Calc. for $C_8H_{10}ONBr.HBr$: N, 4.72%. Found: N, 4.69%.

***p*-Aminophenoxyethyl Bromide**, $p-H_2NC_6H_4OCH_2CH_2Br$.—A portion of the crude hydrobromide was dissolved in water and made alkaline with sodium carbonate solution. The bromide separated as an oil which crystallized almost immediately. The product was quickly filtered off, washed with water, and recrystallized, with bone-blackening, from a little 95% alcohol, forming minute, glistening platelets which are readily soluble in acetone or chloroform, less easily in benzene or alcohol. The bromide melts with preliminary softening at 83–4.5° to a liquid which immediately becomes turbid and decomposes without clearing at about 260°.

Kjeldahl: 0.1958 g. subst.; 9.25 cc. 0.1 *N* HCl.

Calc. for $C_8H_{10}ONBr$: N, 6.48%. Found: N, 6.62%.

***p*-Uraminophenoxyethyl Bromide (*p*-Uraminophenyl Bromoethyl Ether)**, $p-H_2NCONHC_6H_4OCH_2CH_2Br$.—This substance was obtained by reacting crude *p*-aminophenoxyethyl bromide hydrobromide with potassium cyanate in aqueous solution. Recrystallized, with bone-blackening, from 95% alcohol it forms aggregates of flat needles which melt slowly at 160–2° with preliminary softening. It is quite soluble in alcohol or acetone at room temperature, sparingly in ether or chloroform.

Kjeldahl: 0.1501 g. subst.; 11.70 cc. 0.1 *N* HCl.

Hydrolysis: 0.1152 g. subst.; 0.0828 g. AgBr.

Calc. for $C_9H_{11}O_2N_2Br$: N, 10.82%; Br, 30.84%. Found: N, 10.92%; Br, 30.58%.

NEW YORK CITY.

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

THE CONVERSION OF METHYLENEAMINOACETONITRILE TO IMINOACETONITRILE.

By J. R. BAILEY AND H. L. LOCHTE.

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In THIS JOURNAL,¹ Bailey and Snyder state that, contrary to the observation of M. Delépine,² methyleneaminoacetonitrile, $CH_2 = NCH_2CN$ readily adds on prussic acid, "when the compound is subjected to the action of either absolute or an aqueous prussic acid" giving in quantitative yield iminoacetonitrile, $NH(CH_2CN)_2$. In the work referred to above Delépine found that ethylidene- α -propionitrile, $CH_3CH = NCH(CH_3)CN$, and numerous alkylidene amines show an addition reaction with prussic acid but, after trying under modified conditions to effect the reaction that Bailey and Snyder later found proceeds so smoothly between methyleneaminoacetonitrile and prussic acid, Delépine reported as follows: "J'ai constaté que ce corps ($CH_2 = NCH_2CN$) restait absolu-

¹ 37, 935 (1915).

² Bull. soc. chim., 29, 1202 (1903).

ment inaltère sous l'influence de l'acide cyanhydrique à froid, en présence ou en l'absence de solvants."

An explanation of Delépine's failure to effect the addition of prussic acid in the case cited above has now been found. The prussic acid employed by Bailey and Snyder contained a very small amount of hydrochloric acid which had been added to the stock bottle to prevent polymerization and no thought was given to the possible effect this might have in the reaction. We now find, in conformity with Delépine's observation, that prussic acid is without effect on methyleneaminoacetonitrile. However, if the prussic acid contains a little hydrochloric acid, iminoacetonitrile is formed in quantitative yield. In one experiment 225 cc. of absolute HCN were distilled onto 150 g. of $\text{CH}_2 = \text{NCH}_2\text{CN}$. After standing 48 hours the prussic acid was distilled off and the residue proved to be unchanged starting material. The regained prussic acid with the addition of 6 drops of concentrated hydrochloric acid was again placed on the methyleneaminoacetonitrile, allowed to stand 48 hours, and then distilled off at 50° . It was then found that the conversion of the methylene compound to iminoacetonitrile was complete.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON.]

THE ACTION OF BENZENESULFONYLCHLORIDE ON ORGANIC BASES IN ANHYDROUS ETHER.

BY GEORGE L. SCHWARTZ AND WILLIAM M. DEHN.

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These studies were undertaken primarily for the purpose of throwing light on the mechanics of organic reactions in anhydrous ether. Various halides previously¹ were found to yield with organic bases simple additive products. This type of reaction was especially marked in cases of acetyl chloride² and benzoyl chloride,³ which yielded additive products not only with primary and secondary bases but also with tertiary bases.

General conclusions in agreement with previous studies, involving reactions of acyl halides on organic bases and obtained by these studies with benzenesulfonylchloride, are as follows: 1. Sunlight promoted all of these reactions. 2. The initial reactions were uniformly additive. 3. The reactions were non-ionic. 4. Some of the additive compounds formed directly could not be obtained by the action of hydrogen chloride on the respective substituted benzenesulfones.

¹ THIS JOURNAL, 33, 1588, 1598 (1911); 34, 286, 290, 1399, 1409 (1912); 36, 2091 (1914); 37, 2122 (1915); 39, 1717 (1917).

² *Ibid.*, 34, 1399 (1912).

³ *Ibid.*, 36, 2091 (1914).