We conclude that, within our experimental error, phosphorus pentoxide is as efficient a desiccant at 90° as it is at room temperature. Alternatively, if we suppose that a gain in weight of as much as half a milligram escaped our notice, we can state that the aqueous pressure in the air passing the phosphorus pentoxide at 90° under our experimental conditions did not exceed by over 0.0009 mm. the aqueous pressure which passed both magnesium perchlorate and phosphorus pentoxide at room temperature.

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Received September 21, 1937

The Preparation of 1-Naphthonitrile

By Melvin S. Newman

The preparation of 1-naphthonitrile from 1-naphthylamine by the Sandmeyer reaction is tedious and the yields often leave much to be desired. Recently, Rupe and Brentano[1] have reported an improved method by which yields of 75–78% may be obtained, but the process requires much in the way of time and attention.

The replacement of aromatically bound halogen by the cyano group has been carried out in several instances by heating the organic halogen compound with anhydrous cuprous cyanide, with or without added organic base, such as pyridine or quinoline. Thus, 1-naphthonitrile was prepared from 1-chloronaphthalene[2] and other halogen containing compounds[3] have been converted into the corresponding nitriles in excellent yields. The present report deals with the preparation of 1-naphthonitrile from 1-bromo- and 1-chloronaphthalene in yields of over 90% by heating with cuprous cyanide and pyridine.

Experimental

From 1-Bromonaphthalene.—In a dry flask fitted with a ground-in condenser and protected from moisture were placed 33.0 g. (0.16 mole) of bromonaphthalene, b. p. 153–154° at 11 mm., 17.3 g. (0.19 mole) of cuprous cyanide, and 20 cc. of pyridine (dried over barium oxide). The mixture was heated at 220° for fifteen hours, and the resulting brown solution poured into dilute ammonia in a separatory funnel. After vigorous shaking for several minutes, the nitrile was extracted with ether and the extract washed successively with dilute ammonia, water, dilute hydrochloric acid, water, and saturated sodium chloride solution. After the first treatment with ammonia it was usually necessary to remove some dark insoluble matter by filtration as this seriously interfered with separation of the layers. The ether was removed and the residue vacuum distilled. The temperature rose abruptly to the boiling point and the yield of colorless nitrile, b. p. 173–174° at 27 mm., was 22.8 g., or 93%. This material had a melting point of 34–35° and on hydrolysis with sulfuric acid–acetic acid–water yielded pure 1-naphthoic acid, m. p. and mixed m. p. 162–163°.

From 1-Chloronaphthalene.—In an experiment similar to the above, 18.1 g. of 1-chloronaphthalene, b. p. 144–146.5° at 29 mm., 12.0 g. of cuprous cyanide and 10 cc. of pyridine were heated at 245–250° (temperature of bath) for twenty-four hours. The yield of 1-naphthonitrile was 15.6 g., or 92%. In an experiment in which the heating period was only six hours, the yield was 70%, a fore run of unreacted 1-chloronaphthalene being obtained.

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[1] Rupe and Brentano, *Helv. Chim. Acta*, **19**, 581 (1936); see also McRae, This Journal, **52**, 4550 (1930); and Clarke and Read, *ibid.*, **46**, 1001 (1924).

[2] German Patent, 293,094 (1916).

[3] Von Braun and Manz, *Ann.*, **488**, 116 (1931); Koelsch, This Journal, **58**, 1329 (1936); Fieser and Seligman, *ibid.*, **58**, 2482 (1936); Fieser and Hershberg, *ibid.*, **59**, 394 (1937); Lock, *Ber.*, **70**, 926 (1937).

Ethoxyethylphenylurea

By E. Wertheim

Continuing a study of compounds related to Dulcin, as suggested in an earlier paper,[1] the compound ethoxyethylphenylurea has been made. In this compound the aromatic ring and aromatic attachment of the carbamido group previously found to be essential to sweet taste have been retained, but the ethoxy group is given an aliphatic attachment. The sequence of four carbons between the taste groups, as in Dulcin, is retained. The compound was found to have only a very faint sweet taste.

Experimental

Ethylphenethyl Ether, $C_6H_5CH_2CH_2OC_2H_5$.—One hundred twenty grams of phenylethyl alcohol was treated with 5 g. of sodium, and subsequently with 30 g. of ethyl bromide. The precipitated salt was removed by filtration and washed with dry ether. The filtrate was heated and aerated with dry air to remove ether and excess ethyl bromide. The material was again treated with 5 g. of sodium, and the above cycle of operations was repeated until about 20 g. of sodium and some excess over the equivalent amount of ethyl bromide had been used. The material was then washed with water, dried, and fractionally distilled; b. p. 198–199°; $n^{32}\text{D}$ 1.4870.

Anal. Calcd. for $C_{10}H_{14}O$: C, 80.00; H, 9.33. Found: C, 79.81; H, 9.54.

Ethyl-*o*-nitrophenethyl Ether, $C_2H_5OCH_2CH_2C_6H_4NO_2$.—In a typical experiment 59 g. of acetyl nitrate was

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[1] Wertheim, This Journal, **57**, 545 (1935).

added in small portions to a solution of 50 g. of ethylphenethyl ether in 50 g. of acetic anhydride. The temperature was maintained at about −5° during the addition and for several hours thereafter. After twenty-four hours an excess of sodium hydroxide solution was added, and the nitro compound was extracted with ether, washed and dried. Several lots were combined and subjected to repeated fractional distillation, using a short Vigreux column. The fraction of b. p. 129–134° (6 mm.) consisted of the ortho compound. A smaller fraction of b. p. 139–143° (6 mm.) was the para compound. The oxidation of portions of these fractions to the corresponding nitrobenzoic acids for confirmation of structure followed the method of Reimer and Gatewood.[2]

Anal. Calcd. for $C_{10}H_{13}NO_3$: C, 61.54; H, 6.67; N, 7.18. Found: C, 61.60, 61.54; H, 6.72, 6.88; N, 7.15.

***o*-Aminophenethylethyl Ether,** $C_2H_5OCH_2CH_2C_6H_4NH_2$.—Fifteen grams of ethylnitrophenethyl ether was treated in the customary manner with 28 g. of tin scraps and 60 cc. of concd. hydrochloric acid. When the first reaction ceased the flask was heated to 90–100° for one hour. The mixture was then made alkaline and distilled with steam. The distillate was acidified and shaken with ether: the ether layer was rejected. Following the addition of alkali the mixture was again extracted with ether; the ether extract was dried, the ether evaporated, etc. The product was a light yellow oil, b. p. 115–120° (4 mm.) with a pleasant, floral odor and a burning taste.

Anal. Calcd. for $C_{10}H_{15}NO$: C, 72.73; H, 9.09; N, 8.48. Found: C, 72.43; H, 8.99; N, 8.42.

***o*-Ethoxyethylphenylurea,** $C_2H_5OCH_2CH_2C_6H_4NHCONH_2$.—Aminophenethyl ethyl ether (1.65 g.) was dissolved in dilute alcohol and treated with 1.2 g. of nitrourea which was added in small portions. In two hours the precipitated urea was removed and washed with dilute acid, then recrystallized from a mixture of alcohol and ethyl acetate: colorless, amorphous compound, with very faint sweet taste, m. p. 155–156°.

Anal. Calcd. for $C_{11}H_{16}N_2O_2$: C, 63.46; H, 7.69; N, 13.46. Found: C, 63.40; H, 7.85; N, 13.29, 13.40.

The research is being continued in this Laboratory.

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RECEIVED AUGUST 10, 1937

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[2] M. Reimer and E. S. Gatewood, THIS JOURNAL, **42**, 1475 (1920).

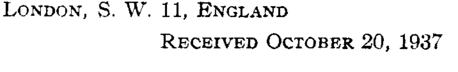
COMMUNICATIONS TO THE EDITOR

BETA-OCTYL THIOCYANATE

Sir:

By the interaction of potassium thiocyanate and (−)-β-octyl bromide Rose and Haller [THIS JOURNAL, **58**, 2648 (1936)] prepared (+)-β-octyl thiocyanate, a compound which had been obtained previously by the interaction of β-octyl *p*-toluenesulfonate and potassium thiocyanate [Kenyon, Phillips and Pittman, *J. Chem. Soc.*, 1081 (1935)]. Although the recorded refractive index and other physical properties of this compound prepared by the two different methods are in excellent agreement, there is a marked difference in the densities of the two specimens and accordingly we have looked into the matter. Our laboratory record shows that while the refractive index of the beta-octyl thiocyanate was determined with the freshly prepared specimen the density was not taken until some six months afterward. We have now redetermined the density of the thiocyanate, using this time a specimen newly prepared from β-octyl *p*-toluenesulfonate and find $d^{20}{}_4$ 0.914, a value in good agreement with that of Rose and Haller; it thus appears that the compound slowly decomposes on keeping.

The specific rotatory powers of (+)-β-octyl thiocyanate in the homogeneous state have been recalculated using the amended value for the density, they are $[\alpha]^{20}_{5893}$ +62.0°, $[\alpha]^{20}_{5461}$ +74.9°, $[\alpha]^{20}_{4358}$ + 121.5°. Since *d*-octanol by one series of reactions gives rise to *l*-octyl thiocyanate and by the other to *d*-octyl thiocyanate, it seems highly probable that, as surmised by Rose and Haller, a Walden inversion occurs in each of the three reactions where a bond of the asymmetric carbon atom is involved and that the two processes take place according to the scheme (where *d*- and *l*- denote configurations)



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