

The removal of halogens from aromatic compounds during the reduction of two activating nitro groups is a well-known phenomenon. Thus the reduction of 2,4-dibromo-3,5-dinitrotoluene with tin and hydrochloric acid gives 3,5-diaminotoluene.³

In contrast to the nitration with mixed acid as described above, nitration with 70% nitric acid alone according to the method of Mayes and Turner⁴ led to a mixture of products from which a considerable amount of 1-nitro-4-bromobenzene was isolated. The other products were not identified.

(3) W. A. Davis, *J. Chem. Soc.*, **81**, 873 (1902).

(4) H. A. Mayes and E. E. Turner, *ibid.*, 500 (1929).

CHICAGO, ILLINOIS

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The Acylation of Thiophene and Furan by Means of Boron Trifluoride¹

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The acetylation of thiophene and furan to form the respective 2-acyl derivatives has been effected previously by means of several catalysts.³ This reaction has now been effected by means of catalytic amounts of boron trifluoride complexes in ether, methanol, and acetic acid. The yields were satisfactory (70%) with 0.03–0.075 mole of the catalyst per mole of acetic anhydride. When acetyl chloride was used instead of acetic anhydride the yield was poor. The analogous reaction with benzoyl chloride was effected in 22% yield.

Although the nucleus of 2-acetylthiophene is acetylated in the presence of zinc chloride, orthophosphoric acid and phosphorus pentoxide,³ acetylation at the side chain of this ketone occurred in the presence of a molecular equivalent of boron trifluoride to form a triacetylthiophene in 17% yield; however, the product has not been identified. Acetylation at the side chain might have been anticipated from the work of Meerwein, Pannwitz and Vossen⁴ and Hauser and Adams.⁵

With furan, acetic anhydride and a catalytic amount of boron trifluoride in methanol, 2-acetylfuran was obtained in 46% yield.

Boron Trifluoride Complexes.—The boron trifluoride etherate was used as received from the Eastman Kodak Co. The boron trifluoride methanol complex and the boron trifluoride acetic acid complex were prepared by saturating methanol and acetic acid with boron trifluoride gas at 100 p. s. i. pressure in a stirring autoclave.

2-Acetylthiophene.—To a mixture of 252 g. (3 moles) of thiophene and 107 g. (1 mole) of 95% acetic anhydride cooled to 10° by means of an ice-bath was added 4 g. of boron trifluoride-methanol complex (60% boron tri-

fluoride). The temperature rose to 13° and when it finally subsided after five minutes to 5° the ice-bath was removed and the flask warmed to 50° for two hours. Two hundred milliliters of water was added, the mixture agitated for fifteen minutes, the lower organic layer drawn off, washed with 10% sodium carbonate solution until neutral, and distilled. Thiophene, 180 g., was recovered and 84 g. (70%) of 2-acetylthiophene, b. p. 87–88° (8 mm.),⁶ n_D^{20} 1.5666, was obtained.

2-Benzoylthiophene.—To 126 g. (1.5 moles) of thiophene and 141 g. (1 mole) of benzoyl chloride was added 4 g. of boron trifluoride-acetic acid complex. No heat of reaction was noted and the mixture was heated at 90–95° for six hours. After cooling, the reaction mixture was washed with 10% sodium hydroxide solution until neutral. Distillation yielded thiophene, 42 g. (22%) of 2-benzoylthiophene, b. p. 146–147° (5 mm.), m. p. 56.5–57°,⁷ after recrystallization from ASTM naphtha, and 21 g. of tarry residue.

2-Triacetylthiophene.—To 42 g. (0.33 mole) of 2-acetylthiophene was added 107 g. (1 mole) of 95% acetic anhydride and 110 g. (0.84 mole) of boron trifluoride etherate. The temperature rose to 38° and after fifteen minutes the mixture was warmed on a steam-bath at 55° for thirty minutes. The hot mixture was poured slowly into one liter of water containing 120 g. of sodium acetate and shaken until the oily liquid crystallized. The crystals were filtered, washed with cold benzene, and purified by vacuum sublimation, yielding 12 g. (17%) of bright yellow crystals, m. p. 176–177°.⁸

Anal. Calcd. for C₁₀H₁₀O₃S: S, 15.31, Found: S, 14.92.

Oxidation with alkaline permanganate gave 2-thiophenecarboxylic acid, m. p. and mixed m. p. 127–128.5°.

2-Acetylfuran.—A procedure, analogous to that employed for 2-acetylthiophene, was used but the temperature of the reaction mixture was maintained at 25° instead of 50° for two hours. Distillation yielded 53 g. (48%) of 2-acetylfuran, b. p. 89–90° (43 mm.),⁹ m. p. 30–32°,⁹ n_D^{20} 1.5015.

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(6) Reported data (ref. 3a): b. p. 77–78° (4 mm.) and n_D^{20} 1.5666.

(7) Reported data (ref. 3b); b. p. 143–144 (4 mm.) and m. p. 56.5–57°.

(8) Alternate purification procedures involved numerous recrystallizations from benzene or precipitation of the material from ethyl acetate by addition of petroleum ether yielding brown crystals, m. p. 173–175°.

(9) Reported data (ref. 3c): m. p. 30–32° and b. p. 45–50° (5 mm.).

SOCONY-VACUUM LABORATORIES

RESEARCH AND DEVELOPMENT DEPARTMENT

PAULSBORO, N. J.

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Derivatives of Diethylamino Compounds

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In connection with studies in progress on reactions of aminoalcohols and aminoketones involving possible rearrangement, it was desirable to obtain readily identifiable derivatives of certain diethylamino compounds. The compounds of interest included amines, aminoethers, aminoalcohols and aminoketones, in all of which the amine function was tertiary. Derivatives have been formed with picric acid, picrolonic acid and ethyl iodide. Diethyl-*n*-propylamine has been obtained

(1) Paper VII of this series.

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(3) (a) Hartough and Kosak, *THIS JOURNAL*, **68**, 2639 (1946); (b) **69**, 1012 (1947); (c) **69**, 3093 (1947); (d) **69**, 3098 (1947); (e) Hartough, Kosak and Sardella, *ibid.*, **69**, 1014 (1947); (f) Hartough and Conley, *ibid.*, **69**, 3096 (1947).

(4) Meerwein, *Ber.*, **66B**, 411 (1933); Meerwein and Pannwitz, *J. prakt. Chem.*, **141**, 123 (1934); Meerwein and Vossen, *ibid.*, **141**, 149 (1934).

(5) Hauser and Adams, *THIS JOURNAL*, **66**, 345 (1944).

pure, as have β -ethoxyethyldiethylamine and γ -ethoxypropyldiethylamine. 2-Diethylamino-2-methyl-1-propanol has been prepared by a method similar to the previously unsuccessful diethylation of 2-amino-2-methyl-1-propanol¹ and the successful ethylation of 2-ethylamino-2-methyl-1-propanol.²

Experimental³

Diethyl-*n*-propylamine.—A mixture of 70 g. of *n*-propyl bromide, 32 g. of ethylene glycol and 61 g. of diethylamine was refluxed for forty hours. The amine was liberated with alkali and extracted with ether. After the ether solution was dried over potassium hydroxide the ether was removed, and 19 g. (27%) of diethyl-*n*-propylamine was distilled at 111.5–112.5° (750 mm.); n_D^{20} 1.4064; d_4^{20} 0.742.

Anal. Calcd. for $C_7H_{17}N$: C, 72.97; H, 14.88; N, 12.16; *MRD*, 38.35. Found: C, 73.10; H, 15.01; N, 12.14; *MRD*, 38.18.

The ethiodide melted at 262–263° (cor.) with decomposition (von Auwers and Mauss reported 255–256°⁴).

The picrate was prepared in and recrystallized from ether as long yellow needles, m. p. 82–84° (cor.).

Anal. Calcd. for $C_{11}H_{23}N_2O_7$: C, 45.34; H, 5.86; N, 16.27. Found: C, 45.41; H, 5.91; N, 16.14.

The picrolonate was prepared in ether and recrystallized from ethanol-ether as orange-yellow elongated prisms, m. p. 140–141° (cor.).

Anal. Calcd. for $C_{17}H_{33}N_2O_6$: C, 53.81; H, 6.64; N, 18.46. Found: C, 53.92; H, 6.69; N, 18.41.

Diethylisopropylamine Picrolonate.—Prepared from diethylisopropylamine⁵ in ether, the picrolonate was recrystallized from absolute ethanol in leafy clusters of yellow prisms, m. p. 164–165.5° (cor.).

Diethylisopropylamine Ethiodide.—Formed by refluxing diethylisopropylamine in benzene with excess ethyl iodide, the microcrystalline ethiodide melted at 264–266° (cor.) with decomposition.

β -Ethoxyethyldiethylamine.—A mixture of a six to one molar proportion of diethylamine (50 g.) and β -ethoxyethyl bromide (16.7 g.) was heated under reflux for twenty-four hours. The product was isolated as in the method for diethyl-*n*-propylamine; b. p. 63–64° (25 mm.); n_D^{20} 1.4179.

Anal. Calcd. for $C_8H_{19}NO$: C, 66.15; H, 13.18; N, 9.64. Found: C, 65.81; H, 12.96; N, 9.64.

No picrate, picrylsulfonate, picrolonate, methiodide or mineral acid salt could be formed.

γ -Ethoxypropyldiethylamine.—Fifty grams of diethylamine and 19 g. of γ -ethoxypropyl bromide were heated under reflux and the product was isolated in the usual manner; b. p. 78–81° (25 mm.); n_D^{20} 1.4223.

Anal. Calcd. for $C_9H_{21}NO$: C, 67.87; H, 13.29; N, 8.80. Found: C, 68.01; H, 13.01; N, 8.84.

Prepared in and recrystallized from ethanol, the picrolonate melted with decomposition at 213–215° (uncor.).

Anal. Calcd. for $C_{13}H_{29}N_2O_6$: C, 53.89; H, 6.93. Found: C, 53.75; H, 6.92.

2-Diethylamino-2-methyl-1-propanol.—2-Diethylamino-2-methyl-1-propanol was prepared by a method similar to that of Olson and Whitacre and Bachman and Mayhew²; b. p. 82–83° (22 mm.); n_D^{20} 1.4421.

Anal. Calcd. for $C_8H_{19}NO$: N, 9.64. Found: N, 9.61.

The picrolonate was recrystallized from benzene containing a small amount of ethanol as elongated yellow prisms; m. p. 185.5–187° (uncor.) with decomposition.

(1) Olson and Whitacre, *THIS JOURNAL*, **65**, 1019 (1943).

(2) Bachman and Mayhew, *J. Org. Chem.*, **10**, 243 (1945).

(3) The microanalyses were performed by Miss Theta Spoor. Boiling points are uncorrected for emergent stem error.

(4) von Auwers and Mauss, *Ber.*, **61**, 2411 (1928).

(5) Caspe, *THIS JOURNAL*, **54**, 4457 (1933).

Anal. Calcd. for $C_{13}H_{27}N_2O_6$: C, 52.80; H, 6.65. Found: C, 52.73; H, 6.67.

The picrate was recrystallized from ethanol-petroleum ether solution as yellow prisms; m. p. 156° (uncor.).

Anal. Calcd. for $C_{14}H_{29}N_2O_8$: C, 44.92; H, 5.92. Found: C, 45.00; H, 5.89.

Diethylaminoacetone Picrolonate.—Formed from diethylaminoacetone⁶ in ether and recrystallized from ethanol, the picrolonate formed clusters of yellow prisms, m. p. 143–144° (cor.).

Anal. Calcd. for $C_{17}H_{33}N_2O_6$: C, 51.90; H, 5.89; N, 17.80. Found: C, 51.74; H, 6.11; N, 17.81.

5-Diethylamino-2-pentanone Picrolonate.—Prepared from Noval ketone in ether and recrystallized from ethanol-ether, the picrolonate formed stout yellow prisms, m. p. 105–107° (cor.).

Anal. Calcd. for $C_{19}H_{37}N_2O_6$: C, 54.14; H, 6.46; N, 16.62. Found: C, 54.32; H, 6.67; N, 16.67.

(6) Stoermer and Dzimiski, *Ber.*, **28B**, 2220 (1895).

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Conversion of Benzylamine to N-Substituted Thiobenzamides

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In a previous publication² the modified Willgerodt reaction³ was applied to styrene in the presence of a series of amines and the yield of phenylacetic acid obtained by hydrolyzing the crude reaction mixture was measured. In some instances there was isolated from the crude reaction mixture a little of the pure thioamide for characterization and analysis. It has been found that the compound isolated and called N-benzylphenylthioacetamide was in reality N-benzylthiobenzamide. Since there was no doubt that it was phenylacetic acid which was obtained from the hydrolysis of the crude reaction mixture, the hydrolysis of pure N-benzylthiobenzamide was investigated. It was found that this thioamide was very slowly attacked by refluxing 50% (by weight) sulfuric acid (the conditions used for hydrolyzing the crude thioamides), thus explaining the absence of benzoic acid in the hydrolysate from the crude reaction mixture of styrene, sulfur and benzylamine. The identity of N-benzylthiobenzamide was established by hydrolysis with refluxing 65% (by weight) sulfuric acid followed by isolation of benzoic acid and benzylamine in the form of its picrate.

Since none of the other amines used to prepare thioamides reported in ref. 2 had the possibility of undergoing a reaction analogous to that which benzylamine underwent, there is no reasonable doubt as to their identity.

Although it is possible that the N-benzylthiobenzamide could have arisen through cleavage⁴

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(2) King and McMillan, *THIS JOURNAL*, **68**, 2335 (1946).

(3) Schwenk and Bloch, *ibid.*, **64**, 3051 (1942).

(4) For discussion of cleavage in Willgerodt reaction cf. McMillan and King, *ibid.*, **60**, 1297 (1947).