Anal. Calcd. for $C_{16}H_{17}ON$: N, 5.84. Found: N, 5.80.

With acetone and nitromethane N-isopropylmethylamine was produced in 59% yield, b. p. 45–55°. It was identified as the picrate, m. p. 133–135° (133–134°).[16]

N - Benzyl - N - *n* - butylaniline.—N - Benzylphenylhydroxylamine was prepared in 75% yield by the method of Vavon and Crajcinovic.[5] When treated with two equivalents of butyraldehyde under the same conditions used for the preparation of N,N-di-*n*-butylaniline from nitrobenzene, this compound yielded 38% of N-benzyl-N-*n*-butylaniline. The product distilled at 175–182° (10 mm.); d^{20}_{20} 1.019; n^{20}_{D} 1.5810; M^{20}_{D} calcd. 78.0; M^{20}_{D} found 78.3. It was identified as the picrate, m. p. 126–128° (129°).[17]

When N-benzylphenylhydroxylamine was treated with two equivalents of butyraldehyde in basic solution following the procedure of Emerson and Mohrman,[1] N-benzylaniline was produced in 54% yield. No N-benzyl-N-*n*-butylaniline could be isolated from the reaction mixture.

N-benzyl-N-*n*-butylaniline was also prepared in 3% yield from N-benzylaniline and two equivalents of butyraldehyde in acid solution by the method described above. In this reaction 64% of the N-benzylaniline was recovered unchanged.

Summary

A method has been developed for preparing tertiary amines by treating an alcoholic solution of a nitro compound and an aldehyde with hydrogen and platinum in the presence of acetic acid. Seven tertiary amines have been prepared in 34 to 92% yield by this procedure.

Under these same conditions ketones give secondary amines, N-isopropylaniline having been prepared in 53% and isopropylmethylamine in 59% yield.

The reaction probably proceeds through the alkylarylhydroxylammonium ion, which has been found to be far more reactive than the corresponding alkylarylammonium ion.

URBANA, ILLINOIS RECEIVED DECEMBER 11, 1940

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(16) Dunstan and Goulding, *J. Chem. Soc.*, **79**, 628 (1901).

(17) Reilly and Drumm, *ibid.*, 1395 (1927).

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

Secondary and Tertiary Amines from Azo Compounds

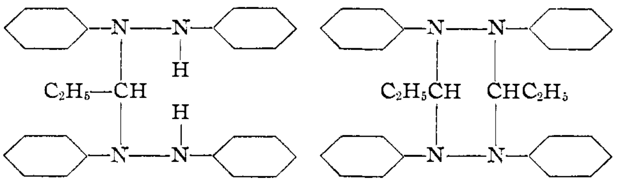
BY WILLIAM S. EMERSON, S. K. REED AND R. R. MERNER

The successful preparation of secondary amines by the reductive alkylation of nitro compounds[1] suggested that this procedure could be made general for other compounds reducible to primary amines with hydrogen and a catalyst. The present communication shows that azo compounds, which belong to this class,[2] can be treated with hydrogen and Raney nickel in the presence of an aldehyde and sodium acetate, to give secondary amines. In this way three alkylanilines have been prepared from azobenzene in 49–74% yield.

When activating groups such as hydroxyl or dimethylamino are ortho or para to the azo group, tertiary amines are produced. Thus with N,N-dimethyl-*p*-aminoazobenzene and *n*-butyraldehyde, 73% of N,*n*-butylaniline was obtained from one-half of the molecule and 76% of N,N-dimethyl-N′,N′-di-*n*-butyl-*p*-phenylenediamine from the other half.

Similarly using butyraldehyde with hydroxyazo compounds, 1-phenylazo-2-naphthol gave 41% of 1-(N,N-di-*n*-butylamino)-2-naphthol and *p*-hydroxyazobenzene gave 46% of N,N-di-*n*-butyl-*p*-aminophenol.

It should be noted that several of the yields are higher than those obtained with the primary amines themselves.[3] Since Rassow[4] has shown that hydrazobenzene reacts with aldehydes to give compounds of the following type



it seems probable that the course of the reaction is reduction to the hydrazo compound, condensation of the latter with the aldehyde, followed by reduction and further alkylation to the secondary or tertiary amine.

Experimental

General Procedure.—All of the reactions were carried out in a machine for catalytic reduction[5] using Raney

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(1) Emerson and Mohrman, THIS JOURNAL, **62**, 69 (1940).

(2) Whitmore and Revukas, *ibid.*, **59**, 1500 (1937).

(3) Emerson and Walters, *ibid.*, **60**, 2023 (1938).

(4) Rassow, *J. prakt. Chem.*, [2] **64**, 129 (1901); Rassow and Lummerzheim, *ibid.*, [2] **64**, 136 (1901); Rassow and Rulke, *ibid.*, [2] **65**, 97 (1902); Rassow and Bauman, *ibid.*, [2] **80**, 511 (1909).

(5) Adams and Voorhees, "Organic Syntheses," Coll. Vol. I, 1932, p. 53.

nickel[6] as the catalyst. In each experiment after 0.1 mole of the azo compound, 0.25 mole of the aldehyde and 2.0 g. of sodium acetate had been dissolved in 150 cc. of alcohol, from 2.0 g. to 40 g. of Raney nickel was added and the mixture placed in the machine at an initial pressure of 45 lb. It was found that 10 g. of Raney nickel was best, since it was the smallest quantity which gave a smooth and rapid reduction. The mixture was shaken until no more hydrogen was absorbed, usually from one to two hours, 0.3–0.4 mole of hydrogen being taken up. After the catalyst had been removed by filtration, the solvent was distilled on the steam bath. In the case of the lower molecular weight amines the reaction mixture was acidified before the evaporation of the solvent. The residue, made basic if necessary, was extracted with ether and the ether dried over sodium hydroxide. After the removal of the drying agent, the ether was evaporated and the products obtained by distillation, usually at reduced pressure.

Amines from Azobenzene.—Using the general procedure described above **N,*n*-butylaniline** was obtained from azobenzene in 71% yield and identified as the *p*-bromobenzenesulfonamide, m. p 85–86° (87°).[7] Similarly **N-*n*-heptylaniline** was obtained in 74% yield and also identified as the *p*-bromobenzenesulfonamide, m. p. 114–115° (115°).[3]

N-Benzylaniline was isolated in 49% yield as the hydrochloride, m. p. 210–212° (214–216°).[8]

N,N-Dimethyl-N′,N′-di-*n*-butyl-*p*-phenylenediamine, prepared similarly from N,N-dimethyl-*p*-aminoazobenzene and *n*-butyraldehyde in 76% yield, b. p. 150–175° (20 mm.), was identified as the picrate, m. p. 121–122°.

Anal. Calcd. for $C_{22}H_{31}O_7N_5$: N, 14.7. Found: N, 14.8.

A 73% yield of *n*-butylaniline was also obtained in this reaction.

N,N-Di-*n*-butyl-*p*-aminophenol was obtained in the same way from *p*-hydroxyazobenzene and *n*-butyraldehyde. It was isolated as the benzoate by treatment with benzoyl chloride and aqueous alkali; yield 46%. This benzoate melted at 232–233° after two crystallizations from acetic acid.

Anal. Calcd. for $C_{21}H_{27}O_2N$: N, 4.31. Found: N, 4.47.

1-(N,N-Di-*n*-butylamino)-2-naphthol was prepared in 41% yield from 1-phenyl-azo-2-naphthol and *n*-butyraldehyde. It was isolated by adding water to the reaction mixture after half of the alcohol had been distilled, m. p. 106–107°. As it darkened rapidly on standing, it was stored as the hydrochloride, m. p. 225–227°.

Anal. Calcd. for $C_{18}H_{26}ONCl$: Cl, 11.6. Found: Cl, 11.5.

Summary

Three alkylanilines have been prepared in 49–74% yield by treating an alcoholic solution of azobenzene and an aldehyde with hydrogen in the presence of Raney nickel and sodium acetate. When an activating group such as hydroxyl or dimethylamino is present in the *ortho* or *para* position, a tertiary amine is produced.

Urbana, Illinois Received December 11, 1940

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[6] Covert and Adkins, This Journal, **54**, 4116 (1932).

[7] Marvel and Smith, *ibid.*, **45**, 2696 (1923).

[8] Brand, *Ber.*, **42**, 3460 (1909).

[Contribution No. 239 from the Research Laboratory of Organic Chemistry of the Massachusetts Institute of Technology]

The Synthesis of Certain Unsaturated Substances from β-Ionone and Substituted Vinylacetylenes

By A. F. Thompson, Jr., N. A. Milas and Ida Rovno[1]

Substances prepared by condensation of β-ionone so that the β-ionone ring is retained, and a longer unsaturated side chain results, are of interest for at least two reasons. First, there is the possibility that such substances may exhibit the physiological activity of Vitamin A, at least in some degree. Second, the physiological properties of such synthetic substances shed light on the specific structural arrangement necessary for a molecule to possess Vitamin A activity.

It was decided to investigate the condensation products of vinylacetylene, and two of its simple derivatives, with β-ionone. The condensation product from β-ionone and vinylacetylene itself has already been prepared by Zal'kind, Zonis and Blokhin[2] who reported that their product was physiologically inactive. However, the unsaturated carbinol derived from this condensation product by partial reduction of the triple bond has never been reported. And there is no published description of any condensation products of β-ionone with derivatives of vinylacetylene.

The series of transformations performed in the present investigation is illustrated by formulas I–VII inclusive. It was hoped at the outset that

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[1] Part of the material of this paper is abstracted from a thesis submitted to the Massachusetts Institute of Technology by Ida Rovno in partial fulfillment of the requirements for the degree of Bachelor of Science.

[2] Zal'kind, Zonis and Blokhin, *Compt. rend. acad. sci., U. S. S. R.*, **2**, 57 (1935).