Conclusions

The saturated multicyclopentyls were found to have physical properties which in most cases increased in almost a linear relationship with respect to their boiling points at atmospheric pressure. The kinematic viscosity increased linearly when the boiling points were plotted on a uniform scale as the abscissa and the kinematic viscosities in centistokes at the different temperatures were plotted on the ordinate scale of an A. S. T. M. viscosity–temperature chart. A straight line was also obtained by plotting the boiling points against the logarithm of the number of rings per molecule. Thus some approximate physical properties of unknown saturated hydrocarbons containing five or more rings per molecule in this series may be estimated. An exact determination of the properties of these unknown compounds, of course, cannot be made in this manner since possible geometric isomers need still to be synthesized and characterized.

The viscosity index was found to decrease as the number of rings increased. However, the quatercyclic hydrocarbon still had a viscosity index of more than one hundred.

Acknowledgment.—The author desires to express his appreciation for the advice and assistance of Dr. Johannes H. Bruun during this investigation. The aid of Messrs. R. E. Ledley, Jr., W. B. M. Faulconer, David Flitter, S. J. Hetzel and W. A. Hoffecker in assisting in the preparation of several intermediates and determination of several physical properties is gratefully acknowledged.

Summary

For the purpose of establishing the physical properties characteristic of multicyclic five-carbon membered rings in the light of any probable relationship to the chemical structure of petroleum products, there has been synthesized a series of multicyclopentyls.

Bicyclopentyl, 1,3-dicyclopentylcyclopentane and 3,3′-dicyclopentylbicyclopentyl have been synthesized from cyclopentadiene and cyclopentanone. 1,3-Dicyclopentylcyclopentane has also been synthesized from cyclopentanone itself.

The physical properties determined were boiling point at atmospheric and reduced pressure, refractive index at two temperatures, density at five temperatures, specific dispersion, kinematic viscosity at five temperatures and aniline point.

NORWOOD, PA. RECEIVED OCTOBER 16, 1940

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

Secondary and Tertiary Amines from Nitro Compounds

BY WILLIAM S. EMERSON AND C. A. URANECK

Since the reductive alkylation of aromatic nitro compounds in a basic medium was known to give secondary amines in good yield,[1] it seemed likely, by analogy with the known alkyl reduction of the corresponding primary amines, that in an acid medium tertiary amines might be obtained. The reductive alkylation of primary amines by such acid reducing agents as formic acid[2] and zinc and hydrochloric acid[3] produces good yields of tertiary amines. Although unhindered aromatic primary amines yield polymers when treated with aldehydes in the presence of acids,[2b,4] this factor should not interfere with the preparation of tertiary amines from aromatic nitro compounds, since Vavon and Crajcinovic[5] have shown that when nitrobenzene is reduced in the presence of benzaldehyde, the reduction goes only as far as phenylhydroxylamine, which then condenses with the aldehyde as fast as it is formed, so that at no time would there be any aromatic primary amine in the reaction mixture.

It was found that, on treatment of an alcoholic solution of one equivalent of nitrobenzene and three of *n*-butyraldehyde with hydrogen and Raney nickel in the presence of trimethylamine hydrochloride, a 63% yield of N,N-di-*n*-butylaniline was obtained. The yield rose to 69% when acetic acid and platinum oxide were used instead of the trimethylamine hydrochloride

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

[2] (a) Wallach, *Ann.*, **343**, 54 (1905); (b) Clark, Gillespie and Weisshaus, THIS JOURNAL, **55**, 4571 (1933).

[3] Emerson, Dorf and Deutschman, *ibid.*, **62**, 2159 (1940).

[4] Emerson and Walters, *ibid.*, **60**, 2023 (1938).

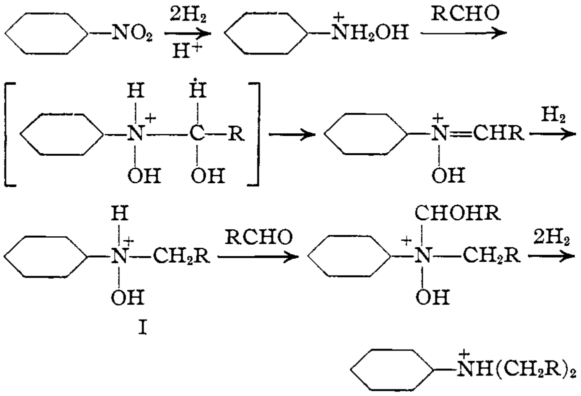
[5] Vavon and Crajcinovic, *Compt. rend.*, **187**, 420 (1928).

and Raney nickel, respectively. This was accordingly adopted as a general procedure by which four dialkylarylamines were prepared in 34 to 70% yield from aromatic nitro compounds and aldehydes.

This procedure was likewise found applicable to the nitroparaffins. For example nitromethane with three equivalents of acetaldehyde, propionaldehyde or *n*-butyraldehyde underwent reductive alkylation to produce the corresponding dialkylmethylamines in 45 to 92% yield.

On the other hand, when this procedure was applied to ketones, secondary amines were formed. In this way N-isopropylaniline was prepared from nitrobenzene in 53% yield and isopropylmethylamine was prepared from nitromethane in 59% yield. Major[6] also has found that ketones give secondary amines under conditions in which aldehydes give tertiary amines in this type of reaction.

The mechanism of this reaction in acid solution is probably analogous to that in basic solution[1,5]



The alkylarylhydroxylammonium ion I is far more reactive than the corresponding alkylarylammonium ion. Thus, in the presence of two moles of *n*-butyraldehyde in acid solution, N-benzylphenylhydroxylamine yielded 38% of N-benzyl-N-*n*-butylaniline whereas under the same conditions N-benzylaniline yielded only 3% of the tertiary amine. This explains why so mild an acidic condensing agent as trimethylamine hydrochloride in dilute solution produces tertiary amines from nitrobenzene whereas the alkylation of aromatic primary and secondary amines requires concentrated hydrochloric acid[3,7] or boiling formic acid[2] as a catalyst.

Experimental

N,N-Di-*n*-butylaniline.—A solution of 12.3 g. (0.1 mole) of nitrobenzene, 21.6 g. (0.3 mole) of butyraldehyde and 10 cc. of glacial acetic acid in 150 cc. of 95% ethyl alcohol was placed in the pressure bottle of a machine for catalytic reduction.[8] After 0.1 g. of platinum oxide[9] was added, the mixture was shaken on the machine for ninety-six hours during which time 0.66 mole of hydrogen was absorbed. Seventeen cubic centimeters of dilute hydrochloric acid was then added and the platinum removed by filtration. After the alcohol had been distilled, the residue was made basic with dilute sodium hydroxide and extracted with ether. After removal of the ether the product was distilled, b. p. 265–275° (lit. 260–263°). The 14.5 g. (69%) of product was identified as the picrate, m. p. 123–125° (125°).[10]

When 2 g. of trimethylamine hydrochloride and 3 g. of Raney nickel[11] were used in place of the acetic acid and platinum and the reaction was otherwise carried out in the same manner except that the mole ratio of butyraldehyde to nitrobenzene was one to one, the yield of N,N-di-*n*-butylaniline was 63% (98% based on the aldehyde).[12] Larger quantities of aldehyde interfered, so that a lower yield resulted.

Other Tertiary Amines.—Using the same procedure as for N,N-di-*n*-butylaniline six other tertiary amines were prepared. Three of them, N,N-diethylaniline, N,N-di-*n*-propylaniline, and N,N-diethylmethylamine, which had already been prepared, were obtained in yields of 70, 34 and 92%, respectively, and were identified, respectively, as the picrate, m. p. 139–140° (142°),[13] the methiodide, m. p. 153–155° (156°),[14] and the picrate, m. p. 183–185° (185°).[15] The properties of the three new amines thus prepared are given in Table I.

TABLE I

NEW AMINES

Amine	N,N-Di-*n*-butylmethyl		N,N-Di-*n*-propylmethyl	N,N-Diethyl-α-naphthyl
Yield, %	56		45	40
Boiling point, °C.	155–163		110–122	155–165 (30 mm.)
d^{20}_{20}	0.782		0.743	1.015
n^{20}_D	1.4302		1.4076	1.5961
Derivative	HCl	Picrate	Picrate	Picrate
M. p. of deriv., °C.	131–131.5	86.0–87.5	92–93	152–154
Analyses, % Calcd.	Cl, 19.8	N, 15.1	16.3	13.1
Found	Cl, 19.7	N, 15.4	16.2	13.1

Secondary Amines.—When acetone was substituted for the aldehyde in the procedure for tertiary amines, a secondary amine was produced. Thus with nitrobenzene and acetone, N-isopropylaniline was obtained in 53% yield, b. p. 198–207°. It was identified as the benzamide, m. p. 63–65°.

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(6) Major, THIS JOURNAL, **53**, 1901, 4373 (1931).

(7) Wagner, *ibid.*, **55**, 724 (1933).

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

(9) Adams, Voorhees and Shriner, *ibid.*, p. 452.

(10) Reilly and Hickinbottom, *J. Chem. Soc.*, **113**, 99 (1918).

(11) Covert and Adkins, THIS JOURNAL, **54**, 4116 (1932).

(12) This experiment was carried out by W. D. Robb.

(13) Singh, *J. Chem. Soc.*, **109**, 780 (1916).

(14) Jones, *ibid.*, **83**, 1400 (1903).

(15) Heilbron, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1936, p. 674.

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

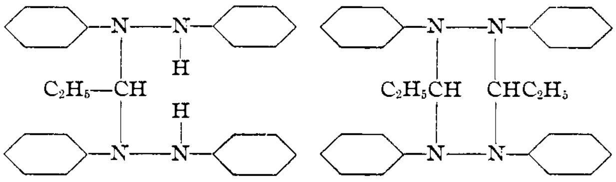
BY WILLIAM S. EMERSON, S. K. REED AND R. R. MERNER

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] **66**, 97 (1902); Rassow and Bauman, *ibid.*, [2] **80**, 511 (1909).

[5] Adams and Voorhees, "Organic Syntheses," Coll. Vol. I, 1932, p. 53.