the $[\alpha]_D$ value for β-ethylgentiobioside heptaacetate is calculated to be $(-12{,}300-1935)/664 = -21.4°$, which agrees satisfactorily with the observed value, $-23.1°$.

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Summary

1. A new crystalline 6-β-gentiobiosido-β-*d*-mannose hendekaacetate has been synthesized by the improved Königs and Knorr reaction and its physical properties determined. This is the first time that a crystalline 6-linked oligosaccharide acetate containing mannose has been synthesized by this method.

2. The epimeric difference relationships of the new 6-β-gentiobiosido-β-*d*-mannose hendekaacetate and the known 6-β-gentiobiosido-β-*d*-glucose hendekaacetate have been correlated with others of the mannose series. The specific rotation as calculated by Hudson's rules is $-19.7°$. The observed specific rotation is $[\alpha]^{25}_D$ $-21.0°$. It has been pointed out that the values of the epimeric differences as required by Hudson's scheme seem to hold for 6-linked sugars although they do not hold for 4-linked sugars.

3. The known 6-β-*d*-glucosido-α-*d*-mannose octaacetate has been made more available by the improved Königs and Knorr reaction. Its preparation represents the second synthesis of a crystalline 6-linked oligosaccharide acetate containing a mannose unit.

4. Ethylgentiobioside heptaacetate has been synthesized and its physical properties determined, m. p. 158–159° (corr.); $[\alpha]^{25}_D$ $-23.1°$. This rotation agrees with that which is calculated $(-21.4°)$ from Hudson's rules.

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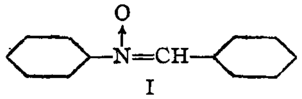
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

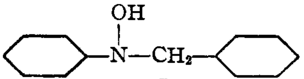
Secondary Amines from Nitro Compounds

BY WILLIAM S. EMERSON AND H. W. MOHRMAN

Since most aromatic primary amines are prepared by the reduction of nitro compounds, it seemed possible that the procedure for reductive alkylation of these amines[1] could be adapted to apply directly to the original nitro compounds. Vavon and Crajcinovic,[2] reduced a mixture of nitrobenzene and benzaldehyde with hydrogen and platinum. By suitably interrupting the reduction they obtained the nitrone I or the alkylarylhydroxylamine II.



I



II

They postulated the course of the reaction as (1) reduction of the nitrobenzene to phenylhydroxylamine, (2) condensation of the phenylhydroxylamine with the benzaldehyde to give the nitrone I and (3) reduction of the nitrone to the substituted hydroxylamine II.

In order to obtain secondary amines it, therefore, appeared necessary to determine satisfactory conditions for the reduction of the hydroxylamine II. From the work of Major[3] it seemed likely that hydrogen and a catalyst would be suitable. He reduced *p*-nitrophenol with hydrogen and platinum in acetone solution to obtain good yields of *p*-hydroxy-N-isopropylaniline. Later he extended the reaction to obtain N,N′-diisopropyl-*p*-phenylenediamine in good yield from *p*-nitroaniline, but states he was unable to obtain alkylation with nitrobenzene and acetone or with *p*-nitrophenol and formaldehyde or acetaldehyde. Benzaldehyde, however, gave *p*-hydroxydibenzylaniline with *p*-nitrophenol. For these reactions Major postulated the same mechanism as that proposed by Vavon and Crajcinovic.

We have found that when an alcoholic solution of an aromatic nitro compound and an aldehyde is reduced with hydrogen and Raney nickel in the presence of sodium acetate as a condensing agent, the corresponding secondary amine is formed in good yield. The reaction is apparently general

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[1] Emerson and Walters, THIS JOURNAL, **60**, 2023 (1938); Emerson and Robb, *ibid.*, **61**, 3145 (1939).

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

[3] Major, THIS JOURNAL, **53**, 1901, 2803, 4373 (1931); *Chem. Abs.*, **29**, 178 (1935) (U. S. Patent 1,978,433).

TABLE I

N-ALKYLARYLAMINES

Amine	Yield, %	Derivative	M. p. of deriv., °C.	Recorded m. p., °C.
N-Methylaniline	50	*p*-Bromobenzenesulfonamide	92	92[a]
N-Ethylaniline	57 63	*p*-Bromobenzenesulfonamide	91	91[a]
N-*n*-Butylaniline	94 96	*p*-Bromobenzenesulfonamide	86–87	87[a]
N-*n*-Amylaniline	84	*m*-Nitrobenzenesulfonamide	74–75	74–75[b]
N-*n*-Heptylaniline	40	*p*-Bromobenzenesulfonamide	115	115[b]
N-Benzylaniline	33	Hydrochloride	210–212	214–216[c]
N-*n*-Butyl-*p*-anisidine	31	*p*-Bromobenzenesulfonamide	72–73	
N-*n*-Butyl-α-naphthylamine	60	*p*-Chlorobenzamide	242–243	
N-*n*-Amyl-α-naphthylamine	43	*p*-Bromobenzamide	226–227	
N-*n*-Butyl-*p*-toluidine	40 85	Hydrochloride	148–149	148–149[d]
N-*n*-Heptyl-*p*-toluidine	35	*p*-Bromobenzenesulfonamide	52.0–52.5	

[a] Marvel and Smith, THIS JOURNAL, **45**, 2696 (1923). [b] See footnote (1). [c] Brand, *Ber.*, **42**, 3460 (1909). [d] Wagner' THIS JOURNAL, **55**, 724 (1933).

TABLE II

PROPERTIES OF AMINES

Amine	B. p., °C.	Mm.	d^{20}_{20}	n^{20}_D	Deriv.	Analyses, % Calcd.	Found
N-*n*-Butyl-*p*-anisidine					*p*-Bromobenzenesulfonamide	Br, 20.06	20.45
N-*n*-Butyl-α-naphthylamine					*p*-Chlorobenzamide	Cl, 10.50	10.62
N-*n*-Amyl-α-naphthylamine	136–146	4	1.102	1.6460	*p*-Bromobenzamide	Br, 20.18	20.17
N-*n*-Heptyl-*p*-toluidine	135–150	4	0.906	1.5055	*p*-Bromobenzenesulfonamide	Br, 18.89	18.54
N,N-Di-*n*-butyl-*p*-toluidine	295–296[a]		.976	1.5514	Picrate, m. p. 186–187°	N, 12.50	12.84
N,N-Di-*n*-heptyl-*p*-toluidine	175–200	2.5	.943	1.5089	Hydrochloride, m. p. 136°	Cl, 10.43	10.53

[a] By Siwoloboff method. Hill and Donleavy, *Ind. Eng. Chem.*, **13**, 504 (1921), give 283–285°/755 mm.

for aromatic nitro compounds and aliphatic or aromatic aldehydes. Our results are summarized in Table I.

Experimental

General Procedure.—All of the reactions were carried out in a machine for catalytic reduction[4] using Raney nickel[5] as the catalyst. In each experiment 0.1 mole of the nitro compound, 0.3 mole of the aldehyde and 2.0 g. of sodium acetate were dissolved in 150 cc. of alcohol. From 3.0 to 6.0 g. of Raney nickel was then added and the mixture placed in the machine at an initial pressure of 40 lb. It was shaken until no more hydrogen was absorbed, usually from twelve to twenty-four hours, 0.42 to 0.62 mole of hydrogen being taken up. After the catalyst had been removed by filtration, the solvent was distilled on the steam-bath. The remaining oil was steam distilled and the residue or distillate, depending on the amine, fractionated to obtain the pure product.

N-Alkylarylamines.—Using the general procedure described above, we have prepared twelve N-alkylarylamines in yields of from 31 to 96%. The compounds prepared, yields, and derivatives used in their identification are shown in Table I. Four of these amines are new and their characterization is summarized in Table II. In all cases except the toluidines the yield of tertiary amine was negligible. No appreciable quantity of high boiling material was isolated except in the case of N-*n*-amylaniline where there was 1.5 cc. of a high boiling oil.

In the case of *p*-nitrotoluene appreciable quantities of the tertiary amines were formed: 53% of N,N-di-*n*-butyl-*p*-toluidine in the first butyraldehyde run and 34% of N,N-di-*n*-heptyl-*p*-toluidine in the heptaldehyde run. The latter is a new compound and is included in Table II. Since our constants for N,N-di-*n*-butyl-*p*-toluidine differ from those previously recorded, this compound is also in Table II.

Summary

A procedure has been developed for preparing N-alkylarylamines from aromatic nitro compounds in 31 to 96% yields by treating an alcoholic solution of the nitro compound and an aldehyde with hydrogen and Raney nickel in the presence of sodium acetate.

URBANA, ILLINOIS RECEIVED NOVEMBER 20, 1939

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[4] Adams and Voorhees, "Org. Syntheses," Coll. Vol. I, 1932, p. 53.

[5] Covert and Adkins, THIS JOURNAL, **54**, 4116 (1932).