alcohol and dried *in vacuo* over calcium chloride. The compound decomposed at 208–209° (corr.).

Anal. Calcd. for $C_{18}H_{22}O_4N_4$: N, 15.64. Found: N, 15.71.

Isolation of Barium Salts.—The gummy barium salt obtained in a sixty-hour oxidation of 25 g. of dulcitol was heated with charcoal and hot water which dissolved all but 0.5 g. of material. The solution was filtered and concentrated at reduced pressure and 55° to a thin sirup. Alcohol was added very slowly to precipitate the barium salt and the mixture then warmed on a steam-bath for one hour. The mixture was cooled and subjected to filtration. The precipitate was washed with alcohol and with ether. It was dried in a vacuum desiccator for one hour, followed by two hours in an oven at 100°.

Anal. Calcd. for barium *dl*-galactonate: Ba, 26.03; for barium *dl*-galacturonate, 26.24. Found: Ba, 26.43, 26.40.

The barium salt obtained by an identical procedure in a seventy-two hour oxidation contained 34.93% barium; calculated for barium mucate dihydrate, 35.80%. Neither salt decomposed at 250° and both gave naphthoresorcin tests.

Summary

A convenient method for the catalytic dehydrogenation of sugar alcohols was developed. Mannitol and dulcitol were the hexitols studied. The advantage of the method lies in the ease of controlling the amount of hexitol dehydrogenated. The results obtained indicate that the method is most satisfactory for aldose isolation in the case of alcohols which yield but one aldose or a *dl*-aldose when dehydrogenated.

Platinic oxide monohydrate was used as the source of the platinum catalyst. The oxide acts first as an oxidizing agent.

The effect of change in the possible variants was studied.

The course of the reaction was determined by a combination of isolation of products and analytical procedures. Mannitol was oxidized to *d*-mannose and *d*-fructose. *d*-Mannose was oxidized, in the main, to *d*-mannonic acid, *d*-mannuronic acid, and finally to *d*-mannosaccharic acid. The *d*-fructose was oxidized, in the main, to *d*-glucosone and 2-keto-*d*-mannonic acid. Other products were also formed in small amounts. The products with dulcitol were similar in nature.

d-Mannose was conveniently prepared by the catalytic dehydrogenation of mannitol. The *d*-mannose was isolated from the reaction mixtures as the phenylhydrazone and as the α-methyl-*d*-mannoside.

dl-Galactose was prepared similarly from dulcitol.

The catalytic dehydrogenation method gives promise of being satisfactory for the preparation of sugars like *dl*-erythrose from the alcohol, erythritol.

The Reductive Alkylation of Aniline

BY WILLIAM S. EMERSON AND PHILIP M. WALTERS

Although the reductive alkylation of amines is a well-known reaction,[1] it has found little application with primary aromatic amines. Clarke, Gillespie and Weisshaus,[1a] using formic acid as their reducing agent, methylated tribromoaniline with formaldehyde to give 77% of N,N-dimethyltribromoaniline. However, they obtained only polymers when aniline was used. While Skita and Keil[2] were able to prepare cyclohexylaniline from aniline and cyclohexanone in the presence of platinum and hydrogen, they did not mention their yield. Wallach[3] obtained di-*n*-amylaniline by heating valeraldehyde with phenylammonium formate, but he also gave no yield. The patent literature[4] contains references to the reductive alkylation of primary aromatic amines. In view of the importance of the reaction as a synthetic method, we felt that its possibilities with primary aromatic amines should be investigated.
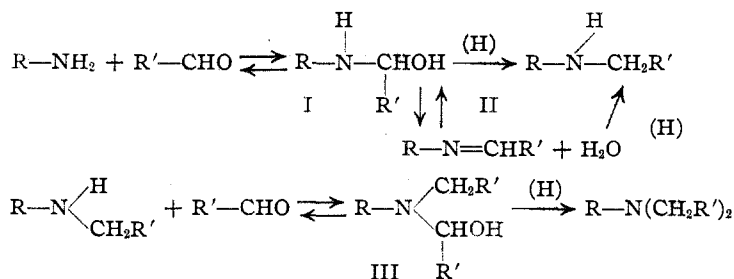
The mechanism of the reaction is probably the following

(1) (a) Clarke, Gillespie and Weisshaus, THIS JOURNAL, **55**, 4571 (1933); (b) Skita, Keil and Havemann, *Ber.*, **66**, 1400 (1933); (c) Forsee and Pollard, THIS JOURNAL, **57**, 1788 (1935).

(2) Skita and Keil, *Ber.*, **61**, 1682 (1928).

(3) Wallach, *Ann.*, **343**, 54 (1935).

(4) German Patents 376,013, 491,856, 503,113.

$$R—NH_2 + R'—CHO \rightleftarrows R—\underset{\underset{R'}{|}}{\overset{\overset{H}{|}}{N}}—CHOH \xrightarrow{(H)} R—\overset{\overset{H}{|}}{N}—CH_2R'$$

$$\text{I} \qquad \text{II} \qquad \uparrow (H)$$

$$R—N=CHR' + H_2O$$

$$R—N\overset{H}{\underset{CH_2R'}{\big\langle}} + R'—CHO \rightleftarrows R—N\overset{CH_2R'}{\underset{\underset{R'}{|}}{\big\langle}CHOH} \xrightarrow{(H)} R—N(CH_2R')_2$$

$$\text{III}$$

It cannot be said definitely that the amino alcohol (I) is reduced directly as suggested by Wallach[3] or that it is dehydrated to the Schiff base (II) before reduction. In either case the product would be the same, and it is quite possible the reaction follows both courses. Schiff bases have been reduced catalytically to secondary amines.[5]

In his study of the reaction between secondary aromatic amines and formaldehyde in the presence of hydrochloric acid, Wagner[6] found that the condensation product on immediate reduction gave the tertiary amine, while on reduction after a few hours of standing it gave the alkyltoluidine. Apparently the amino alcohol (III) which was first produced was dehydrated, forming the hydrochloride of the anhydro-benzyl alcohol as the intermediate in the rearrangement. Clarke, Gillespie and Weisshaus' results with aniline[1a] suggest that this intermediate or some rearrangement product of it polymerizes in the case of primary aromatic amines.

From a consideration of this mechanism, it was felt that in order for the reaction to be of value with primary aromatic amines, it would be necessary to employ a reducing agent powerful enough to reduce the amino alcohol (I) and a condensing agent mild enough to avoid dehydration and polymerization. For this purpose hydrogen and a catalyst seemed ideal. From a series of preliminary studies (Table I), it was found that Raney nickel as the reduction catalyst and sodium ace-

(5) (a) Skita and Keil, *Ber.*, **61**, 1452 (1928); (b) Buck, THIS JOURNAL, **53**, 2192 (1931).
(6) Wagner, *ibid.*, **55**, 724 (1933).

tate as the condensing agent gave the best results.

Using this general procedure, the reaction was extended to other alkylanilines. The method as developed gave N-alkylanilines from aniline and aldehydes in 47 to 65% yields. The results are summarized in Table II.

Experimental

General Procedure.—All of the experiments were carried out in an Adams machine[7] for catalytic reduction. The catalyst was either platinum oxide[8] or Raney nickel.[9] In each case 9.3 g. (0.1 mole) of aniline was dissolved in 150 cc. of ethyl alcohol and from 0.2 to 0.5 mole of aldehyde added. This mixture, along with the catalyst, was then placed in the machine and shaken at an initial hydrogen pressure of about 50 lb. (3 atm.). When no more gas was absorbed (usually from 0.3 to 0.4 mole was taken up), the catalyst was removed by filtration and the alcohol distilled on the steam-bath. After the remaining oil had been steam-distilled, the distillate or the residue (depending on the amine) was fractionated to obtain the product.

TABLE I

ANILINE PLUS ACETALDEHYDE

Expt.	Reduction catalyst	G.	Condensing agent	G.	Product	Yield, %
1	Platinum oxide	0.1	None		Aniline	
2	Platinum oxide	.1	Gl. AcOH	7 (0.11 mole)	Polymer	Quant.
3	Platinum oxide	.2	NaOAc	1	N-Ethylaniline	41
4	Raney nickel	58	None		Mixture of amines	
5	Raney nickel	58	0.1 N NaOH	1 cc.	N-Ethylaniline	25
					N,N-Diethylaniline	10
6	Raney nickel	58	NaOAc	1	N-Ethylaniline	58

TABLE II

ALKYLANILINES

Aniline	Yield, %	Derivative	M. p. of derivative, °C.	Recorded m. p., °C.
Ethyl	58	Picrate	133–135	132[10]
n-Propyl	52	Acetamide	48	47–48[11]
n-Butyl	47	p-Bromobenzene-sulfonamide	85–86	87[12]
n-Amyl	62	m-Nitrobenzene-sulfonamide	74–75	[13]
n-Heptyl	65	p-Bromobenzene-sulfonamide	115	[14]
Benzyl	50	Hydrochloride	210–212	214–216[15]

(7) Adams and Voorhees, "Organic Syntheses," Coll. Vol. I, 1932, p. 53.
(8) Adams, Voorhees and Shriner, *ibid.*, p. 452.
(9) Covert and Adkins, THIS JOURNAL, **54**, 4116 (1932).
(10) Vignon and Evieux, *Compt. rend.*, **147**, 67 (1908).
(11) Pictet and Crepieux, *Ber.*, **21**, 1106 (1888).
(12) Marvel and Smith, THIS JOURNAL, **45**, 2696 (1923).
(13) *Anal.* Calcd. for C₁₁H₂₀O₄N₃S: S, 9.19. Found: S, 9.22.
(14) N,n-heptylaniline is a new compound; b. p. 125–130° (30 mm.); d²⁰₂₀ 0.906; n²⁰D 1.5080; MD calcd. 63.3; MD Found 63.0. *Anal.* of p-bromobenzenesulfonamide. Calcd. for C₁₉H₂₄O₂NSBr: Br, 19.5. Found: Br, 19.7 (Parr bomb).
(15) Brand, *Ber.*, **42**, 3460 (1909).

Preliminary Experiments.—These were carried out using aniline and acetaldehyde with a variety of reduction and condensation catalysts. The results are summarized in Table I.

The products were identified by their physical properties and picrates.

Alkylanilines.—Six alkylanilines were prepared using the procedure developed in preliminary experiment 6. In Table II are summarized the compounds prepared, the yields, and the method of identification. In the case of the first four alkylanilines up to 10% of the tertiary amines were produced, but no tertiary amines were found in the case of N,n-heptylaniline and N-benzylaniline. The re-duction mixture always contained some aniline indicating the equation given above is reversible. This probably accounts for the fact that the yields range from 47 to 65%.

Summary

A procedure has been developed for the reductive alkylation of primary aromatic amines, using aldehydes in the presence of Raney nickel, hydrogen, and sodium acetate. By this method six alkylanilines have been synthesized in 47 to 65% yields.
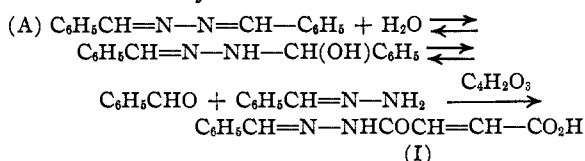
URBANA, ILL.   RECEIVED JUNE 22, 1938

The Reaction of Acid Anhydrides with Anils

BY H. R. SNYDER, R. H. LEVIN AND P. F. WILEY

Conjugated systems of the type —CH=N—N=CH— have not been shown to undergo the Diels–Alder condensation, but observations have been reported[1,2] which suggest that this type of reaction might be brought about under proper conditions. A study of the reaction between benzalazine and maleic anhydride was undertaken to test this idea. Heterocyclic compounds were not isolated, but the study has revealed certain facts which are of interest in connection with the general question of the reaction between acid anhydrides and anils.

When a solution of benzalazine and maleic anhydride in ordinary ether was refluxed, benzalmaleinhydrazine (I) and benzaldehyde were slowly formed. The use of ether containing dissolved water resulted in more rapid formation of the same products. With anhydrous ether solutions only a trace of benzalmaleinhydrazine was produced. The reaction therefore appears due to hydrolysis of benzalazine followed by reaction with maleic anhydride.
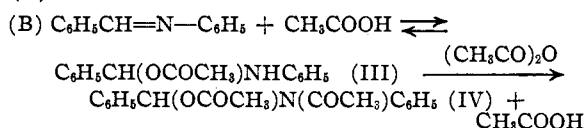
(A) $C_6H_5CH=N—N=CH—C_6H_5 + H_2O \rightleftharpoons$
$C_6H_5CH=N—NH—CH(OH)C_6H_5 \rightleftharpoons$

$C_6H_5CHO + C_6H_5CH=N—NH_2 \xrightarrow{C_4H_2O_3}$
$C_6H_5CH=N—NHCOCH=CH—CO_2H$
(I)

Ekeley and Lefforge[3] recently reported the displacement of one or both of the benzal groups of benzalazine by treatment with acetic anhydride. By analogy with the previous interpretation of the reaction of acetic anhydride with anils,[4] they assumed the initial reaction to be the addition of acetic anhydride yielding C_6H_5-CH=NN(COCH_3)CH(C_6H_5)OCOCH_3$ (II). La Parola[5] used this mechanism to account for the reaction of maleic anhydride with anils in the presence of water. In the present investigation it has been found that the rate of formation of the supposed addition product from benzalaniline and acetic anhydride is considerably increased when small amounts of acetic acid are added. The primary reaction, contrary to the assumption of Ekeley and Lefforge, is therefore addition of acetic acid. In the second step a molecule of acetic acid is liberated and may renew the cycle (B).

(B) $C_6H_5CH=N—C_6H_5 + CH_3COOH \rightleftharpoons$
$C_6H_5CH(OCOCH_3)NHC_6H_5$ (III) $\xrightarrow{(CH_3CO)_2O}$
$C_6H_5CH(OCOCH_3)N(COCH_3)C_6H_5$ (IV) $+$
CH_3COOH

Compounds formed by addition of acetic acid and thioacetic acid to anils have been reported.[6–8] These substances have been formulated as containing the groupings —N(COCH_3)CH(OH)— and —N(COCH_3)CH(SH)—. The cyclization of benzalanthranilic acid, discussed later in this report, indicates the alternate mode of addition (B).

(1) Wagner–Jauregg obtained small amounts of a crystalline substance thought to be a bis-pyrazolidine by refluxing a benzene solution of maleic anhydride and benzalazine [Ber., 63, 3219 (1930)].

(2) W. W. Moyer observed the formation of an apparently neutral solid by heating a mixture of benzalazine and maleic anhydride to the boiling point (private communication).

(3) Ekeley and Lefforge, THIS JOURNAL, 58, 562 (1936).

(4) Ekeley, et al., ibid., 34, 161 (1912); 35, 282 (1913); 36, 603 (1914); 37, 582 (1915); 44, 1756 (1922); Gazz. chim. ital., 62, 81 (1932).

(5) La Parola, ibid., 64, 919 (1934).

(6) Von Auwers, Ber., 50, 1599 (1917).

(7) Eibner, ibid., 34, 659 (1901).

(8) Galatis, ibid., 66, 1774 (1933).