cc.). After standing for forty-eight hours at 0°, the oily product was recovered by the same method as used for *Fraction Va* to give finally *Fraction Vaa;* yield, 0.72 g.

The liquors remaining from the separation of *Fraction V* were evaporated to dryness at reduced pressure. The residue was taken up in chloroform, precipitated into ligroin, filtered, washed with ligroin and dried to give *Fraction VI;* yield, 6.63 g.

Portions of *Fractions I* and *IIa* on analysis[10] for Klason lignin gave 4.3 and 2.4%, respectively, calculated on an acetyl-free basis. Methoxyl analyses[16] on these materials gave 18.2 and 18.6% methoxyl, respectively.

A portion (1.404 g.) of *Fraction VI* heated at 100° with 3% sulfuric acid (200 cc.) for twelve hours in a flask fitted with a reflux condenser gave a brown, amorphous precipitate and a bright yellow solution, the latter showing a positive test for furfural with aniline hydrochloride paper. The insoluble residue was filtered off, washed with hot distilled water and dried; yield, 0.2556 g. *Anal.* Found: OCH_3, 23.8%.

The estimations of methoxyl,[16] acetyl,[17] pentosan,[18] and viscosity[19] (0.100% solutions in chloroform at 25°) were carried out by standard methods. The data are given in Table I, the pentosan yield being taken as 1.71 times the percentage of furfural, and the chain length being deduced from the viscosity by means of the value[20] $K_m = 5.3 \times 10^{-4}$.

The composition of the fractions on an acetyl-free basis as shown in Table I was calculated from the results of the acetyl, methoxyl and pentosan analyses (arbitrarily assuming 23.0% methoxyl in lignin) exemplified for Fraction I as follows:

$$\frac{(0.85)(100)(100)}{(100\text{–}42.6)(23.0)} = 6.5\%\ \text{lignin}$$

$$\frac{(2.08)(100)}{(100 - 42.6)} = 3.6\%\ \text{pentosan}$$

$$100 - (6.5 + 3.6) = 89.9\%\ \text{cellulose}$$

Summary

1. Red oak wood meal previously extracted with alcohol–benzene followed by aqueous alkali was subjected to acetolysis at temperatures of 25, 28 and 35° using acetic anhydride, glacial acetic acid and a catalyst, sulfuric acid; the crude acetylated wood was isolated and investigated.

2. The solubility in chloroform of crude fully acetylated wood increases with the temperature of acetylation, indicating that the extent of acetolysis determines the degree of solubility of the crude acetylated wood in organic solvents.

3. The crude acetylated wood was separated by differential solubilities into the following fractions: (a) dioxane insoluble; (b) dioxane–chloroform insoluble, and (c) dioxane insoluble–chloroform soluble. The dioxane soluble material, using the Schulz re-precipitation technique with increasing methanol to dioxane ratios, was divided into six fractions. Methoxyl, acetyl, pentosan content and yield of the several fractions were determined.

4. Methoxyl-containing substances, apparently lignin, were retained in the dioxane–chloroform insoluble fraction and also in certain dioxane soluble fractions in spite of numerous attempts to remove such materials from both the insoluble and soluble fractions.

5. The results are in apparent harmony with the concept of the reaction as one of acetolysis of intercombined cell wall constituents, the latter involving perhaps a general combination between the lignin and both pentosans and cellulose. Not all these three latter products can be thus united.

MONTREAL, CANADA RECEIVED SEPTEMBER 1, 1939

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(16) Vieböck and Schwappach, *Ber.*, **63**, 2818 (1930).

(17) Friedrich and Rapoport, *Biochem. Z.*, **251**, 432 (1932).

(18) (a) Powell and Whittaker, *J. Soc. Chem. Ind.*, **43**, 36T (1924); (b) see also Kline and Acree, *Bur. Standards J. Research*, **8**, 25 (1932).

(19) Fordyce and Hibbert, THIS JOURNAL, **61**, 1912 (1939).

(20) Staudinger and Daumiller, *Ann.*, **529**, 219 (1937).

[CONTRIBUTION FROM THE ORGANIC CHEMICAL LABORATORY OF THE UNIVERSITY OF FLORIDA]

Reactions of Aldehydes with Amines. I. With *o*-Aminophenol

BY F. G. SINGLETON AND C. B. POLLARD

In an investigation being undertaken in this Laboratory it became necessary to prepare a series of azomethine derivatives in which *o*-aminophenol constituted the amine portion of the molecule. A search of the literature revealed several discrepancies. Levi[1] states that only *p*-aminophenol has been reported as condensing with aldehydes. We found twelve compounds from *o*-aminophenol listed. According to Möhlau and Adam,[2] the compounds obtained from the three nitrobenzaldehydes and *o*-aminophenol are addition compounds containing the group –NH-CHOH– instead of the usual –N=CH– group. They assumed that the presence of the nitro group inhibits the loss of water. Pope[3] found that the usual azomethine compound formed when meta- and para-nitrobenzaldehyde were

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(1) Levi, *Gazz. chim. ital.*, **59**, 544 (1929); *C. A.*, **24**, 351 (1930).

(2) Möhlau and Adam, *Chem. Zentr.*, **78**, 107 (1907).

(3) Pope, *J. Chem. Soc.*, **93**, 532 (1908).

TABLE I

ARYLIDENE DERIVATIVES OF *o*-AMINOPHENOL

Aldehyde	Appearance	Yield, %	M. p., cor., °C.	Formula	Analyses, % N Calcd.	Found
m-Tolualdehyde	Pale yellow leaflets	52	105	$C_{14}H_{13}NO$	6.63	6.67
p-Tolualdehyde	Pale yellow leaflets	81	108.5	$C_{14}H_{13}NO$	6.63	6.64
o-Chlorobenzaldehyde	Yellow leaflets	48	94	$C_{13}H_{10}NOCl$	6.05	6.15
2-Chloro-5-nitrobenzaldehyde	Bright yellow needles	56	164	$C_{13}H_9N_2O_3Cl$	10.12	10.12

condensed with *o*-aminophenol. Senier and Clarke[4] carried out the same reaction with *o*-nitrobenzaldehyde, obtaining the condensation product. Levi[1] studied the same reaction and arrived at a similar conclusion. While differences in melting points were reported, the spread was never more than four degrees. Beilstein apparently overlooked Möhlau and Adam's statement, as all of the compounds are listed as azomethines.

In order to clear up this situation the three nitrobenzaldehydes were allowed to react with *o*-aminophenol under five different sets of conditions: (1) in the cold without a solvent; (2) on the steam-bath without a solvent; (3) in hot alcohol; (4) in hot glacial acetic acid; (5) the hydrochloride of *o*-aminophenol used instead of the free base. For each of the three nitrobenzaldehydes all five procedures led to the same compound as evidenced by melting point and mixed melting point determinations. Nitrogen analysis gave the following results: *o*-nitrobenzylidene-*o*-aminophenol, m. p. 104.5°, 11.59% N; *m*-nitrobenzylidene-*o*-aminophenol, m. p. 132°, 11.54% N; *p*-nitrobenzylidene-*o*-aminophenol, m. p. 161°, 11.51% N. Since calculation shows 11.56% N for the azomethine compound and 10.77% N for the addition compound, this is considered positive proof that the compounds prepared are azomethines.

During the course of this work four new aldehyde condensation products of *o*-aminophenol have been prepared. These are described in Table I.

Summary

1. Attention is called to errors in the literature.

2. The reactions of *o*-aminophenol with the three nitrobenzaldehydes have been studied. Our results show the products of these reactions to be azomethine compounds.

3. Four new arylidene-*o*-aminophenols have been prepared and described.

GAINESVILLE, FLORIDA RECEIVED JUNE 10, 1940

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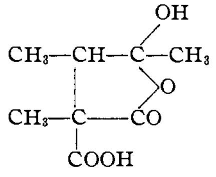
(4) Senier and Clarke, *J. Chem. Soc.*, **105**, 1917 (1914).

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

Structure of Monocrotaline. IV. Monocrotalic Acid[1]

BY ROGER ADAMS AND R. S. LONG[2]



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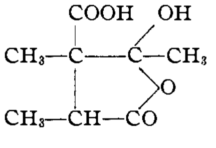

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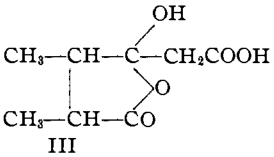
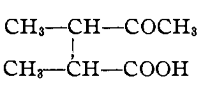


III



IV

Monocrotalic acid, obtained by catalytic hydrogenation of the alkaloid monocrotaline,[3] was assigned three possible structural formulas I, II and III of which I was selected as the most probable. Monocrotalic acid in the presence of alkali is decarboxylated to monocrotic acid (IV) which was postulated as dimethyllevulinic acid on the basis of its oxidation with sodium hypobromite to meso and racemic dimethylsuccinic acids. Dimethyllevulinic acid has been prepared previously; it is an oil, the *p*-nitrophenylhydrazone of which is reported as a solid.[4] However, no *p*-nitrophenylhydrazone of monocrotic acid could be obtained. α,β-Dimethyllevulinic acid, therefore,

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[1] For previous paper see Adams, Rogers and Long, THIS JOURNAL, **61**, 2822 (1939).

[2] An abstract of a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[3] Adams and Rogers, THIS JOURNAL, **61**, 2815 (1939).

[4] Willstätter and Brossa, *Ber.*, **44**, 2191 (1911).