

Short Communications

Nitrobenzene Oxidation of the Products Formed by the Condensation of Resorcinol with Lignin Models *

BENGT LEOPOLD

Organisk-kemiska Institutionen, Kungl. Tekniska Högskolan, Stockholm, Sweden

We have recently shown¹ that when lignin or lignin sulphonic acids are heated with resorcinol in acid solution, the yield of vanillin obtained on subsequent oxidation with nitrobenzene and alkali is decreased by up to 65 %. The present communication deals with the nitrobenzene oxidation of the products obtained from resorcinol and vanillyl alcohol² or the more complex ethers of guaiacyl glycol³, I and II — compounds which closely resemble lignin as regards their condensation with reactive phenols, sulphonation, etc.

Vanillyl alcohol reacted with resorcinol in hot acid solution, yielding a crystalline product which, on the basis of its analysis and analogies with similar compounds, is considered to have the structure III. Similarly, I and II yielded amorphous products which appeared to contain one molecule of resorcinol per guaiacyl residue. The three compounds all gave vanillin on oxidation with nitrobenzene and alkali, and the yields are given in Table 1, the yield of vanillin being expressed as a percentage of the yield obtained from the corresponding compound before heating with resorcinol and acid.

* Part X in the series Studies on Lignin. Part IX. *Svensk Kem. Tid.* 64 (1952) 1.

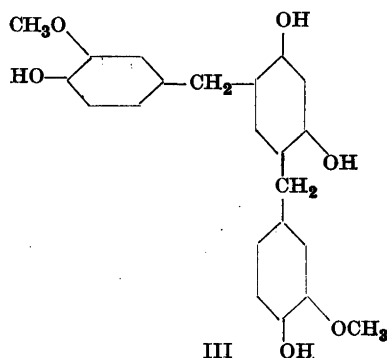
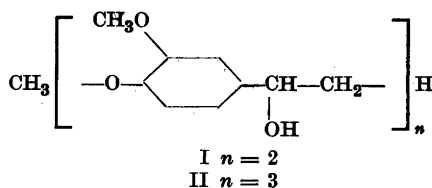


Table 1. Yield of vanillin from compounds heated with resorcinol and acid.

Condensation product of	Yield of vanillin %
Vanillyl alcohol	33
I	30
II	31

When resorcinol alone was oxidized, a 50 % yield of a black, insoluble product was obtained; no unchanged resorcinol could be recovered.

It is evident that prior treatment of the compounds investigated with resorcinol has a marked effect on the subsequent yield of vanillin. However, the formation of vanillin is not entirely suppressed by the

initial condensation, and it is probably more than a coincidence that the decrease brought about by the reaction with resorcinol is of the same order of magnitude as was found in the case of lignin and lignin sulphonic acids subjected to similar treatment.

EXPERIMENTAL. *4,6-Bis(3-methoxy-4-hydroxybenzyl)-resorcinol (III)*. A mixture of vanillyl alcohol (3 g) (conveniently synthesized by the reduction of vanillin, dissolved in dilute sodium hydroxide, with a 50 % excess of sodium borohydride), resorcinol (10 g), and 2 *N* hydrochloric acid (40 ml) was refluxed for one hour. After cooling, the solution was saturated with sodium chloride, and the precipitated oil (3 g) was dissolved in ether. The ether solution was dried over anhydrous sodium sulphate, and evaporated, and the residue was triturated with ether. A large amount of oily material was dissolved and the white powder obtained (0.5 g, 13 %) was repeatedly recrystallized from benzene, yielding transparent plates, m.p. 173–174°. Found OCH_3 , 16.5; required for $\text{C}_{20}\text{H}_{18}\text{O}_4$ (OCH_3)₂, OCH_3 , 16.2.

Condensation of I and II. A mixture of I or II (0.5 g), resorcinol (2 g), 50 % aqueous ethanol (20 ml), and conc. hydrochloric acid (4 ml) was refluxed for one hour. After cooling, water (75 ml) was added and the precipitate was filtered off, washed with water and chloroform and dried.

I: Found OCH_3 , 17.6; required for the condensation product with two molecules of resorcinol, OCH_3 , 17.6.

II: Found OCH_3 , 15.0; required for the condensation product with three molecules of resorcinol, OCH_3 , 15.7.

The nitrobenzene oxidations and vanillin determinations were carried out as described previously⁴.

The author expresses his thanks to Statens Tekniska Forskningsråd for financial support, and to Miss I. Malmström for skilful assistance.

1. Leopold, B. *Acta Chem. Scand.* 6 (1952) 55.
2. Lindgren, B. O. *Acta Chem. Scand.* 3 (1949) 1011.
3. Erdtman, H., and Leopold, B. *Acta Chem. Scand.* 3 (1949) 1358.
4. Leopold, B. *Acta Chem. Scand.* 4 (1950) 1523.

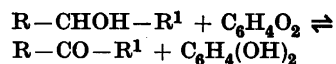
Received November 30, 1951.

On Quinone as Oxidising Agent in the Oppenauer-Oxidation

HENNING LUND

*Department of Organic Chemistry,
University of Technology, Copenhagen*

In his paper on the broad applicability of the Meerwein-Ponndorf reduction of carbonyl groups by means of aluminium *iso*-propanolate Lund in 1937¹ suggested the use of quinones for the opposite reaction: selective oxidation of $>\text{CHOH}$ groups to $>\text{CO}$. The suggestion was based upon the observation that quinone was rapidly reduced to quinol by aluminium *iso*-propanolate and the quinol was immediately precipitated as aluminium quinoate. It might therefore be expected that an alcohol would react quantitatively with formation and precipitation of aluminium quinoate, as the equilibrium



would be displaced practically completely in favour of the right hand side, because the quinol is removed quantitatively from the solution.

In 1941 Adkins and Franklin², apparently without knowledge of the paper cited above, have made use of this reaction on the assumption that the high oxidation potential of quinone as compared with that of the usual aldehydes and ketones would favour the oxidation of the corresponding alcohols.

The reaction, with the use of aluminium *t*-butanolate as catalyst, was now re-examined with the purpose of finding a suitable method for the oxidation of valuable alcohols to ketones, e.g. in the steroid group. A few ordinary alcohols were examined first and it was found that with a reasonable excess of quinone a practically complete conversion of alcohols into ketones could be accomplished.