

REACTIONS OF AROMATIC HYDROXY ALDEHYDES
WITH METALLIC SODIUM IN LIQUID AMMONIA. IV

V. M. Reznikov and V. F. Novitskii

UDC 547.565 + 549.927.2

In the products of the reductive degradation of the lignin of sphagnum moss with Na in liquid NH₃ we identified vanillin and p-hydroxybenzaldehyde by paper and gas-liquid chromatographies [1], and after this by the same methods we showed the presence of the hydroxy alcohols corresponding to them.

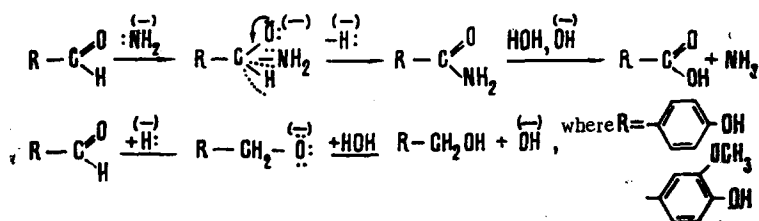
The aldehydes mentioned have never been reported among the phenolic products of decomposition in the literature on the reductive cleavage of lignins. At the same time, various authors have repeatedly found aldehydes among the products of the hydrolytic degradation of lignin [2-6]; however, their origin has not usually been discussed and has remained obscure. The presence of aromatic hydroxyaldehydes in the products of the reductive degradation of moss lignin is difficult to explain, since, even if it is assumed that they are present in the lignin in the form of individual structural fragments connected with the macromolecule by ether bonds, under the conditions of reductive degradation by Na in liquid ammonia the aromatic aldehydes should be reduced to the corresponding hydroxy alcohols.

In order to obtain an idea of the behavior of hydroxy aldehydes of the C₆-C₁ series during the reaction mentioned, we have treated vanillin and p-hydroxybenzaldehyde with Na and NH₃ as described in the literature [7]. Although the reaction was performed for seven days, part of the metallic sodium had not reacted in both vessels.

For the identification and quantitative analysis of the reduction products we separated them chemically by means of ascending chromatography in a thin layer of Al₂O₃ [absolute methanol-benzene (1.5:18) system; chromogenic agent: iodine vapor]. The qualitative and quantitative compositions of the reduction products of the aldehydes mentioned, and also the yields of the products of the reduction of the hydroxy aldehydes by Na in liquid NH₃ (in %) are given below:

Aldehyde	Initial aldehyde, g	Acid	Alcohol	Unchanged aldehyde	Losses
Vanillin	1,71	31,0	26,9	20,5	21,6
p-Hydroxybenzaldehyde	1,50	32,0	29,3	9,0	29,7

The detection among them, in addition to the initial aldehydes, of the hydroxy acids and hydroxy alcohols corresponding to them (in approximately equimolar amounts) shows that in liquid NH₃ the reduction of aromatic hydroxy aldehydes probably takes place by a disproportionation reaction the mechanism of which can be represented in the following way by analogy with the Cannizzaro reaction:



Up to the present time, it has been considered that the Cannizzaro reaction does not take place with hydroxy aldehydes [8]. However, in an anhydrous medium under the influence of such a strong nucleophile as the amide ion it evidently becomes possible. We assume that the saponification of the amide with trans-

S. M. Kirov Belorussian Technological Institute, Institute of Physical Organic Chemistry, Academy of Sciences of the Belorussian SSR. Translated from *Khimiya Prirodnikh Soedinenii*, No. 2, pp. 283-284, March-April, 1975. Original article submitted November 25, 1974.

©1976 Plenum Publishing Corporation, 227 West 17th Street, New York, N.Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$15.00.

formation into a carboxylic acid takes place at the stage of the decomposition of the organometallic compound by moist ether and water; however, this hypothesis requires confirmation.

LITERATURE CITED

1. V. M. Reznikov and V. F. Novitskii, *Khim. Prirodn. Soedin.*, No. 1 (1975).
2. A. Sakakibara and N. Nakajama, *J. Japan Wood Res. Soc.*, 7, 13 (1961).
3. E. Adler and J. Morton, *Acta Chem. Scand.*, 15, 370 (1961).
4. V. M. Reznikov and G. D. Ponurov, *Zh. Prikl. Khim.*, 39, 381 (1966).
5. E. Adler, K. Lundquist, and J. E. Mikshe, *Advan. Chem. Ser.*, 59, 122 (1966).
6. K. V. Sarkanen and A. A. Ludwig, *Lignins*, Wiley-Interscience, New York (1971), p. 228.
7. A. F. Semechkina and N. N. Shorygina, *Izv. Akad. Nauk SSSR, Ser. Khim. Nauk*, No. 5, 884 (1964).
8. R. Adams (editor), *Organic Reactions [Russian translation]*, Vol. 2, Moscow (1950).