Tetrahedron Letters, Vol.22, No.19, pp 1841 - 1842, 1981
Printed in Great Britain

0040-4039/81/191841-02$02.00/0
©1981 Pergamon Press Ltd.

INTRODUCTION OF ONE-CARBON UNITS DURING ANTHRAQUINONE-CATALYSED PULPING OF WOOD

Donald W. Cameron* and Eva L. Samuel

Department of Organic Chemistry, University of Melbourne, Parkville, Vic., 3052, Australia.

Summary. Anthraquinone- and tetrahydroanthraquinone-catalysed pulping of Pinus radiata has given 10-methyl-9-anthrone (2) and derivatives (3) and (4), introduction of the carbon substituent involving carbohydrate constituents of the wood.

Probably the most striking chemical contribution to paper making in recent years has been recognition that anthraquinone derivatives are useful catalysts for wood pulping. Their redox properties lead both to stabilisation of polysaccharides and to delignification.[1] Their detailed role is under intensive study, complicated by the chemical heterogeneity of wood and the severity of pulping conditions.

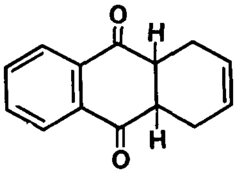
We[2] and others[3] have earlier shown that in such processes part of the catalyst reacts with lignin constituents to give aryl benzanthrones. The present paper provides evidence for covalent bonding to carbohydrate also. Initial experiments were carried out with tetrahydroanthraquinone (1). This is as effective in pulping as anthraquinone itself[4] but it is more convenient for laboratory work in not requiring in situ reduction.

Compound (1) was heated at 180° for 1 hour in aqueous sodium sulphite (4.8%) and sodium bicarbonate (1.2%) ("neutral sulphite conditions"). The chloroform-extractables gave a mixture of anthraquinone (10%) and 9-anthrone (70%), the latter stoichiometrically a dehydration product of (1) formed under the severe conditions.[5] However cooking Pinus radiata chips with (1) (0.1% of the dry wood) under the same conditions gave a new product 10-methyl-9-anthrone (2)[6] [10% based on (1)], m.m.p. 65°, δ_{CH_3} ($CDCl_3$) 1.60 (d), $\delta_{CH(10)}$ 4.30 (q) (J 7.3Hz). None was formed in the absence of (1).

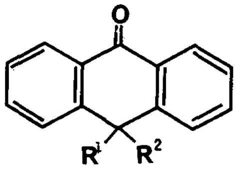
The origin of unexpected C-methylation leading to (2) was explored by heating small quantities of (1) (10% w/w)with chemical models related to wood constituents under neutral sulphite conditions. Thus reaction with glucose also gave (2) [20% based on (1)] as did other carbohydrates mannose (17%), xylose (15%), glyceraldehyde (14%) and powdered cellulose (9%). On the other hand sorbitol, milled wood lignin,[7] and lignin - related materials coniferyl alcohol, guaiacol, vanillin, vanillyl alcohol and acetovanillone were comparatively ineffective. Reaction of (1) with D-[1-^{14}C]-glucose gave (2) with incorporation of activity (87%), all of which was lost on removal of the methyl group by chromic oxidation to anthraquinone.

These data indicate derivation of the C-methyl group by condensation of C-10 of the catalyst onto the reducing carbon of carbohydrate, followed by fragmentation. The course of the latter process is under investigation, it being noted that both 9-anthrone and 10-methylene-9-anthrone (3)[8] also afforded (2) (17, 22% respectively) when reacted similarly with glucose.

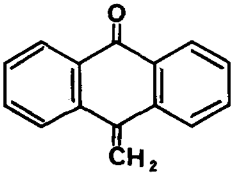
Introduction of one-carbon units has also been observed in soda pulping (aqueous 1 M-sodium hydroxide at 170° for 2 hours). Pinus radiata chips were cooked with catalytic proportions of anthraquinone (0.5% w/w). Rapid extraction of the spent liquors with chloroform to minimize exposure to air gave aryl benzanthrones[2,3] as before but little recovered



1



	R^1	R^2
2	Me	H
4	Me	O)$_2$
5	Me	OOH



3

anthraquinone. Instead there was a mixture of 10-methylene-9-anthrone (3) (10% based on anthraquinone) δ_{CH_2} 6.35 and a new product (10%). The former has recently also been observed by other workers.[9] The latter, $C_{30}H_{22}O_4$, m.p. 225°, was formulated as the peroxy dimer (4), δ_{CH_3} 1.34 (s). Its electronic absorption was similar to that of (2), from which it was independently synthesised by treatment with alkaline potassium permanganate (42%).

Whilst the precursors of compounds (3) and (4) have not been identified, the formation of these products is consistent with alkylation and oxidation. The former process is presumably analogous to the formation of (2), given the redox interactions known to occur under the reaction conditions.[1] The latter forms part of those interactions. Thus compound (2) in aqueous sodium hydroxide was rapidly autoxidised at 60°, via the anthranolate ion, to give the known hydroperoxide (5)[10] (90%) m.p. 161°. Heating either (5) or (2) under soda cooking conditions with an excess of glucose gave the peroxide (4) (32, 35% respectively).

We are grateful to Australian Paper Manufacturers Limited for helpful discussions and for financial support.

References

1. e.g., L. Löwendahl and O. Samuelson, Tappi, 1978, 61(2), 19; S. Lindenfors, Sven. Papperstidn., 1980, 83, 165.
2. D. W. Cameron and E. L. Samuel, Tetrahedron Lett., 1979, 3035.
3. T. J. Fullerton and S. P. Ahern, J.Chem.Soc. Chem.Commun., 1979, 457.
4. A. Satoh, J. Nakano, A. Ishizu, Y. Nomura, and M. Nakamura, Kami Pa Gikyoshi, 1979, 33, 410 (Chem. Abstr., 1979, 91, 75906n).
5. S. Nakatani, R. Matsuura, K. Nagaoka, and K. Hioki, Brit., 1,540,192 (Chem. Abstr., 1979, 91, 58706e).
6. H. Heymann and L. Trowbridge, J.Am.Chem.Soc., 1950, 72, 84.
7. D. E. Bland, Holzforschung, 1961, 15, 102.
8. W. H. Starnes, J.Org.Chem., 1970, 35, 1974.
9. B. F. Hrutfiord, W. T. McKean, and D. Hanson, Paper No. 115 presented at the Cellulose Paper and Textile Division, ACS/CSJ Chemical Conference, Honolulu, April 2-6, 1979.
10. J. Rigaudy, N. K. Cuong, J. Albouy, and A. Chétrit, Tetrahedron Lett., 1976, 1089.

(Received in UK 20 February 1981)