

Acid Degradation of Lignin

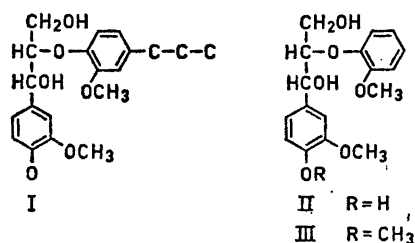
I. The Formation of Ketones of the Guaiacylpropane Series

KNUT LUNDQUIST and KENNETH HEDLUND

Department of Organic Chemistry, Chalmers Institute of Technology and University of Göteborg, Göteborg, Sweden

The behaviour of 1-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone (V) and its isomer, 2-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone (VI), on acidolysis has been investigated. It is shown that an equilibrium between these ketols is established. A method of preparing V from VI is based on this finding.

Acid-catalyzed degradation ("acidolysis", *i.e.* refluxing with 0.2 M hydrogen chloride in dioxane-water 9:1) has proved to be useful in the elucidation of the structure of lignin.¹⁻⁸ The presence of elements of the arylglycerol- β -aryl ether type (I) was concluded, *inter alia*, from the finding that model compound II as well as spruce Björkman lignin on 48 h acidolysis gave the ketones VI, VII, and VIII.¹ These ketones were also found to be formed on



acidolysis of ketol IV,² as could be expected from the behaviour of the latter compound on "ethanolysis" (48 h refluxing with ethanol containing 2 % hydrogen chloride).⁹ The formation of comparatively large amounts of ketol IV on brief acidolysis of model compound II as well as of spruce lignin has recently been demonstrated.²⁻⁴ These results are in agreement with the previously expressed view¹ that ketol IV is an intermediate in the acidolytic degradation of elements of type I in lignin to compounds VI–VIII.

If ketol VI was subjected to acidolysis for 1 h, paper chromatography of the reaction mixture showed the presence of ketol V in addition to unchanged starting material. Similar treatment of ketol V also gave a mixture of both ketols. Reaction mixtures obtained on prolonged acidolysis (4 and 10 h) of either V or VI contained VII and VIII in addition to the two ketols. The appearance of VI (λ_{\max} 278 $m\mu$ and 305 $m\mu$) on acidolysis of V (λ_{\max} 281 $m\mu$) and the decrease in the amount of VI on acidolysis of this ketol were followed by UV spectroscopic examination. After a reaction time of only 0.5 h, the absorption curves of both acidolysis mixtures were indistinguishable. These results prove that an equilibrium between the isomeric ketols V and VI is established. The UV examinations indicate that the equilibrium mixture contains the ketols V and VI in a ratio of 1:4. (For the isolation of ketol V from the equilibrium mixture, see below.)

Černý¹⁶ recently subjected ketol VI to heating with methanolic hydrochloric acid and found, by IR examination, that one of the fractions obtained by paper chromatography was a mixture of the methyl ether of ketol V (IX, OCH₃ instead of OC₂H₅) and ketone VII. This is in accord with the results reported above.

The ketol ether IX obtained on ethanolysis of wood (Hibbert *et al.*¹⁰) as well as of ketol IV (Gardner⁹) was suggested by these authors to arise by allylic rearrangement of the enol form IVa and subsequent enol-keto rearrangement to give ketol V, the latter being finally etherified to yield IX (R = 4-hydroxy-3-methoxyphenyl) : $R-CH_2-CO-CH_2OH(IV) \rightleftharpoons R-CH=C(OH)-CH_2OH(IVa) \rightleftharpoons R-CH(OH)-CH(OH)=CH_2 \rightleftharpoons R-CH(OH)-CO-CH_3(V)$. Thus, the overall reaction $IV \rightleftharpoons V$ was assumed to be reversible. However, the occurrence of the reaction $V \rightarrow IV$ has not been demonstrated; in fact, in the present acidolysis experiments with ketols V and VI, no formation of ketol IV was detected.

Heating equivalent amounts of products VII and VIII under acidolysis conditions did not result in any formation of ketols V and VI. Thus, the formation of compounds VII and VIII, which were suggested by Hibbert^{13,14} to be the products of an oxidoreduction of V, is irreversible. (Regarding the mechanism of this reaction, see further Ref. 8.)

The relationships between the lignin acidolysis products IV–VIII indicated by the results reported above are summarized in Fig. 1. Since ketol IV on acidolysis was found to disappear slowly,^{2,8} step $IV \rightarrow V$ is a slow reaction. Similarly, the formation of VII and VIII proceeds at a low rate. The ketol equilibrium $V \rightleftharpoons VI$, however, is established comparatively rapidly.

Preparation of 1-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone (V)

With the exception of V, Hibbert and co-workers (*cf.* Ref. 17 and preceding work) synthesized all the ketones of the guaiacylpropane series which they obtained as products of or postulated as intermediates in the ethanolysis of spruce wood. The 1-ethyl ether¹⁸ and the diacetate¹³ of V had been prepared, but attempts to deacetylate the latter product provided the rearrange-

ment product VI rather than V.^{14,19} As late as 1962, Gardner, Henderson and MacLean¹⁵ reported the preparation of ketol V in a yield of 9 % by catalytic hydrogenation of the diketone VIII, the isomeric ketol VI being formed as the major product.

The reversible isomerisation $V \rightleftharpoons VI$ reported above offered a further possibility to prepare ketol V. From a reaction mixture obtained after 2 h acidolysis of ketol VI, ketol V could be separated in a yield of 10 %.

Whereas Gardner *et al.*¹⁵ report m.p. 53–54°, our product had m.p. 87–88°. Furthermore, the infrared data (KBr) given by Gardner *et al.*¹⁵ differed in part from those obtained for the acidolysis product. However, the identity of our product with ketol V was established by elemental analysis and by preparing the diacetate according to Gardner *et al.*,¹⁵ which was identical by mixed m.p. and IR spectrum with a sample of the diacetate of V obtained according to Mitchell and Hibbert.¹³ Moreover, our product showed the same behaviour as that of Gardner *et al.*¹⁵ with respect to R_F values as well as the colour reactions with N-chloroquinonimine and diazotized sulphanilic acid. Thus, the chemical identity of the two products with m.p. 53–54° and 87–88° is obvious.

Ketol V with m.p. 87–88° was also obtained in a preparation by the method of Gardner *et al.*¹⁵

EXPERIMENTAL

The dioxane used was purified according to Vogel.²⁰

The ketols IV and XI, previously synthesized by Hibbert and co-workers,^{17,12} were prepared by brief acidolysis of guaiacylglycerol and veratrylglycerol, respectively.^{2,4b} The remaining ketones of the guaiacylpropane and the veratrylpropane series used in this work, with the exception of 1-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone (V) (see the present paper), were obtained according to Hibbert and co-workers (Ref. 21 and preceding work).

For *paper chromatography* use was made of the system described by Kratzl and Schweers.²² For phenolic substances, diazotized sulphanilic acid in 2 % aqueous sodium carbonate was used as a spraying agent. R_F values: IV, 0.04 (red-violet); V, 0.10 (orange); VI, 0.17 (orange-red); VII, 0.56 (red-violet) and VIII, 0.64 (orange-red). Ketol V could also be made visible as a blue spot on spraying with an ethanolic solution of 2,6-dibromo-N-chloroquinonimine followed by dilute aqueous sodium hydroxide. Veratryl compounds were detected by spraying first with a 0.5 % solution of 2,4-dinitrophenylhydrazine in 1 M hydrochloric acid and, after air-drying over night, with 0.5 M aqueous potassium hydroxide. The spots appeared on a gray background. R_F values: XI, 0.28 (brown with a bluish ring); XII, 0.53 (light red); XIII, 0.64 (purple).

Analytical acidolysis experiments. One per cent solutions of the compounds in dioxane-water (9:1) containing 0.2 M hydrogen chloride were refluxed under nitrogen. After the desired time a cooled 1 ml sample of the solution was neutralized with 0.4 M sodium bicarbonate solution and extracted with chloroform. After drying over anhydrous sodium sulphate the solvent was removed by film evaporation. A solution of the residue in 1 ml ethanol was used for paper chromatographic examination.

For UV examination of the acidolysis of ketols V and VI 15.2 mg of either compound was refluxed in 100 ml of the acidolysis mixture. After the desired time 10 ml of a cooled sample of the reaction mixture were neutralized to pH 5–6 with 0.4 M bicarbonate solution, and after dilution to 100 ml with water the UV spectrum of the solution was recorded.

1-Hydroxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone (V). A solution of 5 g of 2-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone (VI)²³ in 200 ml of 0.2 M hydrogen chloride in dioxane-water (9:1) was refluxed for 2 h (nitrogen atmosphere). The

reaction mixture was neutralized with 0.4 M sodium bicarbonate solution and extracted with a total of 600 ml of chloroform. The extract was dried over anhydrous sodium sulphate and the solvent removed in a film evaporator. The remaining oil was dissolved in 175 ml of ether and the separation of V from this solution accomplished according to the directions given by Gardner *et al.*¹⁵ A colourless oil (0.5 g) was obtained, which crystallized (m.p. 81–85°). Recrystallisation from benzene gave rhombical plates, m.p. 87–88°. (Found: C 61.21; H 6.28; OCH₃ 15.74. Calc. for C₁₀H₁₂O₄: C 61.22; H 6.16; OCH₃ 15.82). The IR spectrum (KBr), recorded on a Beckman IR-9 instrument, showed a band at 1725 cm⁻¹ (unconjugated carbonyl).

Acknowledgements. The authors are greatly indebted to professor E. Adler for his kind interest in this work. Financial aid from the *Swedish Council for Applied Research* is gratefully acknowledged.

REFERENCES

1. Adler, E., Pepper, J. M. and Eriksoo, E. *Ind. Eng. Chem.* **49** (1957) 1391.
2. Adler, E. *Paper and Timber (Finland)* **43** (1961) 643; Lundgren, R. *Ibid.* p. 670, and unpublished results.
3. Lundquist, K. *Acta Chem. Scand.* **16** (1962) 2303.
4. Lundquist, K. a) *Svensk Kem. Tidskr.* **75** (1963) 423; b) unpublished results.
5. Adler, E. and Lundquist, K. *Acta Chem. Scand.* **16** (1963) 13.
6. Lundquist, K. *Acta Chem. Scand.* **18** (1964) 1316.
7. Lundquist, K. and Miksche, G. *Tetrahedron Letters* **1965** 2131.
8. Adler, E., Lundquist, K. and Miksche, G. *Advan. Chem. Ser.* **59** (1966) 22.
9. Gardner, J. A. F. *Can. J. Chem.* **32** (1954) 532.
10. West, E., MacInnes, A. S. and Hibbert, H. *J. Am. Chem. Soc.* **65** (1943) 1187.
11. Gardner, J. A. F. and MacLean, H. *Can. J. Chem.* **43** (1965) 2421.
12. Fisher, H. E., Kulka, M. and Hibbert, H. *J. Am. Chem. Soc.* **66** (1944) 598.
13. Mitchell, L. and Hibbert, H. *J. Am. Chem. Soc.* **66** (1944) 602.
14. Mitchell, L., Evans, T. H. and Hibbert, H. *J. Am. Chem. Soc.* **66** (1944) 604.
15. Gardner, J. A. F., Henderson, D. W. and MacLean, H. *Can. J. Chem.* **40** (1962) 1672.
16. Černý, M. *Chem. Zvesti* **20** (1966) 132.
17. Fisher, H. E. and Hibbert, H. *J. Am. Chem. Soc.* **69** (1947) 1208.
18. Kulka, M. and Hibbert, H. *J. Am. Chem. Soc.* **65** (1943) 1185.
19. Wacek, A. and Horak, I. *Monatsh.* **77** (1947) 18.
20. Vogel, A. I. *Practical Organic Chemistry*, 2nd Ed., London 1954, p. 175.
21. Eastham, A. M., Fisher, H. E., Kulka, M. and Hibbert, H. *J. Am. Chem. Soc.* **69** (1944) 26.
22. Kratzl, K. and Schweers, W. *Monatsh.* **85** (1954) 1046.
23. Cramer, A. B., Hunter, J. M. and Hibbert, H. *J. Am. Chem. Soc.* **61** (1939) 2204.

Received April 1, 1967.