[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

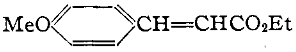
A Synthesis of 3-(4-Hydroxycyclohexyl)-propanol-1, a Product of the Hydrogenation of Lignin

BY EVERETT BOWDEN AND HOMER ADKINS

One of the chief products obtained in the hydrogenation of a certain sample of hardwood lignin was a glycol, $C_9H_{18}O$, to which was tentatively assigned the structure VII.[1] The correctness of this formulation has now been confirmed by synthesis. The preferred synthesis is as follows.

Anisaldehyde, I, was condensed with ethyl acetate under the influence of sodium to give *p*-methoxycinnamic ester, II; the latter was hydrogenated over Raney nickel to β-(*p*-methoxyphenyl)-propionic ester, III; the latter was hydrolyzed to β-(*p*-hydroxyphenyl)-propionic acid, IV, under the influence of hydroiodic acid. The acid was esterified, the benzenoid ring hydrogenated over Raney nickel to give the corresponding cyclohexane compound, VI, which was then hydrogenated over copper chromite to 3-(4-hydroxylcyclohexyl)-propanol-1, VII. The glycol was then oxidized to the solid β-(4-ketocyclohexyl)-propionic acid, VIII. The 2,4-dinitrophenylhydrazone, IX, of the keto acid was also prepared. A comparison of the physical properties of VII, VIII and IX, as obtained by synthesis, with those of the corresponding compounds obtained from lignin established the identity of the latter group of products.


I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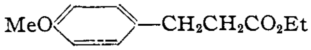
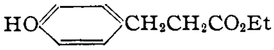

III


IV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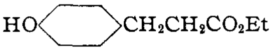
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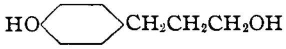
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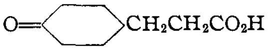
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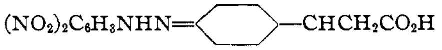
IX

Ethyl *p*-Methoxycinnamate.—Anisaldehyde (106 g.), sodium (30 g.) and ethyl acetate (460 ml.) were allowed to react according to a standard method[2] except that the reaction mixture was kept below 0° before acidifying. The product was fractionated twice through a Widmer column at 132° (1 mm.). The yield was 133 g. (82%), m. p. 48–50° from methanol.

Ethyl *p*-Methoxyphenylpropionate.—The *p*-methoxycinnamic ester (103 g.) in 20 ml. of ethanol was hydrogenated quantitatively to III over Raney nickel within five minutes at 80–90° under 100 atm. of hydrogen.

β-(*p*-Hydroxyphenyl)-propionic Acid.—The ester III (78 g.) was placed with 342 g. of hydroiodic acid (d. 1.7) in a 500-ml. flask under an Allihn condenser. The top of the latter was connected to a condenser set for downward distillation. The reaction mixture was heated gently to drive off the alkyl halides formed in the reaction and finally boiled. The mixture of iodides distilling weighed 108 g. The desired acid separated out of the cold reaction mixture and was filtered off. After washing with cold water there was obtained 60 g. of a salmon-colored well-crystallized solid, m. p. 122°. A small portion recrystallized from water had a m. p. of 128–129°.

Ethyl β-(*p*-Hydroxylphenyl)-propionate.—The acid (75 g.) was refluxed with 500 ml. of ethanol containing 1 ml. of sulfuric acid. The apparatus was so arranged that the alcohol returning from the reflux passed through dehydrated magnesium sulfate. After about twenty-four hours of refluxing, most of the alcohol was removed by distillation, and the residue diluted with water. The ester layer was washed with sodium carbonate solution. The aqueous solution was saturated with salt and extracted with ether. The combined ester and ether was dried over sodium sulfate. Upon fractionation through a Widmer column there was obtained 80 g. of ester, b. p. 140–141° (0.3 mm.).

p-Hydroxyphenylpropionic acid was also prepared by condensing anisaldehyde (100 g.) with malonic ester (120 g.) under the influence of piperidine (5 ml.) to give anisalidene malonic ester (120 g., b. p. 167° (0.3 mm.), a 58% yield), hydrogenating the alkene linkage over Raney nickel at 100° to *p*-methoxybenzylmalonic ester, and hydrolyzing and decarboxylating the latter to the desired acid. This process is not so satisfactory as the synthesis using anisaldehyde and ethyl acetate.

Ethyl β-(4-Hydroxycyclohexyl)-propionate.—The ester V (78 g.) in 20 ml. of ethanol was hydrogenated over Raney nickel at 175–200° within three hours under 150 atm. of hydrogen. The saturated ester, VI, b. p. 102–103° (0.5 mm.), was obtained in a yield of 77 g.

3-(4-Hydroxycyclohexyl)-propanol-1.—The ester, VI, (57 g.) in 20 ml. of ethanol was hydrogenated within five hours over copper chromite at 250° under 200 atm. of hydrogen. The glycol (42 g.) (93%), b. p. 125–127° (1 mm.), was obtained. The glycol crystallized on standing just as did the sample prepared from lignin.

β-(4-Ketocyclohexyl)-propionic acid and its 2,4-dinitrophenylhydrazone.—The glycol, VII, was oxidized with chromic acid to the keto acid (m. p. 60–65°), VIII, as previously described,[1] and also with permanganate. The neu-

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[1] Harris, D'Ianni and Adkins, THIS JOURNAL, **60**, 1467 (1938).

[2] "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, New York, N. Y., 1932, p. 246.

TABLE I

PHYSICAL PROPERTIES AND ANALYTICAL DATA

Compound	B. p. or m. p.	d^{25}_{25}	$n^{25}\mathrm{D}$	Analyses, %			
				Carbon		Hydrogen	
				Calcd.	Found	Calcd.	Found
II Ethyl *p*-methoxycinnamate	B. 132° (1 mm.)	....	....	69.88	69.82	6.84	7.06
III Ethyl β-(*p*-methoxyphenyl)-propionate	B. 103° (0.1)	1.0628	1.5016	69.19	69.17	7.72	7.72
IV β-(*p*-Methoxyphenyl)-propionic acid	M. 128–129°	....	....	65.04	64.83	6.07	6.08
V Ethyl β-(*p*-hydroxyphenyl)-propionate	B. 140° (0.2)	1.1083	1.5153	68.02	67.85	7.26	7.51
VI Ethyl β-(4-hydroxycyclohexyl)-propionate	B. 102–103° (0.2)	1.0309	1.5661	65.96	65.78	10.06	9.96
IX 2,4-Dinitrodiphenylhydrazone of β-(4-ketocyclohexyl)-propionic acid	M. 125–127°	....	....			N, 16.00	16.08
p-Methoxybenzylmalonic ester	B. 138° (0.1)	1.1055	1.4923	64.27	64.31	7.18	7.3

tral equivalent of the sample of keto acid was 174, corresponding to a calcd. molecular weight of 170.

The keto acid, VII, (2 g.) in 10 ml. of hot water was mixed with 2,4-dinitrophenylhydrazine (3 g.) in 15 ml. of hot water. The mixture was boiled under a reflux while 3–6 ml. of concd. hydrochloric acid was added. The solid which separated when the solution was cooled was then dissolved in hot dioxane and precipitated by the addition of hot water. The m. p. of the hydrazone was 125–127°. The hydrazone crystallized from ethanol showed a m. p. 90–94°. A hydrazone similarly prepared from the sample of the keto acid *ex* lignin had a m. p. of 90–93°. The mixed melting point was 90–94°. These hydrazones crystallized from ethanol are apparently derived from the ethyl ester of the keto acid, VIII.

Summary

The glycol 3-(4-hydroxycyclohexyl)-propanol-1 has been prepared by a series of reactions from anisaldehyde, and has been shown to be identical with the chief product of the hydrogenation of a sample of lignin derived from the hard wood aspen by the methanol process.

MADISON, WISCONSIN

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An Electron Diffraction Investigation of the Structure of Propylene Bromide

BY VERNER SCHOMAKER AND D. P. STEVENSON

In a recent communication[1] we presented the results of an electron diffraction investigation of the structures of the racemic and *meso*-2,3-dibromobutanes. We report here the results of a similar investigation of propylene bromide.

The sample (b. p. 42° (15 mm.)) of propylene bromide used was fractionally distilled from a large batch prepared by Mr. Maurice Schlatter of these Laboratories. The electron diffraction apparatus and technique have been described by Brockway.[2] The wave length of the electrons (a_0 for gold = 4.070 Å.) was 0.0615 Å., and the camera distance was 10.85 cm. The gas jet was formed by the high temperature nozzle,[3] the temperature of the boiler being 90–110°. There was no indication of any decomposition of the propylene bromide.

Interpretation

The observed s_0 values $\left(s_0 = \frac{4\pi}{\lambda} \sin \frac{\vartheta}{2}\right)$ for the twenty-four measurable features of the photographs are given in Table I together with the coefficients of the radial distributive function,[4,5] and the quantitative comparison with the simplified theoretical curves G and H of Fig. 1. The positions and designations of the observed features are indicated on the figure by numbered arrows.

The radial distribution function, curve A, shows a number of maxima of which only those at 2.85 and 4.62 Å. give accurate values for interatomic distances in the molecule, since it is only for these two peaks that the individual distribution curves for the maxima and minima are in agreement. These two distances undoubtedly correspond to the shorter non-bonded carbon–bromine and the

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[1] D. P. Stevenson and Verner Schomaker, THIS JOURNAL, **61**, 3173 (1939).

[2] L. O. Brockway, *Rev. Mod. Phys.*, **8**, 231 (1936).

[3] L. O. Brockway and K. J. Palmer, THIS JOURNAL, **59**, 2181 (1937).

[4] L. Pauling and L. O. Brockway, *ibid.*, **57**, 2684 (1935).

[5] V. Schomaker, A. C. S. Meeting, Baltimore, Md., April, 1939.