

benzene (1:1) mixture. After the solution was washed with water and dilute alkali the solvents and unchanged mesitylene were removed by steam distillation. The ketone was recrystallized from methanol; m. p. 93.5–94°. ⁹

*Anal.*¹⁰ Calcd. for $C_{20}H_{24}O$: C, 85.67; H, 8.62. Found: C, 85.52; H, 8.56.

Mesitil Monoxime.—Twenty cubic centimeters of butyl nitrite was added gradually over a period of three hours to a solution of 9.8 g. of desoxymesitoin in 100 cc. of moist ether. The solution was stirred during the addition of the nitrite and dry hydrogen chloride was passed in during this time and for an hour longer. The ether solution was allowed to stand overnight, washed with water and the oxime extracted with 4% potassium hydroxide. The oxime was recrystallized from an ether-petroleum ether mixture; m. p. 215–216°. A specimen of the oxime prepared by the method of Kohler and Baltzly also melted at 215–216°¹¹ and a mixture of the two showed no depression of the melting point.

α -Mesitylvinyl Mesityl Ketone.—A solution of 4.6 g. of desoxymesitoin, 2 g. of paraformaldehyde, 1 g. of anhydrous potassium carbonate and 50 cc. of ethyl alcohol was heated under reflux with efficient stirring for twenty-eight hours. At the end of fourteen hours an additional gram of carbonate was added. The dark brown solution was allowed to cool, poured on 150 g. of cracked ice and acidified with dilute hydrochloric acid. The product, after being decolorized with Norit, crystallized from ethyl alcohol in colorless plates melting at 131.5–133°. The yield was 2.5 g.

Anal. Calcd. for $C_{21}H_{24}O$: C, 86.25; H, 8.27. Found: C, 86.13; H, 8.32.

The unsaturated ketone failed to absorb bromine in car-

(9) Kohler and Baltzly (*THIS JOURNAL*, **54**, 4015 (1932)) obtained a compound by the reduction of mesitil which they believed was desoxymesitoin. However, its physical properties are different from those of the ketone reported here.

(10) The analysis reported in this paper are microanalyses and were carried out by Mr. L. G. Fauble, Mr. W. H. Taylor and Miss Mary S. Kreger.

(11) Kohler and Baltzly reported the melting point as 209–210°.

bon tetrachloride and decolorized permanganate only very slowly when warmed.

1,2-Dimesityl-1-propen-1-ol.—A small amount (0.015 g.) of platinum oxide catalyst in 35 cc. of ethyl alcohol was reduced, then 0.49 g. of α -mesitylvinyl mesityl ketone added and the reduction continued. One mole of hydrogen was absorbed per mole of ketone. The reaction mixture was filtered and divided into two parts.

One portion was concentrated to a small volume on a hot-plate, cooled and allowed to crystallize. The product consisted of 0.2 g. of white cubes melting at 124–126°.

A stream of air was bubbled through the second portion for two hours. Evaporation of the solvent left a white solid which, when crystallized from alcohol, melted at 124–126° and proved by the mixed melting point method to be the same as the product from the first portion. The pure 1,2-dimesityl-1-propen-1-ol crystallized from ethyl alcohol as colorless needles melting at 126–127°.

Anal. Calcd. for $C_{21}H_{26}O$: C, 85.66; H, 8.90. Found: C, 85.48; H, 8.98.

This compound decolorized permanganate instantly and a bromine-carbon tetrachloride solution slowly. It gave no color with ferric chloride and was insoluble in 20% sodium hydroxide solution. A sample could be melted and remelted repeatedly without change in the melting point.

The Acetate of 1,2-Dimesityl-1-propen-1-ol.—A solution of 0.1 g. of the enol and 15 cc. of acetic anhydride was heated under reflux for two hours, allowed to cool and poured on ice. The acetate was recrystallized from ethyl alcohol; m. p. 138–139.5°. The yield was almost quantitative.

Anal. Calcd. for $C_{23}H_{28}O_2$: C, 82.10; H, 8.39. Found: C, 82.24; H, 8.32.

Summary

A stable vinyl alcohol, 1,2-dimesityl-1-propen-1-ol, has been described. It is novel in type; the enol double bond does not form part of a heteroconjugated system.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF BRITISH COLUMBIA]

The Ethanolysis of Western Red Cedar, Douglas Fir and Western Hemlock

By J. S. BRAWN, R. D. HEDDLE AND J. A. F. GARDNER

Hibbert and his co-workers¹ have succeeded in isolating from the phenolic constituents of spruce lignin a relatively simple substance, α -ethoxypropioveratrone, and from maple wood α -ethoxypropiosyringone, in addition to the former compound. The lignin was separated from the cellulose and hemicellulose by digesting with absolute ethanol containing 3% hydrogen chloride, there-after precipitating the soluble "extracted lignin"

(1) A. B. Cramer, M. J. Hunter and H. Hibbert, *THIS JOURNAL*, **61**, 509 (1939).

into a large volume of water. After the removal of the diketone constituents² with sodium bisulfite, and the acidic products with sodium bicarbonate, the remaining phenol constituents were separated by extracting with sodium hydroxide solution.

The purpose of the present investigation was to determine whether western soft woods, using the same procedure, would be found to have the same typical composition as the eastern species.

(2) L. Brickman, J. J. Pyle, J. L. McCarthy and H. Hibbert, *ibid.*, **61**, 836 (1939).

The quantitative data obtained are given in Table I.

TABLE I

	Type of wood	West- ern Red Cedar	Doug- las Fir	West- ern Hem- lock
Lignin in starting materials	Klason lignin % ^a	38	29.3	30.6
	Klason lignin g.	179	155	210
Lignin in residual wood meal	Klason lignin %	34.2	25.8	28.2
	Klason lignin g.	120	93	140
Extracted oil (phenolic constituent)	from Aq. soln. g.	4.63	4.9	8.02
	from EtOH lignin g.	0.82	2.9	1.44
	total, g.	5.45	7.8	9.46
Distilled oils (phenolic constituent)	from Aq. soln. g.	3.25	3.7	5.48
	from EtOH lignin g.	0.53	0.2	...
	total, g.	3.78	3.9	5.48

^a Yields are on an oven dry basis.

The alkaline phenolic extract was methylated with an ether solution of diazomethane³ using 50% excess. After removal of the ether a clear yellow oil was obtained which, after crystallization had been induced by scratching, solidified completely. After repeated recrystallizations from petroleum

(3) E. A. Werner, *J. Chem. Soc.*, **115**, 1093 (1919).

ether a white crystalline product was obtained which melted at 81–82°. This was shown to be α -ethoxy-propioveratrone, by conversion of 0.5 g. of it into its 2,4-dinitrophenyl-hydrazone,⁴ an orange-yellow precipitate which after crystallization from chloroform and then from petroleum ether melted at 140–141°.

Using the procedure developed by Hibbert and co-workers⁵ for the separation of the syringyl and guaiacyl radicals, the former was shown to be absent.

Summary

The ethanolyse of the western soft woods, red cedar, Douglas fir, and western hemlock, gave a phenolic fraction containing the veratryl group, as demonstrated by the isolation of α -ethoxy-propioveratrone, and none of the syringyl group.

(4) J. J. Pyle, L. Brickman and H. Hibbert, *THIS JOURNAL*, **61**, 2193 (1939).

(5) M. J. Hunter and H. Hibbert, *ibid.*, **61**, 2190 (1939).

VANCOUVER, B. C.

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Side-Chain Bromination. II. Negative Catalytic Effects

By JOHN R. SAMPEY AND ELIJAH M. HICKS

In an earlier communication¹ attention was called to the negative catalytic effect of small amounts of sulfur present as impurities in c. p. and Reagent grades of carbon disulfide on the side-chain bromination of toluene derivatives. In the present paper data are presented on the rates of bromination with different amounts of sulfur present in both carbon disulfide and carbon tetrachloride as solvents. A few measurements are made also with changing sulfur concentration and different intensities of the artificial illumination.

Negative Catalytic Effects of Sulfur.—The relative rates of bromination in Table I were obtained as described in the previous paper. The carbon disulfide was carefully purified and was purer than that used previously, which accounts for the higher rates of bromination. The slower rate in carbon tetrachloride, on the other hand, is due to the fact that the bromination reported below was made with the reacting flask at a greater

(1) Sampey, Fawcett and Morehead, *THIS JOURNAL*, **62**, 1839–1840 (1940).

distance from the source of irradiation than that carried out in the earlier work. The brominations in Table I below were made with the Erlenmeyer flask exactly three inches (7.6 cm.) from the two 300-watt clear-glass Mazda lamps. Twenty cc. samples were measured in each run; the small amounts of sulfur reported in Column 2 were obtained by dilution of stronger solutions.

The striking negative catalytic effect of sulfur on the side-chain bromination is apparent from the fact that 0.01 mg. slows down the reaction, while 100 mg. practically stops the bromination of one-hundredth molar quantities of toluene and *p*-bromotoluene in both carbon disulfide and carbon tetrachloride. The sulfur effects on toluene and *p*-bromotoluene are roughly parallel in carbon disulfide; sulfur has a greater retarding action on side-chain bromination in carbon tetrachloride than in carbon disulfide.

Photochemical Effects.—The care which had to be exercised in placing the reaction flask exactly the same distance from the source of radiation in all our side-chain brominations sug-