ethoxy-*aldehydo-d*-galactose pentaacetate (V).

4. The α and β forms of 1-thioethoxy-*aldehydo-d*-glucose hexaacetate (III) have been synthesized by application of the above reactions established for *d*-galactose.

5. *d*-Glucose S-ethyl O-methyl monothioacetal (VII) and its pentaacetate (VI) have been synthesized from α-1-thioethoxy-*aldehydo-d*-glucose hexaacetate (III).

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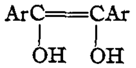
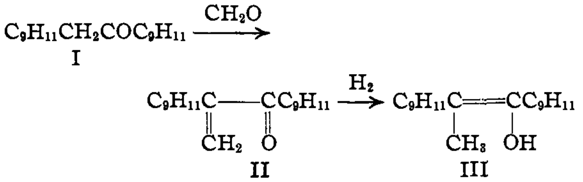
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

A Stable Vinyl Alcohol, 1,2-Dimesityl-1-propen-1-ol

BY REYNOLD C. FUSON, JOSEPH CORSE AND C. H. MCKEEVER[1]

The stability of enediols of the type  $\underset{OH}{\underset{|}{ArC}}=\underset{OH}{\underset{|}{CAr}}$ appears to be conditioned by the steric hindrance afforded by the aryl radicals. When these are mesityl,[2] 2,6-xylyl,[3] 2,4,6-triethylphenyl[4] or 2,4,6-triisopropylphenyl[5] the enediol shows no tendency to ketonize spontaneously. The present work was undertaken to see if the enolic form would persist if one of the hydroxyl groups were replaced by a hydrocarbon radical. The plan was to hydrogenate α-mesitylvinyl mesityl ketone (II) and to study the stability of the resulting product (III).



$$\underset{\mathrm{I}}{C_9H_{11}CH_2COC_9H_{11}} \xrightarrow{CH_2O} \underset{\mathrm{II}}{C_9H_{11}\underset{\underset{CH_2}{\|}}{C}-\underset{\underset{O}{\|}}{C}C_9H_{11}} \xrightarrow{H_2} \underset{\mathrm{III}}{C_9H_{11}\underset{\underset{CH_3}{|}}{C}=\underset{\underset{OH}{|}}{C}C_9H_{11}}$$

The saturated ketone (I) was prepared from α^2-chloroisodurene by the following sequence of changes.

$$C_9H_{11}CH_2Cl \longrightarrow C_9H_{11}CH_2CN \longrightarrow C_9H_{11}CH_2CO_2H \longrightarrow C_9H_{11}CH_2COCl \longrightarrow \mathrm{I}$$

The first three steps had been carried out previously by Hoch.[6] An improved procedure has been developed for the synthesis of the nitrile.

The unsaturated ketone was made by the action of paraformaldehyde on desoxymesitoin (I). The hydrogenation product was a solid melting at 126–127° and proved to be stable in the enolic form (III). It was insoluble in aqueous sodium hydroxide and gave no color with ferric chloride. Heat or long exposure to air caused no change. The compound was unaffected by boiling with alcoholic solutions of hydrogen chloride, or piperidine or with phosphoric acid. It readily reduced permanganate in acetone and formed an acetate when treated with acetic anhydride. Its identity was confirmed by the infrared spectrum; this showed absorption maxima at 2.76 μ, which demonstrates the presence of a hydroxyl group. At higher concentrations a maximum appears at 284 μ, presumably due to the dimer formed by hydrogen bonding.

The new propenol (III) is the first permanent enol to be described in which the enolic double bond does not form part of a hetero-conjugated system.[7]

The authors are indebted to Professors A. M. Buswell and W. H. Rodebush and to Mr. J. B. Patberg for the determination and interpretation of the infrared absorption data.

Experimental

Mesitylacetonitrile.[8]—A solution of 25 g. of sodium cyanide, 35 cc. of water and 50 cc. of alcohol was warmed on a water-bath. Then 50 g. of α^2-chloroisodurene was added gradually, with stirring, over a period of twenty minutes. Heating and stirring were then continued for three hours. The product was dissolved in ether and the solution washed with water and dried over calcium chloride. Distillation gave a nearly quantitative yield of the nitrile, boiling at 160–165° (22 mm.).

Desoxymesitoin.—A solution of 70 g. of mesitylacetyl chloride[6] in 25 cc. of mesitylene was added gradually over a period of forty minutes to an ice cold mixture of 70 cc. of mesitylene, 125 cc. of carbon disulfide and 80 g. of aluminum chloride. The mixture was stirred throughout the addition and for an hour and a half afterward. The temperature was allowed to rise gradually and finally was maintained at the point of reflux for forty minutes.

The reaction mixture was decomposed with ice and hydrochloric acid and the product taken up in an ether-

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(1) Röhm and Haas Research Assistant, 1938–1940.

(2) Fuson and Corse, THIS JOURNAL, **61**, 975 (1939); Thompson, *ibid.*, **61**, 1281 (1939); Fuson, McKeever and Corse, *ibid.*, **62**, 600 (1940).

(3) Fuson, Scott, Horning and McKeever, *ibid.*, **62**, 2091 (1940).

(4) Fuson, Corse and McKeever, *ibid.*, **61**, 2010 (1939).

(5) Fuson and Horning, *ibid.*, **62**, 2962 (1940).

(6) Hoch, *Compt. rend.*, **192**, 1464 (1931).

(7) This enol is formally similar to that isolated by Kohler (*Am. Chem. J.*, **36**, 177 (1906)), and others known to exist in solution (Kohler, Tishler and Potter, THIS JOURNAL, **57**, 2517 (1935)).

(8) This experiment was carried out by Mr. Norman Rabjohn.

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 carbon 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.

Urbana, Illinois Received August 26, 1940

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[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°.

[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-workers[1] 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, thereafter precipitating the soluble "extracted lignin" into a large volume of water. After the removal of the diketone constituents[2] 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.

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[1] A. B. Cramer, M. J. Hunter and H. Hibbert, This Journal, **61**, 509 (1939).

[2] L. Brickman, J. J. Pyle, J. L. McCarthy and H. Hibbert, *ibid.*, **61**, 886 (1939).