

After separating the coagulum from the solution it is redissolved and the procedure repeated twelve or fifteen times. A water-insoluble fraction is obtained at the end amounting to only about 1% of the original amount.

A similar substance was obtained by Kunitz and Northrop when they hydrolyzed a 5% solution of gelatin in *M*/10 hydrochloric acid at 90°.

If the "insoluble gelatin fraction" separated by Kunitz and Northrop is actually no constituent of gelatin at all, but a protein impurity, it seems unlikely that it is essential to the swelling mechanism, as supposed by them. We have obtained a gelatin which had merely a trace of this material, but which showed all the usual swelling properties of gelatin, and equal jelly strength and viscosity. We are continuing investigations on this foreign protein and its removal from gelatin.

Summary

It is found that gelatin prepared from calf-skins usually contains a small amount—less than 1%—of a heat coagulable protein as an impurity. The protein approaches albumin (egg albumen and serum) in nitrogen content (around 14%). Its organic sulfur content is considerably higher than that of gelatin (0.8 compared to 0.24%). Its isoelectric point lies at about *P_H* 4.0. It is suggested that the so-called "insoluble" gelatin of various investigators is identical with this protein impurity.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON]

THE CONSTITUTION OF HOMOMESITYL OXIDE¹

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The homomesityl oxide derived from 2-butanone has been prepared by numerous investigators.² Earlier workers made no attempt to determine its structure, while later investigations produced some evidence that it has the formula $C_2H_5(CH_3)C=CHCO_2H_5$.

Since 2-butanone reacts with aldehydes to give compounds of the type $RCH=C(CH_3)COCH_3$, one would expect the structure $C_2H_5(CH_3)C=C(CH_3)COCH_3$, and as the evidence in favor of the other formula was not conclusive and involved some contradictions, this investigation was undertaken to determine definitely the constitution of the homomesityl oxide.

¹ This paper is an abstract of a thesis offered by C. H. Secoy in partial fulfillment of the requirements for the degree of Master of Science in the University of Washington.

² (a) Pawlow, *Ann.*, **188**, 138 (1877); (b) Schramm, *Ber.*, **16**, 1581 (1883); (c) Descudé, *Ann. chim.*, [7] **29**, 494 (1903); (d) Barbier and Leser, *Bull. soc. chim.*, **31**, 278 (1904); (e) Bodroux and Taboury, *ibid.*, [4] **3**, 831 (1908); *ibid.*, [4] **5**, 950 (1909); (f) Pariselle and Simon, *Compt. rend.*, **173**, 86 (1921); (g) Becker and Thorpe, *J. Chem. Soc.*, **121**, 1303 (1922); (h) Ekeley and Howe, *THIS JOURNAL*, **45**, 1917 (1923); (i) Franke and Köhler, *Ann.*, **433**, 314 (1923).

The formula of the homomesityl oxide from 2-butanone was conclusively shown to be $C_2H_5(CH_3)C=CHCOC_2H_5$ by hydrogenating it and identifying the resulting octanone as 5-methyl-3-heptanone. Guerbet³ prepared 5-methyl-3-heptanone and reported the melting point of its semicarbazone as 96° , whereas Bodroux and Taboury reported 102° as the melting point of the semicarbazone of the octanone obtained from homomesityl oxide. As Guerbet's evidence for the structure of his ketone is not very complete, 5-methyl-3-heptanone was prepared by the oxidation of the 5-methyl-3-heptanol obtained by the Grignard synthesis from 1-bromo-2-methylbutane and propionaldehyde. The semicarbazone of this 5-methyl-3-heptanone melted at 96° , as did that of the octanone obtained by hydrogenating homomesityl oxide, contrary to the findings of Bodroux and Taboury. In addition, the properties of the octanol resulting from reduction of homomesityl oxide corresponded with those of the 5-methyl-3-heptanol mentioned above.

As further evidence, the octanone was oxidized and the resulting acids identified as acetic (by conversion to the *p*-bromophenacyl ester) and *sec*-butylacetic (by comparison of the amide with the amide of known *sec*-butylacetic acid).

Furthermore, a homomesityl oxide with the structure $C_2H_5(CH_3)C=C(CH_3)COCH_3$ would yield on reduction 3,4-dimethyl-2-hexanone. A ketone with this constitution was prepared by the hydrolysis of ethyl *sec*-butylmethylacetoacetate and was found to differ from the octanone obtained from homomesityl oxide.

Of the previous attempts to determine the structure of homomesityl oxide, that of Becker and Thorpe is the only one that furnished any positive evidence. They treated it with sodio ethyl malonate, hydrolyzed the resulting product to an ethyldimethyldihydroresorcinol and oxidized this to β -ethyl- β -methylglutaric acid, a product which could only arise from a homomesityl oxide with the formula $C_2H_5(CH_3)C=CHCOC_2H_5$. Franke and Köhler assumed this structure because they failed to obtain a positive iodoform reaction, which they offer as evidence that the grouping CH_3CO- is absent. In this investigation it was found that chloroform was readily produced by treatment of the homomesityl oxide with sodium hypochlorite and that in the presence of sodium iodide a small quantity of iodoform was also produced. This apparently contradictory evidence is readily explained if preliminary hydrolysis to two molecules of 2-butanone is assumed.

Experimental

Homomesityl Oxide.—This was prepared by a method that is essentially that of Bodroux and Taboury.⁴ It was found that more satisfactory results could be obtained

³ Guerbet, *Compt. rend.*, 150, 183 (1910).

⁴ Bodroux and Taboury, *Bull. soc. chim.*, [4] 3, 831 (1908).

by substituting small muslin bags filled with powdered barium oxide for the lumps of calcium carbide of the original method. In a typical run, 500 g. of 2-butanone yielded 85 g. of homomesityl oxide, b. p. 164–166°, d_4^{21} 0.8633, n_D^{21} 1.4445.

The 2,4-dinitrophenylhydrazones⁵ melted at 46°. Chloroform was readily obtained by warming homomesityl oxide with sodium hypochlorite solution, and a small amount of iodoform was produced when sodium hypochlorite solution was slowly added to a well shaken mixture of homomesityl oxide and sodium iodide solution.

Preparation of the Saturated Ketone.—The reduction was carried out as described by Adams and his students,⁶ using 0.4 g. of platinum oxide, 31.5 g. (0.25 mole) of homomesityl oxide, and 150 cc. of 95% alcohol. The initial hydrogen pressure was 40 lb.; time of reduction nine minutes; yield of saturated ketone, 94% of the theoretical; b. p. 158°; d_4^{24} 0.829; n_D^{24} 1.412.

The semicarbazone after recrystallization from dilute methanol melted at 96°.

Oxidation of the Saturated Ketone.—Twenty-five grams of the ketone was refluxed for six hours with a mixture of 40 g. of sodium dichromate, 53 g. of sulfuric acid and 200 cc. of water. The whole was then distilled until the residue became quite thick. The distillate was neutralized with sodium hydroxide solution and again distilled until no more unchanged ketone passed over. The residue was acidified and distillation continued, collecting three equal-sized fractions. By refractionation the acids more volatile with steam were concentrated in the first fraction, and the least volatile in fraction 3.

Fraction 1 was extracted several times with ether, the ether solution dried with calcium chloride, the ether removed and the residue distilled. The acid was converted by treatment with thionyl chloride to the acid chloride, which was added drop by drop to concd. aqueous ammonia. The amide which separated on cooling was recrystallized from boiling water and melted at 123°. The amide prepared in the same manner from *sec.*-butylacetic acid (obtained by the ethyl malonate synthesis) also melted at 123°,⁷ as did a mixture of the two.

Fraction 3 was neutralized with sodium hydroxide and the solution evaporated to dryness; 0.3 g. of the dry salt was converted into the *p*-bromophenacyl ester according to the directions of Judefind and Reid.⁸ The ester melted at 85° as reported by Judefind and Reid for *p*-bromophenacyl acetate.

Fraction 2, treated in the same manner as fraction 3, proved to contain only acetic acid.

Preparation of the Saturated Alcohol.—Homomesityl oxide was reduced with sodium and moist ether by the method previously described by one of us for the reduction of butylidene ethyl methyl ketone.⁹ From 25 g. of homomesityl oxide there was obtained 10 g. of the saturated alcohol boiling at 155°, d_4^{24} 0.8425, n_D^{24} 1.433.

5-Methyl-3-heptanol.—This was prepared by the Grignard synthesis from 36 g. of magnesium, 192 g. of 2-methyl-1-bromobutane, and 100 g. of propionaldehyde. The boiling point, density and refractive index corresponded with those of the saturated alcohol obtained from homomesityl oxide. This is evidently the same alcohol as that obtained by Guerbet³ by heating 2-butanol with sodium.

5-Methyl-3-heptanone.—Eighteen and one-half grams of 5-methyl-3-heptanol was added drop by drop with constant stirring to a mixture of 15 g. of sodium dichromate, 20

⁵ Allen, *THIS JOURNAL*, **52**, 2955 (1930).

⁶ Adams and Voorhees, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII, pp. 10, 92.

⁷ Van Rombergh, *Rec. trav. chim.*, **6**, 153 (1887).

⁸ Judefind and Reid, *THIS JOURNAL*, **42**, 1043 (1920).

⁹ Powell, *ibid.*, **46**, 2516 (1924).

g. of sulfuric acid and 70 cc. of water, keeping the temperature at about 50°. Stirring was continued for thirty minutes after all of the alcohol had been added, and the mixture then distilled until no more oil passed over. The oil was separated, dried with calcium chloride and distilled. The boiling point, density and refractive index were the same as those of the saturated ketone obtained from homomesityl oxide.

The semicarbazone melted at 96°.

3,4-Dimethyl-2-hexanone.—This was prepared by hydrolyzing ethyl *sec.*-butylmethylacetoacetate by the regular procedure. Ninety grams of ethyl acetoacetate yielded 90 g. of crude ethyl methylacetoacetate, which in turn gave 62 g. of pure ethyl *sec.*-butylmethylacetoacetate. The ketone was obtained by refluxing the ester with 300 cc. of 15% aqueous sodium hydroxide; b. p. 158°, d_4^{22} 0.8295, n_D^{22} 1.412.

The semicarbazone melted at 124–126°.

Summary

1. An improved method for the preparation of homomesityl oxide has been described.
2. The structure of homomesityl oxide is definitely established as $C_2H_5(CH_3)C=CHCO_2H_5$.

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THE CHEMISTRY OF LIGNIN. V. THE DISTILLATION OF ALKALI LIGNIN WITH ZINC DUST IN AN ATMOSPHERE OF HYDROGEN

BY MAX PHILLIPS

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Considerable difference of opinion prevails among investigators of the chemistry of lignin as to whether this substance belongs to the aliphatic, aromatic, hydroaromatic or heterocyclic series.¹ Among the earliest constitutional formulas for lignin may be mentioned the Keto-R-hexene formula of Cross and Bevan² and that proposed by Green.³

Willstätter and Kalb,⁴ as the result of their work on the reduction of lignin with hydriodic acid and red phosphorus, conclude that lignin is structurally related to the carbohydrates. However, none of the products which they obtained were homogeneous, and they were unable to identify any definite chemical substance.

¹ An excellent résumé of the literature up to 1926 dealing with the constitution of lignin is given by K. Kürschner in his monograph, "Zur Chemie der Ligninkörper," p. 141, published in F. B. Ahrens' "Sammlung Chemischer und Chemischtechnischer Vorträge," Vol. 28, Ferd. Enke, Stuttgart, 1926, and in the monograph by W. Fuchs, "Die Chemie des Lignins," Julius Springer, Berlin, 1926, p. 277.

² Cross and Bevan, "Cellulose," Longmans, Green and Co., London, 2d ed., 1895, p. 137; Vol. III, 1912, p. 104.

³ Green, *Z. Farben Textilchemie*, 3, 97 (1904).

⁴ Willstätter and Kalb, *Ber.*, 55, 2637 (1922).