g. of dioxadiene and 5 cc. of dry carbon tetrachloride. Some solid separated during the reaction. After the carbon tetrachloride was removed in a vacuum desiccator, the residue was warmed with petroleum ether and the solution decanted from some insoluble material. The petroleum ether solution on cooling deposited needle-like crystals of 2,5-dichlorodioxane, m. p. 117–118°.[7] The material decomposed on standing. It was readily hydrolyzed by water and the solution yielded the *p*-nitrophenylosazone of glycol aldehyde when treated with *p*-nitrophenylhydrazine; m. p. 300° (uncorr.).

Mercuration of Dioxadiene.—A solution of 1 g. of dioxadiene in 5 cc. of alcohol was added to 71.5 cc. of a cold solution which contained 3.22 g. of mercuric chloride and 6.23 g. of sodium acetate-$3H_2O$. A white precipitate formed immediately. After standing overnight in a refrigerator, the solid was filtered and washed with water several times. The material after air drying weighed 3.28 g. The theoretical yield for a disubstituted compound is 3.30 g. The product showed no definite melting point, and was insoluble in alcohol, dioxane, benzene or a mixture of alcohol and acetic acid. The material was washed several times more with water and dried in a desiccator.

Anal. Calcd. for $C_4H_6O_2Hg_2Cl_2$: Hg, 72.39. Found: Hg, 71.56, 70.11.

(7) 2,5-Dichlorodioxane, needles, m. p. 118–119°, has been isolated as a product of the chlorination of dioxane by L. Rochen of this Laboratory. It is an unstable solid easily hydrolyzed by water.

Summary

1. Dioxadiene has been prepared for the first time.

2. The physical and chemical properties have been studied. These indicate that the unsaturation is modified to a marked extent by conjugation with the ether oxygens.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Sterols. LXXV. Cholesterol Derivatives

BY RUSSELL E. MARKER AND EWALD ROHRMANN

The present work is a continuation of a previously reported investigation[1] on 7-keto-cholesterol derivatives. In the previous work it was observed that 7-ketocholesteryl chloride upon catalytic hydrogenation in acetic acid solution gave a mixture of products from which cholestyl chloride was isolated. Indications of the presence of 7-hydroxycholestyl chloride were also obtained.

We have now observed that when the hydrogenation of $\Delta^{5,6}$-unsaturated 7-keto compounds is conducted in a neutral medium with Adams catalyst the essential product is a saturated 7-keto compound. This selective reduction of the ethylenic linkage most probably is due to the slightly hindered nature of the carbonyl group at C-7.

The catalytic hydrogenation of 7-ketocholesteryl chloride in neutral solution with Adams catalyst yielded 7-ketocholestyl chloride identical with that prepared previously by the oxidation of crude 7-hydroxycholestyl chloride.[1] A similar reduction of 7-ketocholesteryl acetate gave 7-ketocholestyl acetate evidently identical with the product which Windaus and Kirchner[2] obtained by the hydrogenation of 7-ketocholesteryl acetate with palladium catalyst in an acidic medium. When the hydrogenation of 7-ketocholesteryl acetate was carried out in acetic acid solution with Adams catalyst followed by alkaline hydrolysis of the reduction products, 7-hydroxycholestanol was obtained. This was identical with the product obtained by the reduction of 7-ketocholestanol with aluminum isopropylate. Mild oxidation of this diol with chromic anhydride yielded 7-ketocholestanone first reported by Windaus and Kirchner.[2]

Dimroth and Trautmann[3] reported the preparation of $\Delta^{5,6}$-cholestenol-7 by the reduction of $\Delta^{5,6}$-cholestenone-7 with aluminum isopropylate. No analytical data were given on their product which melted at 93–94°. The substance was reported to yield a benzoate, m. p. 108–109°. We have prepared $\Delta^{5,6}$-cholestenol-7 by the reduction of 7-hydroxycholesteryl chloride with sodium and amyl alcohol. The product, m. p. 106°, gave a benzoate, m. p. 147°. Bromination of the substance followed by mild oxidation with chromic anhydride and subsequent debromination gave $\Delta^{5,6}$-cholestenone-7 of m. p. 126°, while catalytic hydrogenation in neutral medium gave cholestanol-7.

It is improbable that our $\Delta^{5,6}$-cholestenol-7 differs from that of Dimroth and Trautmann in the configuration of the hydroxyl group as in both

(1) Marker, *et al.*, THIS JOURNAL, **59**, 619 (1937).

(2) Windaus and Kirchner, *Ber.*, **53**, 614 (1920).

(3) Dimroth and Trautmann, *ibid.*, **69**, 669 (1936).

cases the hydroxyl group was formed by reduction of a carbonyl group with aluminum isopropylate, a reaction which appears to give largely one isomer at C-7. It is possible that the two benzoates may be polymorphic forms.

In the present paper we are also reporting the incidental preparation of 3-acetyl-4-hydroxycholesterol which was prepared by the oxidation of cholesteryl acetate with selenium dioxide.[4-7] The substance was obtained in two polymorphic forms.

We wish to thank Parke, Davis and Company for their generous help and assistance in the various phases of this work.

Experimental Part

7-Ketocholestyl Chloride.—A mixture of 1.6 g. of 7-ketocholesteryl chloride, 400 mg. of Adams catalyst and 120 cc. of ether was shaken with hydrogen at 3 atmospheres pressure for four hours at 25°. The product was crystallized from acetone as thick white prisms, m. p. 136–138°. This gave no depression with an authentic sample of 7-ketocholestyl chloride.

Anal. Calcd. for $C_{27}H_{45}OCl$: C, 77.1; H, 10.7. Found: C, 77.1; H, 10.5.

The substance gave an **oxime** which crystallized from aqueous ethanol, m. p. 152–154°.

Anal. Calcd. for $C_{27}H_{46}OClN$: C, 74.35; H, 10.6. Found: C, 74.35; H, 10.7.

Hydrogenation of the Acetate of $\Delta^{5,6}$-Cholestenol-3(β)-one-7.—A mixture of 5 g. of the acetate, 500 mg. of Adams catalyst and 150 cc. of ether was shaken with hydrogen at 3 atmospheres pressure for seven hours at 25°. The mixture was filtered, the filtrate evaporated and the residue crystallized from acetone–methanol to give white plates, m. p. 147–148°.

Anal. Calcd. for $C_{29}H_{46}O_3$: C, 78.3; H, 10.9. Found: C, 78.4; H, 10.6.

Hydrolysis of the resulting acetate of cholestanol-3(β)-one-7 by refluxing with an excess of ethanolic potassium hydroxide gave a product which crystallized from acetone–methanol as white plates, m. p. 128–130°, solidifying almost at once and remelting at 157–159°.

Anal. Calcd. for $C_{27}H_{46}O_2$: C, 80.5; H, 11.5. Found: C, 80.8; H, 11.7.

The hydrolysis product gave an **oxime** which crystallized from aqueous ethanol as fine white needles, m. p. 232–233°.

Anal. Calcd. for $C_{27}H_{47}O_2N$: C, 77.6; H, 11.3. Found: C, 77.2; H, 11.5.

Cholestanediol-3(β)-7(α). (a) **By Hydrogenation of 7-Ketocholesteryl Acetate.**—A mixture of 5 g. of 7-ketocholesteryl acetate, 500 mg. of Adams catalyst and 150 cc. of glacial acetic acid was shaken with hydrogen at 3 atmospheres pressure at room temperature for fourteen hours. The mixture was filtered and the filtrate evaporated *in vacuo*. The residue which would not crystallize was hydrolyzed with ethanolic potassium hydroxide and the product crystallized from acetone to give white plates, m. p. 164–166°.

Anal. Calcd. for $C_{27}H_{48}O_2$: C, 80.1; H, 11.95. Found: C, 80.2; H, 11.9.

The filtrate containing crude 7-hydroxycholestanol was evaporated to dryness and the crystalline residue dissolved in 125 cc. of glacial acetic acid. To this solution was added 2 g. of chromic anhydride in 20 cc. of 80% acetic acid. After standing at room temperature for two hours the solution was diluted with water and the precipitated solid taken up in ether. The ethereal extract was washed with sodium carbonate solution and the ether evaporated. The residue was crystallized from acetone as white needles, m. p. 186–187°.

Anal. Calcd. for $C_{27}H_{44}O_2$: C, 80.9; H, 11.1. Found: C, 81.2; H, 11.2.

(b) **By Aluminum Isopropylate Reduction of the Acetate of Cholestanol-3(β)-one-7.**—A mixture of 1.2 g. of cholestanol-3(β)-one-7 acetate, 1.5 g. of aluminum isopropylate and 40 cc. of dry isopropyl alcohol was refluxed on the steam-bath for fourteen hours. Most of the solvent was distilled off over a period of three hours. The residue was diluted with water and the precipitate extracted with ether. The product crystallized from acetone as white plates, m. p. 163–165°. It gave no depression with the product of the catalytic hydrogenation of 7-ketocholesteryl acetate.

$\Delta^{5,6}$-Cholestenol-7.—To a boiling solution of 3 g. of 7-hydroxycholesteryl chloride was added 6 g. of sodium over a period of four hours. The mixture was then cooled, diluted with ether and washed well with water. The ether and amyl alcohol was evaporated on the steam-bath. The residual oil which would not crystallize was sublimed in high vacuum. The material distilling at 130–160° was crystallized from acetone to give 800 mg. of thick white prisms, m. p. 105–106°.

Anal. Calcd. for $C_{27}H_{46}O$: C, 83.9; H, 12.0. Found: C, 83.9; H, 12.0.

When treated with benzoyl chloride in pyridine at room temperature for two days the product yielded a benzoate which crystallized from methanol as white needles, m. p. 145–147°.

Anal. Calcd. for $C_{34}H_{50}O_2$: C, 83.2; H, 10.3. Found: C, 83.1; H, 10.1.

Hydrogenation of $\Delta^{5,6}$-Cholestenol-7.—A mixture of 400 mg. of $\Delta^{5,6}$-cholestenol-7, 500 mg. of Adams catalyst, 50 cc. of ether and 25 cc. of absolute ethanol was shaken with hydrogen at 45 pounds (3 atm.) pressure for ninety minutes. The mixture was filtered, the filtrate diluted with water and the ether layer separated. The ether was evaporated and the residue crystallized from ethanol to give white needles, m. p. 115–117°. This gave no depression with an authentic sample of cholestanol-7, m. p. 116–117°.

$\Delta^{5,6}$-Cholestenone-7.—To a solution of 500 mg. of $\Delta^{5,6}$-cholestenol-7 in 5 cc. of ether was added a slight excess of bromine in 2 cc. of glacial acetic acid. No crystalline bromide was obtained. The solution was diluted with

(4) Rosenheim and Starling, *J. Chem. Soc.*, 377 (1937).
(5) Butenandt and Hausmann, *Ber.*, **70**, 1154 (1937).
(6) Marker, Kamm and Wittle, THIS JOURNAL, **60**, 1071 (1938).
(7) Marker and Rohrmann, *ibid.*, **60**, 1073 (1938).

water, extracted with ether and the ether evaporated at room temperature. The residue was dissolved in 10 cc. of benzene. To this solution was added a solution of 500 mg. of chromic anhydride in 15 cc. of 80% acetic acid, and the mixture stirred for five hours at room temperature. The benzene layer was washed with water and the solvent evaporated. The residue was dissolved in 20 cc. of glacial acetic acid and the solution heated on the steam-bath for thirty minutes with 2 g. of zinc dust. The solution was decanted into water and the precipitated solid extracted with ether. After washing with dilute sodium carbonate solution the ether was evaporated and the residue crystallized from acetone to give white needles, m. p. 125–126°.

Anal. Calcd. for $C_{27}H_{44}O$: C, 84.3; H, 11.5. Found: C, 84.3; H, 11.7.

3-Acetyl-4-hydroxy-cholesterol.—A mixture of 50 g. of cholesteryl acetate in 250 cc. of benzene was oxidized with a solution of 20 g. of selenium dioxide in 500 cc. of 98% acetic acid as described in a previous paper for sitosteryl acetate. The product was crystallized from acetic acid and after treatment with Norite it was crystallized from methanol to give white needles, m. p. 163–165°.

Anal. Calcd. for $C_{29}H_{48}O_3$: C, 78.3; H, 11.1. Found: C, 78.2; H, 10.9.

The acetic acid filtrate from the above initial crystallization upon standing deposited pale tan plates. After treatment with Norite and crystallization from methanol–ether the product formed white plates, m. p. 189–191°. The mixture with the product of m. p. 163–165° melted over an intermediate range of 163 to 184°.

Anal. Calcd. for $C_{29}H_{48}O_3$: C, 78.3; H, 11.1. Found: C, 78.3; H, 11.0.

Both polymorphic forms yielded the diacetate of 4-hydroxycholesterol, m. p. 162–163°, on refluxing with acetic anhydride. Hydrolysis of both forms with ethanolic potassium hydroxide yielded 4-hydroxycholesterol, m. p. 174–175°.

Summary

Reduction of 7-ketocholesterol derivatives with hydrogen and Adams catalyst in neutral medium tends to reduce the ethylenic linkage, yielding a saturated 7-keto compound.

$\Delta^{5,6}$-Cholestenol-7 has been prepared by the reduction of 7-hydroxycholesteryl chloride with sodium and amyl alcohol.

The preparation of 4-hydroxycholesteryl acetate by the oxidation of cholesteryl acetate with selenium dioxide is reported.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Photolysis of Azomethane and of Azomethane–Acetaldehyde Mixtures

BY FRANCIS E. BLACET AND ALVIN TAUROG

Several investigators are in agreement that at elevated temperatures the thermal[1,2] and photochemical[3,4] decomposition of acetaldehyde involves the reactions

$$CH_3 + CH_3CHO \longrightarrow CH_4 + CH_3CO \quad (1)$$
$$CH_3CO + M \longrightarrow CH_3 + CO + M \quad (2)$$

However, the evidence for these reactions in room temperature photolysis is indirect,[5] being based upon analyses of decomposition products, and is opposed by the experimental proof that CH_3CO is fairly stable[6] below 60°, as well as by a rather high calculated minimum value of 17 kcal. for the energy of activation of reaction 2.[7] By mixing azomethane and acetaldehyde vapors at room temperature, and irradiating the mixture with λ 3660 Å., which is not absorbed by the aldehyde but which dissociates azomethane to give free methyl radicals,[8] the present authors have obtained additional information which pertains to this mechanism. A brief study has been made also of the gaseous decomposition products and the quantum yield of azomethane photolysis.

Experimental Method

Azomethane was obtained by preparing dimethylhydrazine dihydrochloride after the manner of Hatt[9] and oxidizing this with cupric chloride by the method suggested by Jahn.[10] This oxidation process was found to be definitely superior to the potassium chromate method of Thiele.[11] Ramsperger's procedure[12] was followed in purifying the azomethane.

Radiant energy was obtained from a high pressure mercury arc and a quartz monochromator. The gas train was similar to that which has been described[13] except that a second storage reservoir and mercury trap was added to accommodate the azomethane. This reservoir was pro-

(1) Rice and Herzfeld, THIS JOURNAL, **56**, 284 (1934).
(2) Allen and Sickman, *ibid.*, **56**, 1251 (1934).
(3) Leermakers, *ibid.*, **56**, 1537 (1934).
(4) P. A. Leighton, *J. Phys. Chem.*, **42**, 749 (1938).
(5) Blacet and Volman, THIS JOURNAL, **60**, 1243 (1938).
(6) Spence and Wild, *J. Chem. Soc.*, 352 (1937).
(7) E. Gorin, *J. Chem. Phys.*, **7**, 256 (1939).
(8) Burton, Davis and Taylor, THIS JOURNAL, **59**, 1038 (1937).
(9) Hatt, "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., Vol. XVI, 1936, p. 18.
(10) Jahn, THIS JOURNAL, **59**, 1761 (1937).
(11) Thiele, *Ber.*, **42**, 2575 (1909).
(12) Ramsperger, THIS JOURNAL, **49**, 912 (1927).
(13) Leighton and Blacet, *ibid.*, **54**, 3165 (1932).