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

Studies on Hexamethylethane and Related Compounds*

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Hexamethylethane, 2,2,3,3-tetramethylbutane, is of great interest, not only because of its unusual physical properties, but because it is the simplest compound containing two "neo" carbon atoms, that is, two carbons joined only to other carbon atoms. It has been shown that compounds containing such an atom are susceptible to rearrangement and that the products of rearrangement can be predicted.[2] Since no compound with two "neo" atoms has been investigated, hexamethylethane and its derivatives were prepared and studied to determine if their reactions were different in any respect from compounds having only one "neo" carbon.

The abnormal physical properties of hexamethylethane make purification difficult. Crude hydrocarbon made by the method of Marker and Oakwood[3] was fractionated through a special column to give material of better than 99.4% purity as calculated from the cooling curve and the data of Parks and Todd.[4] The true melting point is in the range 101.0–101.5°.

In order to prepare derivatives of hexamethylethane, the pure hydrocarbon was chlorinated to give the monochloride (52% yield). Careful study failed to reveal any *t*-butyl derivatives which might have been formed by splitting of the molecule during chlorination. Proof that the molecule had not rearranged was obtained by conversion of the chloride to the Grignard reagent and the regeneration of the original hydrocarbon by water.

Some twenty-seven distinct reactions were carried out on hexamethylethane and its derivatives and are here reported for the first time. The following condensed summary indicates these reactions and the products obtained.

Whitmore and Homeyer[5] studied the Hofmann rearrangement of *t*-butylacetamide and obtained a nearly quantitative yield of neopentylamine. Additional study of this reaction by Oakwood[6] failed to show any evidence of rearrangement of the carbon skeleton of the neopentyl group. The products of the Hofmann reaction on 3,3,4,4-tetramethylvaleramide are shown in the summary and represent a 94% recovery of material with the hexamethylethane nucleus intact. Proof of structure of the amine was obtained by its synthesis from 2,2,3,3-tetramethyl-1-butanol by methods which do not cause rearrangement.

Chlorohexamethylethane, like neopentyl chloride, is remarkably stable and unreactive except with metals. Iodohexamethylethane, however, is very reactive. It behaves in a manner analogous to neopentyl iodide.[7] Thus treatment of iodohexamethylethane with concentrated alcoholic potassium hydroxide gave an 84% yield of hexamethylethane and equivalent amounts of hydrogen and acetate. The lack of rearrangement in this reaction, as well as the lack of rearrangement of the hexamethylethane nucleus in the Hofmann reaction, is in harmony with the theory of rearrangements used in this Laboratory.[2,5] In these reactions the hexamethylethane nucleus keeps its full complement of electrons so that the necessary conditions for rearrangement are not satisfied.

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Experimental

The Purification of Hexamethylethane.—Crude hexamethylethane, 300 g., m. p. 98–100°, prepared by the method of Marker and Oakwood[3] was fractionated through a partial condensation type column[8] with an electrically heated take-off tube so that the distillate was delivered to the receiving vial as vapor. The purified material, b. p. 105–106° (732–749 mm.), m. p. 101–102° (sealed tube), 258 g., was used in the present studies. Determination of the m. p. range of 250–300 mg. samples from every fourth fraction of fifty fractions showed the material to be better than 99.4% pure as calculated from the "half melted point" value,[4] assuming no solid solution formation.

Chlorination of Hexamethylethane.—This was carried out in liquid phase in carbon tetrachloride solution. Vari-

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[2] Whitmore, THIS JOURNAL, **54**, 3274 (1932), and subsequent work from this Laboratory.

[3] Marker and Oakwood, *ibid.*, **60**, 2598 (1938).

[4] Parks and Todd, *Ind. Eng. Chem.*, **21**, 1235 (1929).

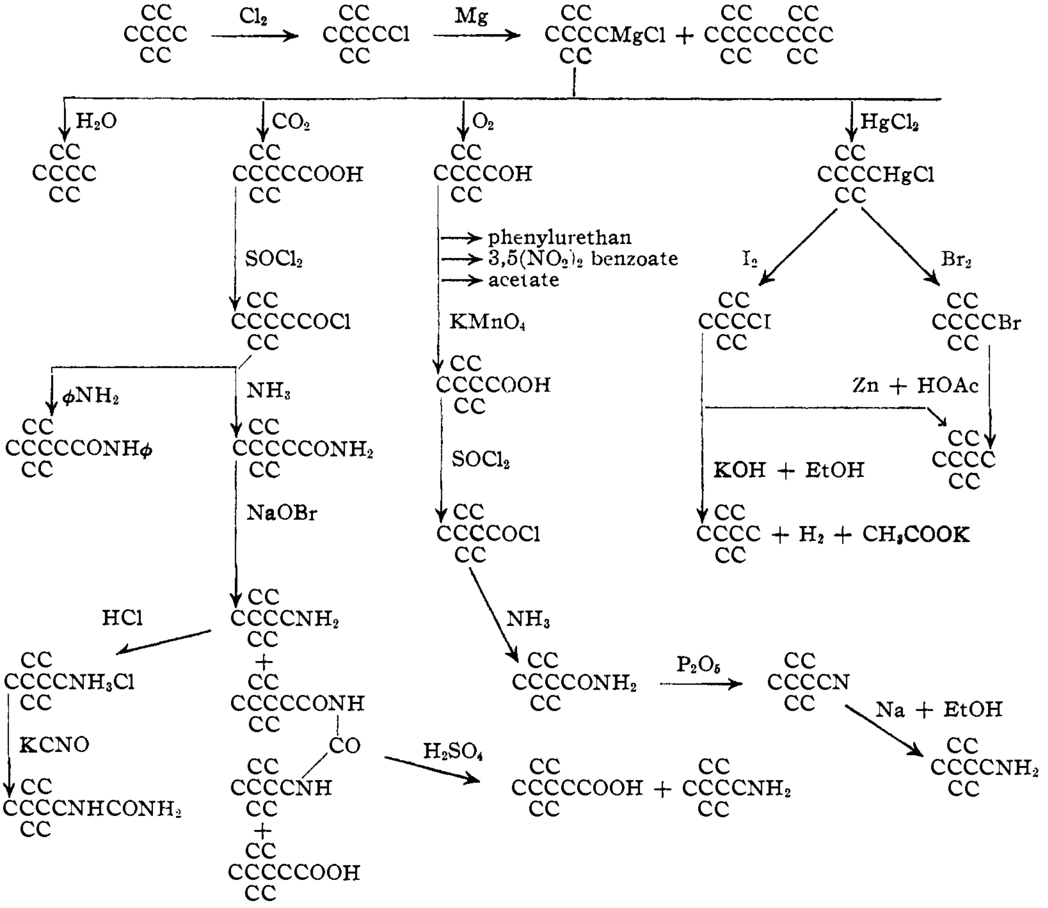
[5] Whitmore and Homeyer, THIS JOURNAL, **54**, 3435 (1932).

[6] Oakwood, unpublished work, this Laboratory, 1937.

[7] Whitmore, Wittle and Harriman, THIS JOURNAL, **61**, 1585 (1939); Whitmore, Popkin and Wittle, *ibid.*, **61**, 1586 (1939).

[8] Laughlin, Nash and Whitmore, *ibid.*, **56**, 1396 (1934).

SUMMARY OF REACTIONS OF HEXAMETHYLETHANE



ous methods were tried but a batch process in sunlight proved the most satisfactory. A typical run is described. In a 500-ml. three-necked flask with sealed stirrer, thermometer, and dropping funnel was placed 0.5 mole of hexamethylethane in 28.5% solution in carbon tetrachloride. The flask was cooled with ice and placed in bright sunlight while 160 ml. of a 2.5 molar solution of chlorine in carbon tetrachloride (0.4 mole of chlorine) was added with stirring as fast as the chlorine reacted. The time of addition varied from one to six hours depending on the brightness of the sunlight. The reaction temperature was 0–10°.

The product from 2.42 moles of hydrocarbon was washed with saturated aqueous sodium bicarbonate, dried over anhydrous sodium sulfate, and most of the solvent distilled off through an indented column. The unreacted hydrocarbon was then distilled through the partial condensation column. The chlorohexamethylethane was fractionated at 15 mm., b. p. 57–59°. The products obtained were unreacted hydrocarbon 37.5%, chlorohexamethylethane 33%, and dichlorohexamethylethane 14.5%. The 15% loss was largely mechanical and involved in handling the highly volatile hexamethylethane. A total of 855 g. of hydrocarbon was chlorinated to give 320 g. of the monochloride. The solvent fractions were carefully refractionated and tested for evidence of *t*-butyl derivatives, especially the chloride, but none was found.

Chlorohexamethylethane is a soft, waxy solid with the characteristic alkyl halide odor. On long standing the opaque crystalline structure of the material disappears and the product is colorless and transparent; b. p. 80–81° at 40 mm.; m. p. 52–53°.

Anal. Calcd. for $C_8H_{17}Cl$: Cl, 23.9. Found: Cl, 24.1.

Grignard Reagent of Chlorohexamethylethane.—In the usual apparatus[9] were placed 5.5 g. (0.23 mole) of magnesium turnings and a small crystal of iodine. The flask was heated to volatilize the iodine. Ethyl bromide, 2 ml. in 70 ml. of ether, was added and the mixture heated to boiling and 29.6 g. (0.2 mole) of chlorohexamethylethane in 135 ml. of ether added over a period of eight hours. The mixture was kept at reflux for an additional nineteen hours. An aliquot of the clear solution was titrated by Gilman's method.[10] The yield of reagent was 70% after correcting for the ethyl bromide used to initiate the reaction.

To an ether solution of the Grignard reagent from 3 g. (0.02 mole) of chlorohexamethylethane was added 40 ml. of ether which had been saturated with water. The resulting solution was poured into cold dilute sulfuric acid, the ether separated, dried, and then distilled to yield a solid, m. p.

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[9] Greenwood, Whitmore and Crooks, THIS JOURNAL, **60**, 2028 (1938).

[10] Gilman, Wilkinson, Fishel and Meyers, *ibid.*, **45**, 150 (1923).

101–102°, which gave no depression when mixed with authentic hexamethylethane.

Preparation of 3,3,4,4-Tetramethylpentanoic Acid.—The Grignard reagent from 44.5 g. (0.3 mole) of chlorohexamethylethane was cooled to −5° and carbon dioxide added with stirring. The solid acid was obtained in the usual way and was crystallized from dilute methanol; 28 g., 59% yield, m. p. 66–67°.

Anal. Calcd. for $C_9H_{18}O_2$: C, 68.29; H, 11.47. Found: C, 68.48; H, 11.61.

Preparation of 3,3,4,4-Tetramethylpentanoyl Chloride.—A solution of 28 g. (0.177 mole) of the above acid in 100 ml. of benzene was added dropwise to 26 ml. (0.36 mole) of boiling thionyl chloride. The product was refluxed for an hour and the benzene and unreacted thionyl chloride distilled off. The residue was distilled to give 25.1 g., 80% yield, of colorless **acid chloride**; b. p. 87–8° at 20 mm., n^{20}_{D} 1.4557, d^{20} 0.9821.

Anal. Calcd. for $C_9H_{17}OCl$: Cl, 20.07. Found: Cl, 19.6.

A small sample of the acid chloride was treated with aniline and the resulting **anilide** recrystallized from petroleum ether, m. p. 175–176°.

Anal. Calcd. for $C_{15}H_{23}ON$: C, 77.19; H, 9.94. Found: C, 77.19; H, 9.93.

Preparation of 3,3,4,4-Tetramethylvaleramide.—A solution of 26 g. (0.14 mole) of 3,3,4,4-tetramethylpentanoyl chloride in 250 ml. of dry ether was cooled in an ice–salt-bath and treated with anhydrous ammonia under a pressure of 10–20 mm. for five hours with stirring. The product was warmed to drive off excess ammonia and the solid separated and thoroughly washed with hot chloroform which was added to the ether solution. Concentration and cooling of this solution gave 17 g. of crystalline **amide**, 77% yield, m. p. 137–138° after two recrystallizations from chloroform. The amide exists in two crystalline forms; recrystallization of 137–138° material from dilute methanol gives large crystals, m. p. 149–150°, which remelt at 137–138°.

Anal. Calcd. for $C_9H_{19}ON$: C, 68.72; H, 12.19. Found: C, 68.80; H, 12.18.

Hofmann Rearrangement of 3,3,4,4-Tetramethylvaleramide.—Sodium hypobromite was prepared by adding dropwise 2.82 ml. (0.055 mole) bromine to a solution of 8.8 g. (0.22 mole) sodium hydroxide in 75 ml. of water. The addition was made at 0°. To this solution 7.85 g. (0.05 mole) of the amide was added all at once and the mixture was stirred for two and a half hours at ice temperature. The ice-bath was removed, 4 g. of sodium hydroxide in 75 ml. of water added, and the amine steam-distilled out of the mixture into 30 ml. of dilute hydrochloric acid. The distillate, about 125 cc., was extracted with three 50-ml. portions of ether to remove a small amount of acid insoluble oil. The aqueous layer was evaporated to dryness to give a white crystalline residue which, after crystallization from ether–ethanol, gave 6.5 g. of white, needle-like crystals of the **hydrochloride** of 2,2,3,3-tetramethylbutylamine. The hydrochloride sublimes at about 330°.

Anal. Calcd. for $C_8H_{20}NCl$: C, 57.96; H, 12.17. Found: C, 58.02; H, 12.38.

Amine hydrochloride, 0.3 g., was mixed with an equal weight of moistened potassium cyanate and warmed on the steam-bath. The inorganic salts were washed out with water and the **monosubstituted urea** crystallized from dilute methanol to give a white crystalline powder, m. p. 176–177°.

Anal. Calcd. for $C_9H_{20}ON_2$: C, 62.73; H, 11.71. Found: C, 62.77; H, 11.70.

The mixture remaining in the flask after the steam distillation was extracted with two 50-ml. portions of ether, the ether dried over magnesium sulfate, the ether evaporated, and the residue recrystallized from methanol; 0.8 g. of brownish-white crystals, m. p. 217–18°. This is the acyl monosubstituted urea $(CH_3)_3C\text{-}C(CH_3)_2\text{-}CH_2CONH\text{-}CONHCH_2\text{-}C(CH_3)_2\text{-}C(CH_3)_3$.

Anal. Calcd. for $C_{18}H_{36}O_2N_2$: C, 69.17; H, 11.62. Found: C, 69.39; H, 11.52.

When 0.3 g. of this material was boiled for fifteen minutes with 10 ml. of 50% sulfuric acid, 3,3,4,4-tetramethylpentanoic acid, m. p. and mixed m. p. 66–67°, was formed and distilled out of the mixture. On making the hydrolysis mixture alkaline with sodium hydroxide, 2,2,3,3-tetramethylbutylamine was formed and distilled into hydrochloric acid. By heating with potassium cyanate, this amine hydrochloride was converted to the monosubstituted urea, m. p. 169–173°; mixed m. p. 173–175°.

The ether extracted aqueous reaction mixture above was made acid and 150 mg. of 3,3,4,4-tetramethylpentanoic acid was precipitated, m. p. and mixed m. p. 66–67°. The reaction products obtained represent a 94% recovery of materials with the hexamethylethane nucleus intact.

Preparation of 2,2,3,3-Tetramethylbutylamine.—To a solution of 9.4 g. (0.057 mole) of 2,2,3,3-tetramethylbutylamine hydrochloride in 50 ml. of water was added an excess of sodium hydroxide solution. The free amine was a sticky, waxy solid, b. p. 100° (110 mm.), m. p. 88.2–88.5°, with a strong, unpleasant, ammoniacal odor. It reacts rapidly with the carbon dioxide in the air to form a white powdery carbonate.

Preparation of 2,2,3,3-Tetramethyl-1-butanol.—Chlorohexamethylethane, 36 g. (0.245 mole), was converted to the Grignard reagent in 75% yield. A gas inlet tube was inserted and dry oxygen bubbled into the solution cooled to −5° with stirring for four hours. The reaction seemed to be complete at the end of the first hour. The product was decomposed with ice and dilute sulfuric acid, the ether layer separated, dried over anhydrous potassium carbonate, and the ether distilled off. Crystallization of the semi-solid residue from petroleum ether gave 17 g. of the *alcohol*, m. p. 149–50°, 53% based on the halide used. It had a pronounced camphor-like odor and was very volatile. No consistent analytical results were obtained due to the great volatility of the compound.

The phenylurethan and 3,5-dinitrobenzoate were prepared from 0.5-g. portions of the carbinol; **phenylurethan**, m. p. 65–66°.

Anal. Calcd. for $C_{15}H_{23}O_2N$: C, 72.24; H, 9.30. Found: C, 72.24; H, 9.25.

The **3,5-dinitrobenzoate** melted at 88–90°.

Anal. Calcd. for $C_{15}H_{20}O_6N_2$: C, 55.53; H, 6.22. Found: C, 55.90; H, 6.21.

Preparation of 2,2,3,3-Tetramethylbutyl Acetate.—A mixture of 2.6 g. (0.02 mole) of 2,2,3,3-tetramethyl-1-

butanol and 20 ml. of acetic anhydride was heated on the steam-bath for three hours. The product was poured into sodium carbonate solution which was then extracted with ether. The ether was removed and the residue distilled to give 2.4 g. of *acetate*, b. p. 191–192° at 739 mm., $n^{20}D$ 1.4291–2, yield 70%.

Oxidation of 2,2,3,3-Tetramethyl-1-butanol.—The carbinol, 2.6 g. (0.02 mole), was oxidized with 4.2 g. of potassium permanganate and 0.5 g. of sodium hydroxide at 70–5°. Acidification of the filtrate from the manganese dioxide gave 2.4 g. of **2,2,3,3-tetramethylbutanoic acid**, m. p. 196–7° after recrystallization from petroleum ether.

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.61; H, 11.19; neut. eq., 144. Found: C, 66.44; H, 11.13; neut. eq., 144.

Preparation of Pentamethylpropionamide.—The above acid was converted to the **amide** which was recrystallized from ammonium hydroxide; m. p. 201–202°.

Anal. Calcd. for $C_8H_{17}ON$: C, 67.07; H, 11.97. Found: C, 66.84; H, 12.01.

Preparation of Pentamethylpropionitrile.—The above amide was heated under a condenser with an equal weight of phosphorus pentoxide. The nitrile collected as a white deposit on the condenser. The resublimed **nitrile** formed white feathery needles, m. p. 131–132°, and had a distinct camphor odor.

Reduction of **Pentamethylpropionitrile.**—The nitrile above was refluxed with 5 ml. of absolute ethanol and 0.3 g. of sodium in an apparatus which led to a trap containing hydrochloric acid. The trap contents were evaporated to dryness to yield a small amount of the amine hydrochloride. This was heated with an equal quantity of potassium cyanate to give the substituted urea, m. p. 170–173°, mixed m. p. with the urea from the amine obtained from the Hofmann reaction, 171–175°.

Hydrocarbon from Coupling of Grignard Reagent.—The mother liquors from the crystallization of 2,2,3,3-tetramethyl-1-butanol were evaporated to remove solvent and the residue treated with warm, dilute permanganate solution until no more permanganate was reduced. The filtrate was freed of manganese dioxide by treatment with sodium bisulfite solution and the organic residue crystallized from methanol to give 6.7 g. of white solid, m. p. 74.0–74.5°. This substance crystallized from methanol in thin lustrous platelets and sublimed readily. It contained no halogen and was not affected by warming with concentrated sulfuric acid. Refluxing in dioxane with sodium-potassium alloy had no effect. The product appears to be 2,2,3,3,6,6,7,7-octamethyloctane from the coupling of the Grignard reagent and represents a 24% yield from the halide.

Anal. Calcd. for $C_{16}H_{34}$: C, 84.86; H, 15.14; mol. wt., 226. Found: C, 84.59; H, 15.21; mol. wt., 218 (benzene).

Preparation of 2,2,3,3-Tetramethylbutylmercuric Chloride.—To a solution of 70 g. of mercuric chloride in 250 ml. of dry ether was added slowly with stirring a solution of the Grignard reagent from 33.4 g. (0.225 mole) of chlorohexamethylethane in 300 ml. of solution. After addition, the product was refluxed for four hours, the ether distilled off, 300 ml. of water and 10 ml. of hydrochloric acid added, and the mixture warmed on the steam-bath. The alkyl mercuric chloride was filtered off, washed with water, and crystallized from aqueous alcohol. Recrystallization from methanol gave a white product, m. p. 125–155°. Recrystallization from petroleum ether gave 28 g., 35% yield, of feathery white crystals, m. p. 170–171°.

Preparation of **Iodohexamethylethane.**—Iodine, 13 g. (0.051 mole), tetramethylbutylmercuric chloride, 17.5 g. (0.05 mole), 20 ml. of ether and 50 ml. of a 1.4 *M* solution of potassium iodide were placed in a flask and shaken vigorously with the addition of more potassium iodide from time to time to dissolve the mercuric iodide formed. When all the iodine had reacted, the ether layer was separated, the water extracted twice with ether, the combined extracts washed with sodium thiosulfate solution and dried over potassium carbonate. Removal of the ether and distillation of the residue gave 10.8 g., 90%, b. p. 112–113° (40 mm.), $n^{20}D$ 1.5101, d^{20} 1.3907.

Anal. Calcd. for $C_8H_{17}I$: I, 52.9. Found: I, 52.9.

Iodohexamethylethane is a colorless liquid with the characteristic alkyl halide odor. It reacts rapidly in the cold with solid silver nitrate to give a precipitate of silver iodide. When an attempt to prepare the Grignard reagent was made, the C_{16} hydrocarbon from the coupling reaction was all that could be isolated. The structure of the iodide was established by warming with glacial acetic acid and zinc to give hexamethylethane, mixed m. p. 99.5–100.5°.

Preparation of Bromohexamethylethane.—This was prepared from 9.6 g. (0.027 mole) of the substituted mercuric chloride, bromine and sodium bromide solution as in the above preparation. Distillation gave 3.1 g., 58%, of a colorless *bromide*, b. p. 92–93° (40 mm.), $n^{20}D$ 1.4692, d^{20} 1.1562.

Anal. Calcd. for $C_8H_{17}Br$: Br, 41.4. Found: Br, 40.8.

As in the case of iodohexamethylethane, reduction with zinc and acetic acid gave hexamethylethane.

Reaction of Iodohexamethylethane with Alcoholic Potassium Hydroxide.—In a side arm test-tube fitted with a reflux condenser were placed 476 mg. (0.002 mole) of iodohexamethylethane, 1.8 g. of U. S. P. stick potassium hydroxide and 0.6 ml. of "aldehyde free" ethanol. The side arm of the test-tube was connected to a gas-measuring buret filled with saturated sodium chloride solution. The entire apparatus was flushed out with nitrogen and the tube heated gradually to 160° for one hour and then to 160–180° for another hour. At 140° there was a noticeable increase in the rate of gas evolution and at 145–150° solid appeared on the condenser. After forty minutes there was little change in the gas volume. The total volume of gas was 48.0 ml. Analysis showed it to be 33% nitrogen, 66% hydrogen, and 0.6% hydrocarbon. Allowing for the nitrogen present in the apparatus, the reaction evolved 0.0017 mole of hydrogen or 86% of the theoretical; an 84% yield of hexamethylethane was obtained.

The residue in the reaction flask was completely soluble in water; 3 ml. of sulfuric acid and 100 ml. of water were added and the solution distilled. The main portion of the distillate contained no halogen but 0.00165 equivalent of a volatile acid. On the assumption that this is acetic acid, the yield is 83%.

Summary

1. Hexamethylethane has been obtained in a

pure state, chlorinated, and many derivatives made and reactions studied.

2. The Hofmann rearrangement of 3,3,4,4-tetramethylvaleramide has been studied and products recovered in 94% yield without rearrangement of the hexamethylethane nucleus.

3. The reaction of iodohexamethylethane with potassium hydroxide failed to give any evidence of rearrangement.

4. Twenty-two compounds containing the hexamethylethane carbon skeleton have been prepared and described. They include such difficultly obtainable materials as 2,2,3,3-tetramethyl-1-butanol, 1-amino-2,2,3,3-tetramethylbutane, 2,2,3,3-tetramethylbutanoic acid (dimethyl-*t*-butylacetic acid), 3,3,4,4-tetramethylpentanoic acid and 2,2,3,3,6,6,7,7-octamethyloctane.

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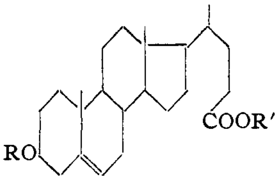
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Certain Ethers and Esters of 3-Hydroxy-5-cholenic Acid

BY BYRON RIEGEL, JAMES A. VANDERPOOL AND MELVIN F. W. DUNKER

In an effort to protect the nuclear hydroxyl group of 3-hydroxy-5-cholenic acid two labile ethers have been prepared. Because of the low solubility of the free acid, its methyl ester has been used. The usual procedure of tritylation, namely, treatment with trityl chloride in pyridine which has been applied to cholesterol by Josephson[1] gave, on modification, methyl 3-triphenylmethoxy-5-cholenate. The trityl ethers of steroids[1,2] are reported to be stable to alkaline reagents but easily hydrolyzed by mineral acids. Refluxing an acetic acid solution of methyl 3-triphenylmethoxy-5-cholenate resulted in an exchange of the trityl for the acetyl group.

Direct benzylation of hydroxylated steroids has proven difficult. The benzyl ether was prepared by heating methyl 3-*p*-toluene-sulfonoxy-5-cholenate with benzyl alcohol, analogous to the preparation[3] of benzyl cholesteryl ether. However, under the conditions of the reaction partial alcoholysis of the methyl ester took place. This fact together with the liberation of *p*-toluenesulfonic acid which probably promoted tar formation, as well as other reactions, not only militated against a good yield but also increased the difficulty of isolating a pure product. The equation for this reaction is $\mathrm{I} + 2\mathrm{C_6H_5CH_2OH} \xrightarrow{100°} \mathrm{II} + \mathrm{CH_3OH} + \mathrm{C_7H_7SO_3H}$.



I, R = $p\text{-}\mathrm{CH_3C_6H_4SO_2}$—; R′ = $\mathrm{CH_3}$
II, R = R′ = $\mathrm{C_6H_5CH_2}$—

The benzyl 3-benzyloxy-5-cholenate exists in dimorphic forms, one melting at 87–88° and the other at 108.5–109.5°. When the lower melting form is melted, allowed to stand several months or crystallized several times, it is converted to the higher melting form.

The benzyl ester-ether was also formed in small amounts when 3-hydroxy-5-cholenic acid and benzyl alcohol were heated with a few drops of sulfuric acid. The main product from this reaction was the expected benzyl 3-hydroxy-5-cholenate.

To confirm the formula of the benzyl ester-ether, isolated in the reaction illustrated above, it was converted to the methyl 3-benzyloxy-5-cholenate. Saponification of the benzyl ester-ether gave 3-benzyloxy-5-cholenic acid which was esterified with diazomethane. The methyl ester benzyl ether melted at 99–100.5°.

The authors wish to thank the Rockefeller Foundation for aiding this research.

Experimental[4]

Methyl 3-Hydroxy-5-cholenate.—The authors wish to thank Dr. Erwin Schwenk of the Schering Corporation, Bloomfield, New Jersey, for supplying us with generous amounts of two different materials from which the pure 3-hydroxy-5-cholenic acid was isolated. The first material was a rather crude mixture containing sodium 3-acetoxy-5-cholenate. A procedure for obtaining the pure bile acid

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(1) Josephson, *Ann.*, **493**, 174 (1932).

(2) (a) Girard and Sandulesco, French Patent 817,340; British Patent 488,801; (b) Williams, British Patent 467,161; U. S. Patent 2,180,762.

(3) Stoll, *Z. physiol. Chem.*, **207**, 147 (1932).

(4) All melting points are corrected. Microanalyses are by Dr. T. S. Ma, University of Chicago.