methylhexane occurs in sulfuric acid.[9] Evidently the triethylmethyl structure has a strong tendency to rearrange.

Experimental

Ethylmagnesium bromide was allowed to react with ethyl carbonate[10] to give 3-ethyl-3-pentanol and with methyl propyl ketone[5] to give 3-methyl-3-hexanol. The corresponding chlorides were prepared by stirring the alcohols with two volumes of concentrated hydrochloric acid for one hour at 25°.[8] The layers were separated, the chloride was washed with water, dried over calcium chloride and distilled through a glass-packed column at 100 mm. Both chlorides were contaminated with olefin, which did not, however, interfere with analysis of the spectra.

Partial spectra of the alcohols and chlorides are given in Table I. The symmetrical compounds have small peaks corresponding to the loss of a propyl group. The unsymmetrical compounds have sizable peaks at these masses and the ratio of the relative intensities corresponding to the loss of ethyl and propyl groups is 2:3. The spectra are consistent with the assigned structures. This same correlation is observed with 3-methyl-3-phenylhexane and other secondary and tertiary alkylbenzenes.[11]

In both alkylations, 0.1 mole of the chloride was dissolved in 1.0 mole of benzene and the solution was cooled to 5°. To this was added 0.06 mole of anhydrous ferric chloride. The solution was allowed to warm slowly and, when evolution of hydrogen chloride ceased, water was added. The hydrocarbon layer was washed successively with 10% hydrochloric acid, 5% sodium bicarbonate and water, and was dried over calcium chloride. Both alkylates were purified by fractionation in a spinning-band column 90 cm. long × 5 mm. in diameter.[12] Selected cuts from the principal plateaus were analyzed with a Consolidated model 21-102 mass spectrometer. The 2-methyl-2-phenylpentane, 98% pure, boiled at 89.5° (20 mm.), n^{20}_D 1.4930. The 3-methyl-3-phenylhexane boiled at 110° (20 mm.), n^{20}_D 1.4950.

Reference samples of 2-methyl-2-phenylpentane and 2-phenylhexane were kindly supplied by Professor Herman Pines of Northwestern University. Reference samples of 3-methyl-3-phenylpentane and 3-ethyl-3-phenylpentane were prepared by sodium-catalyzed ethylation of ethylbenzene and toluene.[13]

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Ketones Contained in a Gilsonite Distillate

BY JAMES M. SUGIHARA AND THOMAS F. MCCULLOUGH

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During the investigation of a Gilsonite coker-distillate,[1] the presence of carbonyl compounds was detected in a low-boiling fraction, by the formation of 2,4-dinitrophenylhydrazones. Acetone,[2,3] 2-butanone[2] and 3-pentanone,[2] have been found in shale oil.

The portion of the Gilsonite distillate boiling at 27–125°[1] was fractionated. The fractions collected at 29–52°, 59–64° and 67–81° were found to react with a 2,4-dinitrophenylhydrazine reagent[4] to form crystalline hydrazones. Intervening, lower and higher fractions gave extremely faint or no visible evidence of reaction.

The 2,4-dinitrophenylhydrazones isolated were identified as those of 2-butanone, 3-methyl-2-butanone and 2-pentanone. In addition the *p*-nitrophenylhydrazone of 2-butanone was obtained.

The presence of carbonyl compounds in the three separate fractions suggested an efficient separation, possibly as azeotropes. Ketones are known to form azeotropes with hydrocarbons such as cyclohexane and hexane.[5]

Chromatography of mixtures of 2,4-dinitrophenylhydrazones of carbonyl compounds has been described as a satisfactory method of separation of these compounds.[6] Derivatives of monocarbonyls, containing not more than four carbon atoms, have been separated. Paper chromatography is reported[7] to enable separation of some of the higher homologs. In our hands the chromatography of the mixture of the 2,4-dinitrophenylhydrazones of 2-butanone, 3-methyl-2-butanone and 2-pentanone on silicic acid failed to effect a satisfactory separation.

Experimental[8]

Separation of Ketones.—The portion of the Gilsonite coker-distillate[1] boiling between 27 and 125° (300 ml.) was fractionated in a Todd precise fractionation assembly using a column (850 × 12 mm.) packed with glass helices. At periodic intervals a few drops of distillate were collected and tested with the carbonyl reagent.[4] Formation of colored hydrazones was observed for fractions of boiling ranges 29–52° (24 ml.) (A), 59–64° (26 ml.) (B), and 67–81° (14 ml.) (C). The fraction, b.p. 64–67° (11 ml.), gave a faint test. The fractions, b.p. 27–29° (4 ml.), 52–59° (25 ml.), and 81–125°, gave negative tests.

2,4-Dinitrophenylhydrazones.—Each of the fractions A, B and C was shaken with 5 ml. of the hydrazine reagent. The resulting precipitates were collected, washed with 50 ml. of water and dissolved in 25 ml. of ether. The ether solutions were washed in succession with equal volumes of water, 5% aqueous sodium bicarbonate, water, and concentrated. The hydrazones were recrystallized from ethanol and water to constant m.p. From A, a 2,4-dinitrophenylhydrazone of m.p. 111–112° (reported[9] for 2-butanone 2,4-dinitrophenylhydrazone, 115°) was obtained. From B, a 2,4-dinitrophenylhydrazone of m.p. 123–124° (reported[10] for 3-methyl-2-butanone 2,4-dinitrophenylhydrazone, 122–122.5°) was obtained. The purified compound isolated from C had a m.p. of 140–141° (reported[9] for 2-pentanone 2,4-dinitrophenylhydrazone, 141°). Melting points of mixtures of these compounds with authentic samples of like melting points were not depressed. Yields were 80 mg. from A, 30 mg. from B and 40 mg. from C (crude).

The infrared spectra of the three 2,4-dinitrophenylhydrazones, determined with a Perkin-Elmer recording spectrophotometer, model 21, with pressed potassium iodide discs, were indistinguishable from those of authentic samples.

Other Derivatives.—The *p*-nitrophenylhydrazone of 2-butanone, m.p. 125–126.5° (reported[9] 128–129° (124°)),

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did not depress the m.p. of authentic 2-butanone *p*-nitrophenylhydrazone. *p*-Nitrophenylhydrazones were not obtained from fractions B or C. Semicarbazones were not obtained from any of the fractions.

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17β-Methyl-Δ^5-androstene-3β-ol

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A report by Ghosh[1] on the isolation of a $C_{20}H_{32}O$ compound, called serposterol from a Rauwolfia serpentina plant, suggested the tentative structure as methylandrostenol. We have prepared the postulated compound, 17β-methyl-Δ^5-androstene-3β-ol, previously unknown, and found that it is not identical with the natural material.[2]

The mixture of 17-methylene-3β-acetoxy-$\Delta^{5,6;17,20}$-androstadiene and 17-methyl-3β-acetoxy-$\Delta^{5,6;16,17}$-androstadiene, resulting from dehydration of 3β-acetoxy-17α-methyl-$\Delta^{5,6}$-androstene-17β-ol, was selectively reduced with palladium-on-charcoal catalyst to give a single compound. Hydrolysis gave the compound proposed as serposterol. Comparison of the X-ray pattern and a mixed melting point determination showed that the two compounds were different. Comparison of the infrared spectra however showed great similarities but the curves were not superimposable.

That the hydrogenation gave the 17β-methyl compound was shown by the work of Heusser[3] in the hydrogenation of the same 17-methylene-3β-acetoxy-$\Delta^{5,6;17,20}$-androstadiene with platinum catalyst to give, after mild hydrolysis, the known 17β-methylandrostane-3-ol. Furthermore, Hershberg[4] obtained a 17β-ethyl compound by the reduction of $\Delta^{5,16}$-pregnadien-20-yne-3β-ol with palladium-on-charcoal as in the present series.

Experimental

3β-Acetoxy-17α-methyl-Δ^5-androstene-17β-ol.—The acetate was prepared from 2.0 g. of 17α-methyl-Δ^5-androstene-3β-17β-diol in 12 cc. of anhydrous pyridine and 6 cc. of acetic anhydride. After 6 hours the mixture was poured into ice, and the product filtered. Recrystallization from ethyl acetate yielded 1.15 g. of colorless needles, m.p. 164–165° (first crop), and 0.750 g., m.p. 162–164° (second crop); lit.[5] reports m.p. 160–161°.

A Mixture of 3β-Acetoxy-17-methyl-$\Delta^{5,6;16,17}$-androstadiene and 3β-Acetoxy-17-methylene-$\Delta^{5,6;17,20}$-androstadiene.—The acetate was dehydrated by the procedure of Julia and Heusser[3] using phosphorus oxychloride–pyridine. From 1.9 g. of acetate there was obtained 0.8 g. of product, m.p. 116–118°. This was found to be a mixture of dienes which could be used directly in the hydrogenation without separation.

3β-Acetoxy-17β-methyl-Δ^5-androstene.—The reduction of the mixture of dienes (800 mg.) in absolute ethanol was carried out using 400 mg. of prereduced 5% palladium-on-charcoal catalyst in an atmosphere of hydrogen. One mole of hydrogen was absorbed in 20 minutes. Recrystallization of the product from methanol, after removal of catalyst and solvent, gave 250 mg. of fine needles, m.p. 129–131°, $[\alpha]^{26}\text{D}$ −64°.

Anal. Calcd. for $C_{22}H_{34}O_2$: C, 79.95; H, 10.37. Found: C, 79.71; H, 10.21.

17β-Methyl-Δ^5-androstene-3β-ol.—To a solution of 500 mg. of potassium carbonate in 10 cc. of water, 10 cc. of dioxane and 100 cc. of methanol was added 250 mg. of the acetoxyandrostene. The solution was refluxed for one hour, then evaporated to dryness and water added. The solid was collected and recrystallized from methanol to give 0.190 g. of colorless rods, m.p. 163–165°. The analytical sample was recrystallized two additional times from methanol, m.p. 164–165°, $[\alpha]^{26}\text{D}$ −65.7°; $\lambda_{\max}^{\text{CHCl}_3}$ 2.84, 3.40, 6.85, 7.27, 9.56.

Anal. Calcd. for $C_{20}H_{32}O$: C, 83.27; H, 11.18. Found: C, 83.09; H, 11.30.

Upon admixture with authentic serposterol (m.p. 151–153°) there was a depression in melting point to 124–131°. In addition, X-ray pattern and infrared spectra were not identical.

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Derivatives of Piperazine. XXVIII. Synthesis of 1-Aryl-4-thioaryloylpiperazines and 1-Aryl-4-thioalkanoylpiperazines by the Kindler Modification of the Willgerodt Reaction

BY C. B. POLLARD AND JOHN C. BRAUN

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The Kindler modification of the Willgerodt reaction has been found to be applicable to both ketones[1,2] and aldehydes of the aromatic series[3,4] and the aliphatic series.[5,6]

Heterocyclic amines such as morpholine[7] and piperazine[8] were found to be especially suitable, since their use permitted reactions to be run in vessels which were open to the atmosphere.

The authors have found that N-phenylpiperazine and N-phenylpiperazines which have substituents on the benzene ring also undergo the reaction when refluxed with an aldehyde or ketone and sulfur in pyridine solution.

Purification of the products was rather difficult, and considerable differences in procedure were required, depending on whether the aldehyde or ketone was aliphatic or aromatic. Thioamides derived from the latter are moderately to slightly soluble in ethanol, while those derived from the former are generally very soluble.

Experimental

The N-phenylpiperazines were prepared by the methods of Pollard and Wicker[9] and Pollard and MacDowell.[10] The

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