mixture with an authentic specimen. Identity was established further by comparison of the infrared spectra and formation of a quinoxaline derivative, m.p. 218–220°.

In another experiment,[16] the reaction was carried out as above except that equimolar proportions were used, and there was isolated 18% of phenanthrenequinone. The original black precipitate was refluxed with sodium sulfite[3] in dilute ethanol for two hours, filtered, and the filtrate was extracted thoroughly with ether. The ether residue after recrystallization from hexane–acetone furnished 11% of **9,10-dihydrophenanthrene-9,10-diol** with m.p. 175–177°, undepressed upon admixture with a sample prepared with osmium tetroxide.[3]

Reaction of Diphenyl Sulfide with Ruthenium Tetroxide.—A large excess of sulfide was employed in order to isolate any intermediate oxidation product.

An ice-cold solution of 4.798 g. (0.0257 mole) of diphenyl sulfide in 150 cc. of carbon tetrachloride was treated exactly as described above with 25 cc. of a carbon tetrachloride solution of ruthenium tetroxide (containing 1.043 g., 0.0063 mole of tetroxide). Precipitation of ruthenium dioxide started immediately and after 14 hours in the refrigerator, the precipitate was centrifuged and washed thoroughly with carbon tetrachloride and ether. The residue after evaporation of the organic solvents was chromatographed on 100 g. of alumina. The unreacted sulfide was removed by the original hexane–benzene (7:3) eluates, while **diphenyl sulfone** (0.58 g., 42%) with m.p. 124.5–125.5° was obtained from the hexane–benzene (1:9) fractions. Identity was established by a mixture melting point and infrared comparison with an authentic sample; the two typical sharp sulfone bands[17] at 8.65 and 9.0 μ were present.

Anal. Calcd. for $C_{12}H_{10}O_2S$: C, 66.05; H, 4.62. Found: C, 66.32; H, 4.91.

Evaporation of the benzene and benzene–ether (1:1) eluates to dryness and recrystallization from benzene–petroleum ether furnished 0.4 g. (32%) of **diphenyl sulfoxide** with m.p. 68–69°. Identity was established in the usual manner including infrared comparison (typical[18] sulfoxide band at 9.6 μ).

Anal. Calcd. for $C_{12}H_{10}OS$: C, 71.28; H, 4.99. Found: C, 71.18; H, 5.28.

When an equimolar ratio of diphenyl sulfoxide and ruthenium tetroxide was mixed in carbon tetrachloride solution and worked up in the above manner, a 93% yield of diphenyl sulfone was realized.

Reaction of Methyl *p*-Tolyl Sulfide with Ruthenium Tetroxide.—Methyl *p*-tolyl sulfide (3.90 g., 0.0281 mole) was oxidized with 1.165 g. (0.007 mole) of ruthenium tetroxide exactly as indicated for diphenyl sulfide and purified by chromatography. **Methyl *p*-tolyl sulfone** was obtained in 31% yield, m.p. 85–86° (lit.[19] m.p. 86–87°) but no sulfoxide could be detected in the later eluates of the chromatogram.

Anal. Calcd. for $C_8H_{10}O_2S$: C, 56.46; H, 5.92. Found: C, 56.35; H, 5.82.

Reaction of Methyl Benzyl Sulfide with Ruthenium Tetroxide.—The oxidation was carried out in the above described manner with 0.0252 mole of methyl benzyl sulfide and 0.0067 mole of ruthenium tetroxide. **Methyl benzyl sulfone** was isolated in 58% yield, m.p. 125–126°,[20] but no sulfoxide was found in the latter chromatogram fractions.

Anal. Calcd. for $C_8H_{10}O_2S$: C, 56.46; H, 5.92. Found: C, 55.98; H, 5.69.

Reaction of Triphenylmethyl Phenyl Sulfide and Ruthenium Tetroxide.—The oxidation of the triphenylmethyl phenyl sulfide[11] was carried out in the standard manner except that equimolar amounts were employed. As in the above-described cases, ruthenium dioxide separated immediately upon addition of the tetroxide. After centrifugation, the carbon tetrachloride solution was evaporated to dryness yielding a residue with m.p. 77–87° which was partitioned between water[21] and ether. The ether solution was washed until neutral, dried, evaporated and dissolved in warm cyclohexane from which 33% of triphenylcarbinol (m.p. 160–162°) separated. The filtrate was evaporated and the residue was chromatographed on alumina yielding 13% of recovered sulfide and an additional 8% of triphenyl carbinol. No disulfide[11] was found in any chromatogram fractions. Acidic products formed were not investigated.

Reaction of Androstan-17-one Ethylene Hemithioketal (I) and Ruthenium Tetroxide.—A mixture of 0.48 g. (0.0011 mole) of the hemithioketal (I)[9] and 0.34 g. (0.0021 mole) of ruthenium tetroxide in carbon tetrachloride was left in the refrigerator overnight. After centrifugation the supernatant liquid was evaporated to dryness and triturated with acetone yielding 0.35 g. of the **sulfone II** with m.p. 187–190°. Two recrystallizations from acetone raised the m.p. to 199–200°, undepressed upon admixture with an authentic sample[9] prepared by perphthalic acid oxidation of I. The infrared spectra of the two specimens were identical.

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(16) This experiment was performed at the University of Mexico with Dr. Alberto Sandoval.

(17) K. C. Schreiber, *Anal. Chem.*, **21**, 1168 (1949).

(18) D. Barnard, J. M. Fabian and H. P. Koch, *J. Chem. Soc.*, 2442 (1949).

(19) R. Otto, *Ber.*, **18**, 154 (1885).

(20) Reported, m.p. 124.5° (A. Freiman and S. Sugden, *J. Chem. Soc.*, 263 (1928)).

(21) The ruthenium tetroxide probably contains a small amount of water since it is obtained by co-distillation with water. It is therefore not necessary to postulate that the hydrogen necessary for the formation of triphenylcarbinol is furnished during the ether–water partition. Indeed, direct chromatography of the carbon tetrachloride residue gave essentially the same results.

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Δ^5-Pregnen-20-one[1]

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In a study of the hydrogenolyses of toluenesulfonates with lithium aluminum hydride Schmid and Karrer[2] observed that the tosylate of cholesterol yielded both Δ^5-cholestene and 3,5-cyclocholestane. In contrast reduction of the tosylate of Δ^5-pregnen-3β-ol-20-one followed by reoxidation of the 20-hydroxy group furnished only a single pure product[3] of the composition $C_{21}H_{32}O$. This was held probably to be the hitherto undescribed[4] Δ^5-pregnen-20-one, as it showed a well-defined infrared absorption maximum in the region of the bending vibrations of hydrogen attached to a trisubstituted double bond. However, the spectrum which possessed absorption maxima near 12.67 and 12.37 μ failed to conform to the generalizations which had emerged from a study of the spectra of Δ^5-unsaturated steroids.[5] These compounds showed in general two maxima in this region that could be associated with the presence of the double bond. If no functional group other than one at C-3 was present in the vicinity of the double bond one of these peaks was close to 12.50 μ (800 cm.$^{-1}$) while the position of the other depended on the nature and the configuration of the substituent at C-3. Since Δ^5-cholestene showed maxima at 12.52, 12.37 (w) and 12.01 μ (799, 809, 833 cm.$^{-1}$) an absorption peak near 12.50 μ was to be expected also for the spectrum of Δ^5-pregnen-20-one. As it

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(1) Supported by grants from the Hanna Research Fund and from the National Cancer Institute of the National Institutes of Health, Public Health Service.

(2) H. Schmid and P. Karrer, *Helv. Chim. Acta*, **32**, 1371 (1949).

(3) P. Karrer, H. Asmis, K. N. Sareen and R. Schwyzer, *ibid.*, **34**, 1022 (1951).

(4) The preparation of this substance has been recorded in the patent literature (R. E. Marker and E. L. Wittle, U. S. Patents 2,397,424, 2,397,425 and 2,397,426). However, the product was not characterized in any way.

(5) H. Hirschmann, THIS JOURNAL, **74**, 5357 (1952).

seemed important to ascertain whether the spectrum of this compound was indeed anomalous we undertook its preparation by an unambiguous route.

3β-Chloro-Δ^5-pregnen-20-one was prepared from Δ^5-pregnen-3β-ol-20-one with phosphorus pentachloride and reduced with sodium and propanol. The resulting mixture of the two Δ^5-pregnen-20-ols was oxidized according to the method of Bladon, *et al.*,[6] which proved superior to the customary procedure with bromination of the 5–6 double bond. The reaction product was identified as Δ^5-pregnen-20-one by its composition, its rotation, and by its conversion to the known allopregnan-20-one. It is clearly different from the product described by the Swiss workers as shown by a comparison of the infrared spectra and the melting points. The absorption maxima of our preparation (12.54 (v.s.), 12.36 (w), and 12.02 (v.s.) μ (798, 809, 832 cm.$^{-1}$) in carbon disulfide, and near 12.50, 12.34 and 11.95 μ (800, 811, 837 cm.$^{-1}$) in Nujol) were in close accord with the corresponding peaks of Δ^5-cholestene[5] and of 20α-acetoxy-Δ^5-pregnene. Since no peaks of comparable height were seen in the reduction products[7] cholestane[6] and allopregnan-20-one it is probable that all three frequencies are characteristic of Δ^5-unsaturated steroids that lack a substituent at C-3 and are not subject to disturbing influences from other vicinal groups.

The results serve to re-emphasize that the presence even of a strong maximum in the 12 μ range is insufficient proof for the presence of a trisubstituted double bond and indicate the greater reliability of a spectral comparison with closely related structures.

Experimental[8]

Δ^5-Pregnen-20-one.—A solution of 62 mg. of phosphorus pentachloride in 2.8 cc. of dry chloroform was added dropwise to a stirred solution of 37 mg. of Δ^5-pregnen-3β-ol-20-one in 4.6 cc. of the same solvent (50 minutes at $-15°$). The mixture was stirred at 0° for 10, and at room temperature for 60 minutes and worked up in the usual manner.[9] The resulting 3β-chloro-Δ^5-pregnen-20-one which was purified by chromatography on alumina and by recrystallization from dilute methanol and from petroleum ether melted at 148.5–150.5°; lit.[10] m.p. 146.5° uncor. The absorption peaks at 13.15, 12.51 and 12.18 μ (760, 799, 821 cm.$^{-1}$) are in good accord with the corresponding maxima of other Δ^5-3β-chlorosteroids.[11] Another strong peak was at 12.10 μ (827 cm.$^{-1}$). A solution of 46.8 mg. of 3β-chloro-Δ^5-pregnen-20-one in 8 cc. of propanol was reduced with 540 mg. of sodium as described for other 3-chlorosteroids.[9] The crude diols (42.3 mg.) in 6 cc. of acetone were oxidized with 0.13 cc. of 8 *N* chromic acid reagent[6] for 5 minutes at 34°. The excess oxidant was reduced by adding immediately a mixture of 110 mg. sodium bisulfite, 1.2 cc. of *N* sulfuric acid and 6.4 cc. of acetone. The reaction mixture was distributed between ether and water. The ether layer was washed with potassium carbonate and water. The ether residue (35.7 mg.) was freed of a high melting impurity which was rather insoluble in petroleum ether and recrystallized from this solvent and from methanol; yield of Δ^5-pregnen-20-one 16.2 mg., m.p. 133–135°, $[\alpha]^{27}\mathrm{D}$ $+6°$ (*c* 0.5, chloroform) $[\mathrm{M}]\mathrm{D}$ $+18°$ ($[\mathrm{M}]\mathrm{D}$ calcd. $+26°$ from $[\mathrm{M}]\mathrm{D}$ for cholesterol[12] $-154°$, Δ^5-cholestene[12] $-207°$ and of Δ^5-pregnen-3β-ol-20-one[12] $+79°$); carbonyl peak at 5.86 μ (1706 cm.$^{-1}$).

Anal. Calcd. for $C_{21}H_{32}O$: C, 83.94; H, 10.74. Found: C, 83.81; H, 10.72.

Allopregnan-20-one.—A mixture of 8.7 mg. of Δ^5-pregnen-20-one, 200 mg. of prereduced palladium–calcium carbonate catalyst and 8.5 cc. of 95% ethanol were shaken in an atmosphere of hydrogen. The uptake of gas ceased after 15 minutes. The reduction product was isolated in the usual manner[9] and recrystallized from methanol to give 5.3 mg. of allopregnan-20-one. The m.p. (136.5–137.5°) remained unchanged by admixture with a specimen[13] prepared from allopregnane-3,20-dione. The infrared spectra of both preparations were in good agreement. In the 12 μ region allopregnan-20-one showed very weak peaks near 12.56 and 12.09 μ (796, 827 cm.$^{-1}$). The ketone peak was at 5.86 μ (1706 cm.$^{-1}$). The compound has been prepared by a variety of methods. Several of these are cited by Mancera, *et al.*[14]

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[6] P. Bladon, J. M. Fabian, H. B. Henbest, H. P. Koch and G. W. Wood, *J. Chem. Soc.*, 2402 (1951).

[7] This is in contrast to the peaks seen near 12.0 μ in many Δ^5-3β-acetoxy steroids. These weaker maxima were considered to be unrelated to the presence of the double bond since reduction caused little or no spectral change (*cf.* Fig. 1 in ref. 5).

[8] All m.p.'s reported are corrected. Details on spectrographic technique have been given previously.[5] The solvent was carbon disulfide unless indicated otherwise. Weak bands are designated as (w), very strong ones as (v.s.). The analysis is by Dr. E. W. D. Huffman, Wheatridge, Colorado.

[9] H. Hirschmann and F. B. Hirschmann, *J. Biol. Chem.*, **184**, 259 (1950).

[10] A. Butenandt and W. Grosse, *Ber.*, **70**, 1446 (1937).

[11] H. Hirschmann, *Ciba Foundation Colloquia*, in press.

[12] D. H. R. Barton and J. D. Cox, *J. Chem. Soc.*, 783 (1948).

[13] H. Hirschmann, F. B. Hirschmann and M. A. Daus, *J. Biol. Chem.*, **178**, 751 (1949).

[14] O. Mancera, G. Rosenkranz and C. Djerassi, *J. Org. Chem.*, **16**, 192 (1951).

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β-Fattyalkylaminopropionaldehydes[1]

BY KENDRICK R. EILAR AND OWEN A. MOE

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It has been found that aliphatic amines having long chain (twelve or more carbon atoms) alkyl groups undergo the Mannich reaction[2] with formaldehyde and other lower aldehydes which contain α-hydrogen atoms in much the same manner as do the lower alkylamines. The products are obtained in good yields (81–92%) in every case except those involving primary fatty amines and acetaldehyde; in such cases mixtures are obtained which are difficult if not almost impossible to separate.

The aldehyde function of the β-fattyalkylaminopropionaldehydes is singularly unreactive for an aldehydo group. It is noteworthy that all attempts to prepare the usual aldehyde derivatives (2,4-dinitrophenylhydrazone, semicarbazone and oxime) were unsuccessful, although positive Tollens tests[3] were obtained. However, the elemental analyses, the mode of formation, and the infrared spectrum of one of the compounds (α,α-dimethyl-β-didodecylaminopropionaldehyde; bands at 880, 1100, 1310, 1730 and 2700 cm.$^{-1}$) constitute strong evidence in favor of the β-alkylaminopropionaldehyde structure.

Experimental

α,α-Dimethyl-β-didodecylaminopropionaldehyde.—Didodecylamine (71 g.) was dissolved in 95% ethanol (100 ml.)

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[1] Paper No. 148, Journal Series, General Mills Research Laboratories.

[2] C. Mannich, U. S. Patent 1,824,676; Blicke, in "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 303.

[3] S. M. McElvain, "The Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., 1945, p. 133.