When the partially purified product (0.350 g.) was recrystallized from benzene (7 ml.) and washed with pentane-hexane, it yielded a solid (0.185 g.) melting at 123–125°; melting point of an admixture with authentic dodecanedioic acid (m.p. 128–129°) was 123–127°. Gas-liquid chromatography showed 93% dodecanedioic acid.

Characterization of the volatile reaction product. The volatile cleavage product was isolated by saturating the condensate with sodium chloride then extracting with ether; the ether extract was worked up in the usual manner. The crude reddish yellow liquid (2.02 g.) was distilled, yielding a pale yellow liquid (0.94 g., b.p. 165–185°). The distillate was treated with saturated sodium bisulfite solution (15 ml.) and let stand for 6 hr. The resulting addition product was successively filtered, washed with ether, then decomposed with 2*N* hydrochloric acid. The liberated product was taken up in ether and worked up in the usual manner to yield a liquid (0.024 g.). This product (0.024 g.) in ethanol (3 ml.) was treated with 2,4-dinitrophenylhydrazine (0.045 g.) solution.[11] The resulting 2,4-dinitrophenylhydrazone (0.010 g.) melted at 53–57°; recrystallization from ethanol (0.5 ml.) yielded a solid (0.004 g.) melting at 54.5–56°; melting point of an admixture with the 2,4-dinitrophenylhydrazone of authentic 2-octanone (m.p. 57–58°) was 55.5–57°. The ethereal solution of the unchanged product was purged with water (4 × 25 ml.) and dried over sodium sulfate, the ether was evaporated under reduced pressure to yield a liquid (0.85 g.), $[\alpha]_D^{25} - 0.2°$ (c 1.92, ethanol), which did not form a 2,4-dinitrophenylhydrazone. Gas-liquid chromatography indicated about 90% 2-octanol. The yield, based on gas-liquid chromatography analyses, is about 15%, compared to 23–25% reported for a similar cleavage of ricinoleic acid.[1]

Chromium trioxide oxidation of the alcohol.[12] A solution of chromium trioxide (0.7 g. in 1 ml. of water and 12 ml. of acetic acid) was added dropwise to a stirred solution of the alcohol (0.035 g. in 5 ml. of acetic acid). The reaction temperature rose rapidly to 35°, and it was maintained at 30–39° for 3.5 hr. The solution was diluted with water (150 ml.) and saturated with sodium chloride; the oxidation product was taken up in ether. The ether phase was washed with dilute sodium hydroxide, then with water, and was dried over sodium sulfate. When the ether was removed under reduced pressure, the yield was 0.015 g. of product which, when treated with a slight excess of 2,4-dinitrophenylhydrazine solution, yielded a 2,4-dinitrophenylhydrazone (0.015 g.) melting at 38–50°.

A combination of recrystallizations from ethanol and chromatography on alumina (eluting with benzene) yielded a product melting at 51–55°; mixed melting point with the 2,4-dinitrophenylhydrazone of authentic 2-octanone (m.p. 57–58°) was 51.5–56°.

A second crop of 2,4-dinitrophenylhydrazone derivative (0.007 g.), which melted at 55–65°, was obtained from the initial filtrate residue by a similar recrystallization and chromatography procedure.

The two crops of 2,4-dinitrophenylhydrazone derivative were chromatographed on paper[13] simultaneously with the 2,4-dinitrophenylhydrazone of authentic 2-octanone. The observed R_f value was 0.89 for each major spot, however, a 2,4-dinitrophenylhydrazone derivative, not easily discernible, was resolved from each of the two crops of 2,4-dinitrophenylhydrazone derivative, R_f 0.66.

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β-Haloethyl Acetoacetates

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The preparation of β-chloroethyl acetoacetate is described in the literature.[1] The preparation of β-bromoethyl acetoacetate from diketene and β-bromoethanol has been reported.[2] The preparation of β-iodoethyl acetoacetate to our knowledge has not been reported.

The β-bromo derivative was prepared by ester interchange of β-bromoethanol with ethyl acetoacetate. The iodo ester was prepared by the reaction of sodium iodide with β-bromoethyl acetoacetate to yield β-iodoethyl acetoacetate. Unsuccessful attempts were made to prepare β-fluoroethyl acetoacetate by halogen replacement from both the β-bromo and β-iodo esters with organic soluble fluorides. The previously unreported copper(II)chelate of β-bromoethyl acetoacetate was readily prepared.

EXPERIMENTAL

β-Bromoethyl acetoacetate. Two hundred sixty grams (2.0 moles) of ethyl acetoacetate, 300 g. (2.4 moles) of β-bromoethanol, and 10 g. of litharge were mixed and heated at 100–160° with stirring until 116 ml. of distillate was collected. Gas chromatography showed that the distillate was largely ethanol, and treatment of the distillate with *p*-nitrobenzoyl chloride yielded ethyl *p*-nitrobenzoate.[3] The mixture in the still pot was cooled, diluted with ether, and filtered. The ether was removed from the filtrate by distillation and the residue distilled at 10 mm. to yield 197 g. (48%) of material, b.p. 124–127°, n_D^{25} 1.4728. The forecuts in the distillation were unchanged starting materials.

Anal. Calcd. for $C_6H_9O_3Br$: C, 34.4; H, 4.3. Found: C, 34.67; H, 4.69.

The product gave a positive test for bromine[3] and had an infrared spectrum consistent with the structure of β-bromo-

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(11) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, 4th ed., Wiley, 1956, p. 219.

(12) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

(13) D. F. Meigh, *Nature*, **170**, 579 (1952).

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(2) C. O. Parker, *J. Am. Chem. Soc.*, **78**, 4944 (1956).

(3) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, John Wiley & Sons, Inc., New York, 1957, p. 61, 212.

ethyl acetoacetate. Treatment of 20.9 g. (0.1 mole) of the product with 20 g. (0.104 mole) of cupric acetate in 400 ml. of water yielded a solid copper chelate (13.5 g.; 56%) which after cooling, filtration, and recrystallization from hexane melted at 143–146°.

Anal. Calcd. for $C_{12}H_{16}O_6Br_2Cu$: C, 30.0; H, 3.34; Cu, 13.13. Found: C, 30.54; H, 3.26; Cu, 13.07.

β-Iodoethyl acetoacetate. Forty-two grams (0.2 mole) of β-bromoethyl acetoacetate was dissolved in the smallest quantity of acetone capable of dissolving 60 g. (0.4 mole) of sodium iodide. After refluxing the solution for 3 hr., the mixture was poured into 1.5 l. of water and extracted with ether. The ether was removed under a nitrogen stream. The residue was rectified to yield 31.7 g. (62%) of product b.p. (10 mm.) 140–144°, b.p. (0.5 mm.) 83–85°, n_D^{25} 1.5151.

Anal. Calcd. for $C_6H_9O_3I$: C, 28.1; H, 3.52. *Found:* C, 28.21; H, 3.66.

The product gave a positive test for iodine[3] and had an infrared spectrum consistent with the structure of β-iodoethyl acetoacetate.

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Isomeric 16-Bromo-D-homo Steroids

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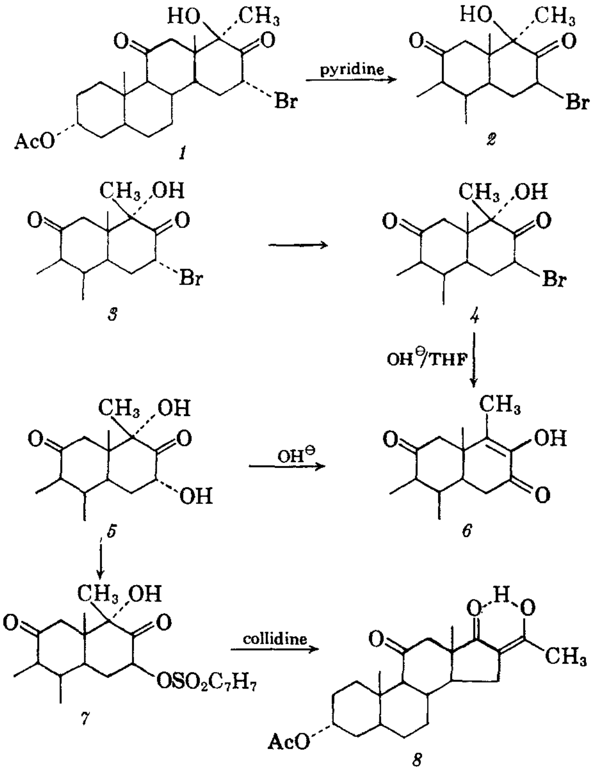
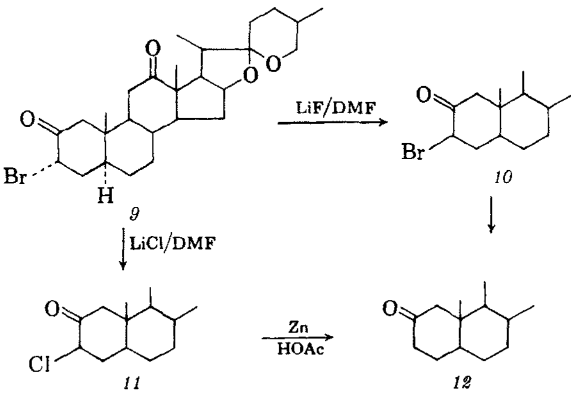
The primary monobromination products of 3α-acetoxy-17a,β-hydroxy-17a,α-methyl-5β-androstane-11,17-dione and 3α-acetoxy-17a,α-hydroxy-17a,β-methyl-5β-androstane-11,17-dione[1] are respectively the axial 16α-bromo derivatives *1* and *3*. Both of these derivatives are labile and pass readily into the corresponding equatorial 16β-isomers *2* and *4* (see below). The axial configuration of *1* and *3* was ascertained in the case of the latter isomer, *3*, by bromination of the free diol, 3α-17a,α-dihydroxy-17a,β-methyl-5β-androstane-11,17-dione to a product possessing a single carbonyl band in the infrared at 5.86 μ; the latter is consistent with the combined absorption of the 11-carbonyl together with an unperturbed 16-axial (α) bromo-17-ketone function.[2] After isomerization of this product with hot pyridine, its infrared spectrum exhibited in addition to the 11-carbonyl absorption at 5.86 μ a new band at 5.76 μ indicating a 16 equatorial (β) bromo-17-ketone group.[2]

All attempts to dehydrohalogenate the isomeric bromo ketones *1*–*4* with either refluxing pyridine, collidine, or sodium acetate in acetic acid at 100° were unsuccessful. The products in all cases were essentially the respective equatorial isomers *2* and *4*. It is apparent that the rate of epimerization exceeds the rate of elimination wherein the equatorial bromides are geometrically unfavorable and the β-hydrogens probably less accessible for *trans*-elimination. This is doubtlessly an over-simplification since the epimeric 3-bromo-2-keto sapogenin derivatives *9* and *10* also resist dehydrohalogenation with refluxing pyridine or collidine. Treatment of *9* on the other hand with lithium chloride in dimethylformamide at 100° produced the 3β-chloro ketone *11* whereas lithium fluoride under the same conditions converted *9* to *10*.[3]





Treatment of *4* with hot aqueous alkali in tetrahydrofuran afforded the known diosphenol *6*, also formed from the diolone *5* under comparable

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(2) R. N. Jones, D. A. Ramsey, F. Herling, and K. Dobriner, *J. Am. Chem. Soc.*, **74**, 2828 (1952).

(3) R. R. Engle and C. Djerassi (Abstracts of the 134th Meeting of the American Chemical Society, September 1958, p. 15–0) have indicated unusual behavior in the dehydrohalogenation of a comparable 3-bromo-2-ketone.