2ξ, 3-(3'-Oxocyclohex-4'-eno)-cholest-4-ene
and
2ξ, 3-(3'-Oxocyclohex-4'-eno)-5α-cholestane
(Preliminary Note)

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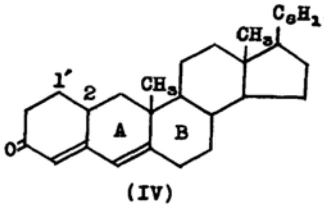
(Received December 10, 1958)

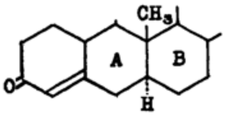
Chololest-4-en-3-one (I) was condensed with ethyl formate by the action of sodium methoxide to give 2-hydroxymethylene-cholest-4-en-3-one (II), m. p. 110°C[1]. The substance II was then condensed with freshly distilled methyl vinyl ketone in ethyl acetate in the presence of trimethylamine[2], and chromatography of the product on alumina and recrystallization from ethanol-methanol yielded 2ξ-(3'-oxobutyl)-cholest-4-en-3-one (III), m. p. 86~88°, λ_{max} 242 mμ(ethanol) (ε=14500), infrared absorptions 5.813, 5.970, and 6.160 μ (Found: C, 82.11; H, 11.19. Calc. for $C_{31}H_{50}O_2$: C,81.88; H, 11.08%). The diketone (III) gave a dioxime melting at 84°C (Found: N, 5.83. Calcd. for $C_{31}H_{52}O_2N_2$: N, 5.78%).

Treatment of the diketone (III) with alcoholic potash in the stream of nitrogen, chromatography of the product on alumina and recrystallization from ethanol, gave 2ξ,3-(3'-oxocyclohex-4'-eno) - cholest - 4 - ene (IV), m. p. 149—150° (Found: C, 85.08; H, 11.17. Calcd. for $C_{31}H_{48}O$: C, 85.26; H, 11.08%). The substance IV dissolved in ethanol showed an absorption maximum at 296 mμ (ε=30000) and in Nujol gave infrared absorptions at 6.000, 6.143 and 6.301 μ, which are proofs of the dienone structure IV.

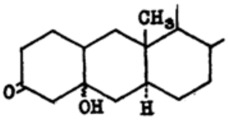
Reaction of 2-hydroxymethylene-cholest-4-en-3-one (II), methanolic sodium methoxide and freshly prepared 4-(diethylamino)-2-butanone methiodide[3], followed by chromatography of the product on alumina and recrystallization from ethanol, gave directly the same dienone (IV), m. p. 141°C, which could be purified with difficulty.



(IV)



(IX)



(VIII)

5α-Cholestan-3-one (V) was transformed into a monohydroxymethylene derivative, m. p. 180~185°C, in the same way as mentioned above(Found: C, 81.14; H, 11.31. Calcd. for $C_{28}H_{46}O_2$: C, 81.13; H, 11.11%). The structure of the product was proved to be 2-hydroxymethylene-5α-cholestan-3-one (VI)[4] by the formation of 2,3-seco-5α-cholestane-2,3-dioic acid, m. p. 193~194°C, on oxidizing the substance with hydrogen peroxide and caustic soda[5]. The dicarboxylic acid was identified with the specimen prepared from 5α-cholestan-3β-ol by the method of Windaus et al.[6]

Reaction of 2-hydroxymethylene-5α-cholestan-3-one (VI), 4-(diethylamino)-2-butanone methiodide and ethanolic potash, followed by chromatography of the product on alumina and recrystallization, gave 2ξ-(3'-oxobutyl)-5α-cholestan-3-one (VII), m. p. 113~114°C, infrared absorption 5.808~5.840μ (Found: C, 81.63; H, 11.52. Calc. for $C_{31}H_{52}O_2$: C, 81.52; H, 11.48%), and 2ξ,3-(3'-oxocyclohexano)-5α-cholestan-3ξ-ol (VIII), m. p. 230~231°C, infrared absorptions 2.826 and 5.790 μ (Found: C, 81.80; H, 11.70. Calcd. for $C_{31}H_{52}O_2$: C, 81.52; H, 11.48%).

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[1] J. G. Burr, Jr., W. F. Holton and C. N. Webb., *J. Am. Chem. Soc.*, **72**, 4903 (1950); R. B. Woodward., A. A. Patchett, D. H. R. Barton, D. A. J. Ives and R. B. Kelly, *J. Chem. Soc.*, **1957**, 1131.

[2] G. I. Poos, G. E. Arth, R. E. Beyler and L. H. Sarett, *J. Am. Chem. Soc.*, **75**, 422 (1953).

[3] Cf. E. C. Du Feu, F. J. McQuillin and R. Robinson, *J. Chem. Soc.*, **1937**, 53.

[4] Cf. L. Ruzicka, U. S. Patent, 2,281,622; *Chem. Abstr.*, **36**, 5958 (1942).

[5] Cf. D. Arigoni, H. Bosshard, H. Bruderer, G. Büchi, O. Jeger and L. J. Krebbaum, *Helv. Chim. Acta*, **40**, 1733 (1957); D. H. R. Barton et al., *J. Chem. Soc.*, **1954**, 4660.

[6] A. Windaus and Cl. Uibrig, *Ber.*, **47**, 2384 (1914).

Compounds VII and VIII yielded the same 2ξ, 3-(3′-oxocyclohex-4′-eno)-5α-cholestane (IX), m. p. 153°C, on treatment with sodium hydroxide in the stream of nitrogen, followed by chromatography of the product on alumina and recrystallization from ethyl acetate (Found: C, 84.75; H, 11.57. Calcd. for $C_{31}H_{50}O$: C, 84.86; H, 11.49%). The substance IX dissolved in ethanol showed an absorption maximum at 243 mμ(ε=15000) and in Nujol infrared absorptions at 5.970 and 6.160μ, which prove the structure IX.

2-Hydroxymethylene-5α-cholestan-3-one (VI) reacted with methyl vinyl ketone on addition of a few drops of 10% ethanolic potash in the heat, and treatment of the product, m. p. 134~135°C, probably the 2-formyl intermediate, with ethanolic potash in the stream of nitrogen gave the same 2ξ-(3′-oxobutyl)-5α-cholestan-3-one (VII).

The 2ξ, 3-(3′-oxocyclohexano)-5α-cholestan-3ξ-ol (VIII), m. p. 231~232°C, and its 3-stereoisomeride, m. p. 217~219°C (Found: C, 81.16; H, 11.42. Calcd. for $C_{31}H_{52}O_2$: C, 81.52; H, 11.48%), were obtained by the action of *N*-ethylanilinomagnesium bromide on 2ξ-(3′-oxobutyl)-5α-cholestan-3-one (VII) followed by hydrolysis of the intermediate product with dilute hydrochloric acid⁷⁾.

No experimental evidence has yet been obtained concerning the configuration around the carbon atom 2 in compounds III, IV, VII, VIII and IX⁸⁾, but it seems almost certain for these deformylated compounds that carbon atom 1′ is situated at the more stable α-configuration and consequently the hydrogen in position 2 is attached there with the β-bond, axial to both ring A and the added ring.

Details will follow.

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7) Cf. J. Colonge, *Bull. soc. chim. France*, (5), 1, 1101 (1934).

8) Cf. S. A. Szpilfogel, W. J. van Der Burg, C. M. Siegmann and D. A. van Dorp, *Rec. trav. chim.*, **75**, 1043 (1956) and A. Wettstein, K. Heusler, H. Ueberwasser and P. Wieland, *Helv. Chim. Acta*, **40**, 323 (1957).