boxylation was obtained. The crude product, a lactone (infrared C = O: 1748 cm.$^{-1}$), was obtained in 70% yield as a liquid which very slowly partially crystallized. By gas phase chromatography this product mixture consisted of a major component (>95%) and two or possibly three trace components. The lactone could be sublimed, but no satisfactory melting point could be obtained.[12] Saponification of the lactone, however, gave the readily purified hydroxy acid, m.p. 118–119° (recrystallized from water) lit.,[12] m.p. 118.5°).

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[12] The melting point range was persistently 5–10° below that reported for camphytolactone. Bicyclic compounds of this sort are notorious for their large cryoscopic constants and difficulty of purification. From a published report [W. A. Noyes and R. S. Potter, *J. Am. Chem. Soc.*, **34**, 1067 (1912)] this lactone is no exception.

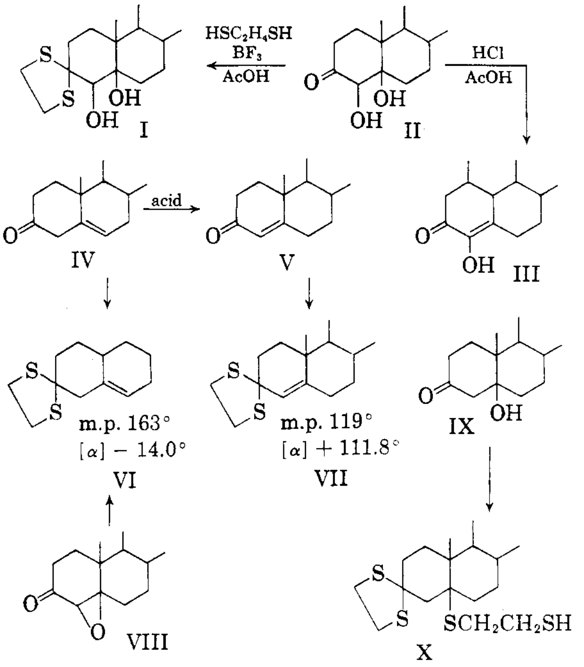
The Reaction of Certain Acid-Sensitive Steroid Ketones with Ethanedithiol–Borontrifluoride

JEROME F. EASTHAM AND GEORGE B. MILES

Received November 18, 1959

Recently we were successful in obtaining thioketal derivatives (I) from 4,5-dihydroxy-3-keto steroids (II) with ethanedithiol and boron trifluoride in acetic acid.[1] It was somewhat surprising that these strongly acid conditions, originated by Fieser,[2] gave derivative I in good yield, because the diolone II is easily dehydrated by acid to a diosphenol (III).[1] To check these conditions with another acid-sensitive functional arrangement, a thioketal derivative has been prepared from Δ^5-cholesten-3-one (IV), which is easily isomerized by acid to Δ^4-cholestenone (V). The derivative (VI) from the Δ^5-isomer (IV) is distinct from the derivative (VII) obtained[2] from the Δ^4-isomer (V). The negative specific rotation of VI is in accord with the structure assigned.[3]

Attempts to prepare thioketal derivatives of two other acid-sensitive functional arrangements under boron trifluoride catalysis have met with less success. 5-Hydroxycoprostan-3-one (IX) was treated with ethanedithiol and borontrifluoride in acetic acid, as a step in an attempted synthesis of the relatively rare monofunctional 5-hydroxy-steroids. Toward this end, 4,5β-oxidocoprostan-3-one (VIII) was treated with the acidic reagent. The yield of crystalline material from each compound was very slight. The small amount of crystalline product from the epoxide (VIII) proved to be the derivative (VI) from Δ^5-cholesten-3-one. The product from the ol-one (IX) was not fully characterized but has an analysis in agreement with structure X. Although formation of compounds VI and X from VIII and IX respectively is intriguing, further discussion of their formation seems unwarranted until they are obtained in significant yield.



EXPERIMENTAL

Reaction of Δ^5-cholesten-3-one (IV) *with ethanedithiol.* A solution of 1.0 g. of Δ^5-cholesten-3-one in 20 ml. of acetic acid was treated with 1 ml. of ethanedithiol and 1 ml. of boron trifluoride etherate. The solution was stirred for a few minutes and allowed to stand for 3 hr. The crystalline material which precipitated was filtered, washed with water, and recrystallized from ethanol. No additional crystalline material could be isolated from the reaction mixture. After recrystallization the yield of the thioketal (VI) was 0.26 g., m.p. 162–163°, $[\alpha]^{26}_{D}$ −14.0° (c, in chloroform, 0.895).

Anal. Calcd. for $C_{29}H_{48}S_2$: C, 75.60; H, 10.50. Found: C, 75.48; H, 10.34.

Reaction of 4,5β-oxidocoprostan-3-one (VIII) *with ethanedithiol.* A solution of 1 g. of 4,5β-oxidocoprostan-3-one[4] in 10 ml. of acetic acid was treated with 1 ml. of ethanedithiol and 1 ml. of boron trifluoride etherate. Only a small amount of crystalline material precipitated from the reaction mixture. After recrystallization from ethanol, this material melted at 161–162° and showed no depression with Δ^5-cholesten-3-one ethylene thioketal (VI).

Reaction of 5-hydroxycoprostan-3-one (IX) *with ethanedithiol.* To a solution of 0.38 g. of 5β-hydroxycoprostan-3-one in 5 ml. of acetic acid were added 0.5 ml. of ethanedithiol and 0.5 ml. of boron trifluoride etherate. The solution was stirred and allowed to stand for several hours. The small amount of crystalline material which separated was collected and washed with water. The acetic acid was allowed to evaporate slowly to leave a dark oil which resisted all attempts at crystallization. After the crystalline material

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[1] J. F. Eastham, G. B. Miles, and C. A. Krauth, *J. Am. Chem. Soc.*, **81**, 3114 (1959).

[2] L. F. Fieser, *J. Am. Chem. Soc.*, **76**, 1945 (1954).

[3] *Cf.* W. Klyne in E. A. Braude and F. C. Nachod, *Determination of Organic Structures by Physical Methods*, Academic Press Inc., New York, N. Y., 1955, p. 108 ff.

[4] P. A. Plattner, H. Heusser, and A. B. Kulkarni, *Helv. chim. Acta*, **31**, 1822 (1948).

was recrystallized from methanol, it melted at 166–168°, showed no absorption in the ultraviolet region, and had a weak, well-defined absorption at 2685 cm.$^{-1}$ characteristic of SH stretching.[5]

Anal. Calcd. for $C_{31}H_{54}S_4$: C, 67.11; H, 9.81; S, 23.07. Found: C, 67.02, 66.79; H, 9.56, 9.83; S, 23.20.

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(5) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley & Sons, New York, N. Y., 1958, p. 351.

5-Dibenzo[b,f]azepine

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Received October 27, 1959

Six-membered ring systems of the general type I have been shown to undergo dehydration on solvolysis with ring enlargement to seven-membered systems (II), *i.e.* 9,10-di(hydroxymethyl)-9,10-dihydroanthracene (I, X=CH(CH_2OH)),[1,2] 9-hydroxymethylxanthene (I, X=O)[3] and 9-hydroxymethylthioxanthene (I, X=S).[4]

In the present study, the transformation of 9-hydroxymethylacridane (I, X=NH) into 5-dibenzo[b,f]azepine (II, X = NH) is described.

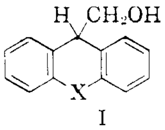
The primary alcohol (I, X=NH) was obtained by reduction of acridine-9-carboxylic acid (III) with lithium aluminum hydride. This reagent reduced not only the carboxyl group, but also the *ortho*-quinoid C=N system. Analogous observations have been made in other acridine derivatives.[5] Treatment of the alcohol with polyphosphoric acid at 160° caused the desired dehydration. Structure II, X = NH for the product, m.p. 189–191°, follows from the similarity of its spectrum with that of 2-amino-*cis*-stilbene:[6] II, X=NH: 262 mμ (4.60); 310 mμ (3.35; inflection); 360 mμ (2.90; inflection); 2-amino-*cis*-stilbene: 245 mμ (3.25; inflection); 2.80 mμ (3.05), and its nonidentity with 9-methylacridine (IV), m.p. 114°,[7] which would probably have formed spontaneously from 9-methylene-9,10-dihydroacridine (V).[8] The spectrum of II, X=NH is also very similar to that of II,X=O,[3] II, X=S[4] and II, X=CH_2.[2]

II,X=O: 230 mμ (4.35); 290 mμ (3.95)

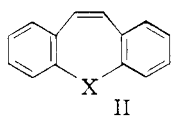
II,X=S: 227 mμ (4.36); 262 mμ (4.47); 295 mμ (3.70)

II,X=CH_2: 288 mμ (4.19)

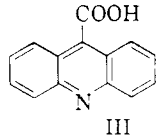
10,11 - Dihydro - 5 - dibenzo[b,f]azepine ("*o*-iminodibenzyl") has been described by Thiele and Holzinger,[9] but no derivatives of II, X=NH carrying a double bond in the 10,11- position appear to have been prepared.



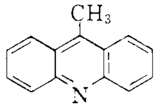
I



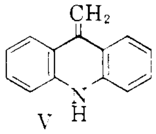
II



III



IV



V

EXPERIMENTAL

9-Hydroxymethyl-9,10-dihydroacridine (I, X = NH). In an atmosphere of nitrogen and at the temperature of an ice-salt mixture, 13 g. of lithium aluminum hydride was added in small portions to a suspension of 40 g. of acridine-9-carboxylic acid (III)[10] in ether. The mixture was gently refluxed for 3 hr. and decomposed by the successive addition of acetone and water. The ethereal solution was then decanted from the solid and the latter extracted several times with ether and benzene. When the solvents were evaporated (at a temperature not exceeding 40°), a colorless solid remained which was triturated with petroleum ether and recrystallized from benzene-petroleum ether or methanol. The compound formed white needles, m.p. 135–136°, and was very sensitive to oxygen, which caused quick discoloration to brown. The yield was 30 g. (80%). That the acridine system had been reduced, followed from the absence of the typical green fluorescence of the acridine derivatives in concentrated sulphuric acid solution.

Anal. Calcd. for $C_{14}H_{13}NO$: C, 79.6; H, 6.2. Found: C, 79.6; H, 6.6.

5-Dibenzo[b,f]azepine (II, X = NH). A mixture of 2.5 g. of the foregoing substance and 150 ml. of polyphosphoric acid was heated at 160° for 3 hr. with vigorous agitation. Water was added and the product extracted with ether and benzene. The organic layer was washed with sodium bicarbonate solution, dried, and evaporated *in vacuo* and the ethereal solution of the residue chromatographed twice on activated alumina. The product contained in the yellow fraction (50-ml. fractions) was dissolved in petroleum ether and chromatographed again. The third fraction gave yellow leaflets which melted at 189–191°; the melting point did not change upon recrystallization from cyclohexane. The infrared spectrum (in potassium bromide pellet) showed 3333 cm.$^{-1}$ (strong, N—H stretching), 3030, 1587, 1481 (str.) (*ortho*-disubst. benzene), 1316 (C—N stretching), 1266, 1163, 1117, 939, 810, 746 (broad, strong) (*ortho*-disubst. benzene), 700 cm.$^{-1}$

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(2) E. D. Bergmann and M. Rabinovitz, *Bull. Res. Counc. Israel*, in press (1960).

(3) F. A. L. Anet and P. M. G. Bavin, *Can. J. Chem.*, **35**, 1084 (1957).

(4) E. D. Bergmann and M. Rabinovitz, *J. Org. Chem.*, in press (1960).

(5) F. Bohlmann, *Ber.*, **85**, 390 (1952); G. M. Badger, J. H. Seidler, and B. Thomson, *J. Chem. Soc.*, 3207 (1951).

(6) D. L. F. De Tar and L. A. Caprino, *J. Amer. Chem. Soc.*, **78**, 475 (1956).

(7) H. Jensen and F. Rethwisch, *J. Amer. Chem. Soc.*, **50**, 1144 (1928).

(8) This can be assumed from analogy to 9-methylene-9,10-dihydroanthracene.[2] However, Decker, *Ber.*, **38**, 2493 (1905), has described some derivatives of V.

(9) J. Thiele and O. Holzinger, *Ann.*, **305**, 100 (1899).

(10) K. Lehmstedt and F. Dostal, *Ber.*, **72**, 804, 1071 (1939). G. I. Braz and T. V. Gortinskaya, *J. Gen. Chem.* (*U.S.S.R.*), **10**, 1751 (1940); *Chem. Abstr.*, **35**, 4025 (1941).