TABLE I

RESULT OF KINETIC ANALYSIS OF TRICHLOROHYDRINS

Time (min.)	7	12	20	30	40	50	60	80	100
Titre (ml.)	1.03	1.15	1.37	1.57	1.70	1.83	1.96	2.10	2.25
$a - x(M)$	0.01770	0.01674	0.01500	0.01340	0.01236	0.01134	0.01030	0.00918	0.00798
$\frac{1}{a-x}\ (M)^{-1}$	56.5	59.5	66.5	74.5	81.0	88.0	97.0	109.0	125.5

mixture did not contain any other impurity. This mixture was used for the kinetic analysis.

Kinetic determination.[6] A sample bottle containing 0.3253 g. (0.2 ml.) of the mixture of trichlorohydrins was dropped into 50 ml. of alcohol solution. The corrected volume of the final mixture was 50.2 ml. To this mixture, 50 ml. of 0.0398*N* alkali was added at 25°. At intervals, 5 ml. samples were taken with the aid of a syringe and added to 2.5 ml. of 0.0518*N* hydrochloric acid. The solution was back-titrated with 0.0398*N* alkali.

The data are summarized in Table I. The plot of $1/a - x$ against t was used to find the composition of the mixture. A straight line with a slope k_2 gave an intercept at $1/a$ on the $1/a - x$ axis. The percentage of 2,3,3-trichloropropan-1-ol was obtained by comparing the "a" value with the known total concentration of the mixed trichlorohydrins.

The values found were: slope, $k_2 = 0.74$ (liter) (mole)$^{-1}$ (min.)$^{-1}$; intercept, $\frac{1}{a} = 51.4M^{-1}$; a (calcd.) $= 0.01946M$; a' (known total concentration) $= 0.01986M$; 2,3,3-trichloropropan-1-ol (98%); 1,1,3-trichloropropan-2-ol (2%).

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CLEVELAND 6, OHIO

[CONTRIBUTION FROM FRICK LABORATORY, PRINCETON UNIVERSITY]

The Solvolysis of 4,4-Dimethylcholesteryl *p*-Toluenesulfonate

ROBERT M. MORIARTY[1] AND EVERETT S. WALLIS

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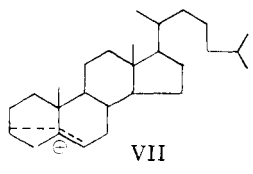
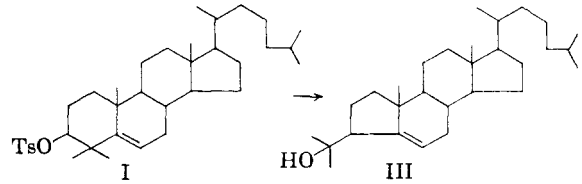
The solvolysis of 4,4-dimethylcholesteryl *p*-toluenesulfonate (I) was carried out in 60% aqueous acetone in the presence of potassium acetate. Under these conditions cholesteryl *p*-toluenesulfonate rearranges to 3,5-cyclocholestan-6β-ol ("*i*-cholesterol"). In the case of 4,4-dimethylcholesteryl *p*-toluenesulfonate no 3,5-cyclosterol was obtained. Nearly 70% of the product was a mixture of isomeric, conjugated dienes (II). Twenty per cent of the product was an A-ring contracted alcohol for which structure III is proposed and 7% 4,4-dimethylcholesterol (IV) was also obtained. A preliminary study of the rate of solvolysis indicated that the rate of acetolysis is 10 times faster than that of cholesteryl *p*-toluenesulfonate. The mechanistic implications of these results are discussed.

A general reaction of 3β-hydroxy-Δ⁵-sterols is solvolysis *via* an intermediary homoallylic type carbonium ion to yield a 3,5-cyclosteroid as the kinetically determined product of the reaction.[2] Winstein and Adams have shown this process to be a case of neighboring group participation of the π-electron system at carbon atoms C_5–C_6 in the rate determining ionization step. This postulate accounted for the retention of the β-configuration at C_3 and the solvolytic rate enhancement of this compound compared to the saturated cholestanyl tosylate. These authors chose to represent the intermediate ion by formula (VII).

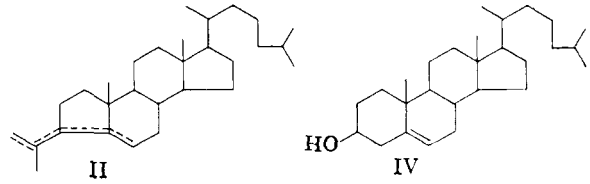
If the solvolytic reaction medium is buffered with an added salt such as potassium acetate, the product of kinetic control is formed. If no buffer is added the product resulting from thermodynamic control is formed, namely 3β-substituted-Δ⁵-com-



VII



I III

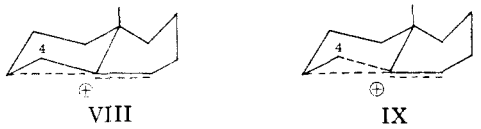


II IV

(1) Allied Chemical and Dye Corporation Fellow 1958–59.

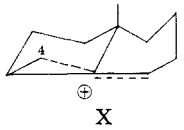
(2) (a) E. S. Wallis, E. Fernholz and F. T. Gephart, *J. Am. Chem. Soc.*, **59**, 137 (1937). (b) E. G. Ford and E. S. Wallis, *J. Am. Chem. Soc.*, **59**, 1415 (1937). (c) M. M. Hafez, G. Halsey and E. S. Wallis, *Science*, **110**, 474 (1949). (d) S. Winstein and R. Adams, *J. Am. Chem. Soc.*, **70**, 838 (1948). (e) C. W. Shoppee, *J. Chem. Soc.*, 1147 (1946).

pounds. Later work by Winstein and Kosower[3] demonstrated that the solvolysis of cholesteryl *p*-toluenesulfonate and the epimeric 3,5-cyclocholestan-6-yl trichloroacetates proceeded through a common homoallylic hybrid carbonium ion intermediate. This intermediate ion was represented by structures (VIII–X).



VIII

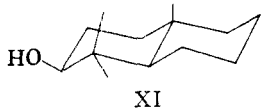
IX



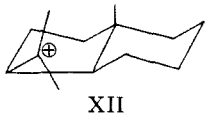
X

Structures VIII and X were termed "unsymmetrical" and structure IX "symmetrical." One would expect the contributions of structures IX and X to be minimal since in each case, the primary carbon C_4 would bear positive charge.

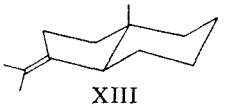
The object of our research on this problem was to study the course of the reaction in a substituted case in which a stabilizing influence would be operative at C_4. The molecule selected was 4,4-dimethylcholesterol, an intermediate in the synthesis of lanosterol.[4] If one were to apply the same symbolism as above to an analogous homoallylic ion derived from 4,4-dimethylcholesterol, the contribution of the structures IX and X would be quite important. Since the C_4 carbon is tertiary it would be capable of stabilizing a relatively large amount of the delocalized positive charge present in the homoallylic ion. In the case of 3β-hydroxy 4,4-dimethyl triterpenoids, dehydration by an ionic process[5] leads to rearrangement of the C_4–C_5 bond to yield a teritary carbonium ion as shown by XI–XIII.



XI



XII



XIII

In the solvolysis of 4,4-dimethylcholesteryl *p*-toluenesulfonate the reaction might occur by participation of the C_4–C_5 single bond rather than the C_5–C_6 double bond leading to a ring-contracted product. From a consideration of steric strain it is unlikely that a 3,5-cyclosteroid would result since the stereochemistry of the homoallylic ion requires attack from the β-side to yield a 6β-axial configuration.[6] In the case of the 4,4-dimethylcholesteryl ion, this would lead to 3,5-cyclo-4,4-dimethylcholestan-6β-ol which would possess the unfavorable feature of having the three groups at positions C_4, C_6, and C_{10} axial and on the same side of the molecule. This however, is not an impossible situation since Barton has prepared an analogous compound in the structure elucidation of zerorin.[7] This compound, epideoxyzeorin, has an axial hydroxyl group at C_6 while C_4 and C_{10} both have axial methyl groups all on the β-side of the molecule. Epideoxyzeorin is quite hindered compared to deoxyzeorin in which the hydroxyl group at C_6 is equatorial. It would not be unlikely that the solvolysis of 4,4-dimethylcholesteryl *p*-toluenesulfonate might proceed with homoallylic participation of the C_5–C_6 double bond to yield a homoallylic ion. This ion might then react at position C_4 in preference to either C_3 or C_6 resulting in ring contraction of the A-ring in a manner analogous to the same phenomenon observed in the dehydration of 4,4-dimethyl triterpenoids.

Results. Under conditions which favor the formation of 3,5-cyclosteroids (aqueous acetone buffered with potassium acetate) 4,4-dimethylcholesteryl *p*-toluenesulfonate (I) was solvolyzed. The product of the reaction was fractionated by absorption chromatography on alumina. About 70% of the total product was eluted with pentane. This oil was cleanly separated from a crystalline fraction which was eluted from the column with an ether-chloroform solution. This latter crystalline material was rechromatographed and separated into 4,4-dimethylcholesterol (25%) and 3-isopropanol-A-norcholest-5-ene (III) (75%) m.p. 120–22°, $[\alpha]_D^{22}$ − 21.90° (C, 2). This structure for the alcohol is proposed on the basis of the following experimental data. Its elemental analysis corresponded to a substance isomeric with 4,4-dimethylcholesterol. That the alcohol group was tertiary was ascertained from the fact that it resisted acetylation with acetic anhydride–pyridine at room temperature for 24 hours or at 100° for two hours and could not be oxidized under Oppenauer conditions using aluminum *tert*-butoxide and acetone or under Sarett conditions.[8] In each case unchanged alcohol was recovered from the reaction. A 3,5-cyclosterol structure for the alcohol was eliminated since it was unaffected by acidic, aqueous acetone (conditions which cause rearrangement of 3,5-cyclocholestan-6β-ol to cholesterol). The alcohol decolorized a solution of bromine in carbon tetrachloride and gave a yellow color with tetranitromethane of about the same intensity as the color

(3) S. Winstein and E. M. Kosower, *J. Am. Chem. Soc.*, **78**, 4353 (1956).

(4) R. B. Woodward, A. A. Patchett, D. H. R. Barton, D. A. J. Ives, and R. B. Kelley, *J. Chem. Soc.*, 1131 (1957).

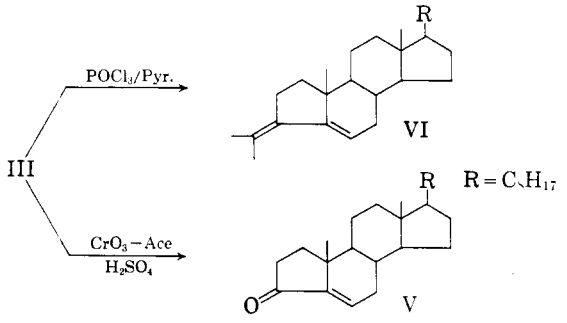
(5) D. H. R. Barton, *Experientia*, **6**, 316 (1950).

(6) R. M. Dodson and B. M. Riegel, *J. Org. Chem.*, **13**, 424 (1950).

(7) D. H. R. Barton and T. Bruun, *J. Chem. Soc.*, 1683 (1952).

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

obtained with cholesterol. Oxidation with 8*N* chromium trioxide sulfuric acid solution[9] led to the formation of a conjugated ketone (V), $\lambda_{max}^{CCl_4}$ 5.81, 6.02 μ, λ_{max}^{MeOH} 245 mμ. The melting point of the ketone and oxime were in agreement with those reported by Windaus for A-norcholest-5-en-3-one.[10] Furthermore, it did not depress the melting point of an authentic sample of A-norcholest-5-en-3-one and their infrared curves were essentially identical.[11] The formation of A-norcholest-5-en-3-one by this retroaldol type change in the oxidation can be rationalized in terms of the accepted mechanism for chromic acid oxidation.[12] Upon treatment of III with phosphorus oxychloride–pyridine, a conjugated diene was obtained, m.p. 102–104°, $[\alpha]_{22}^{D}$ −168.4° (C,2), λ_{max}^{EtOH} 249 mμ, e 12,590. On the basis of the absorption of this diene and the structure of the parent alcohol we suggest that the diene is 3-isopropylidene-A-norcholest-5-ene (VI).

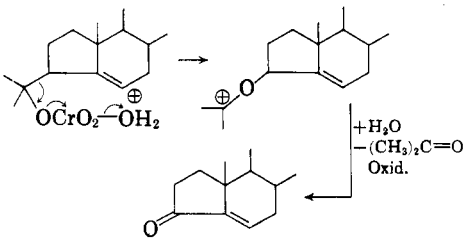


(9) P. Bladon, J. M. Fabian, H. B. Henbest, M. P. Koch, and G. W. Wood, *J. Chem. Soc.*, 2407 (1951).

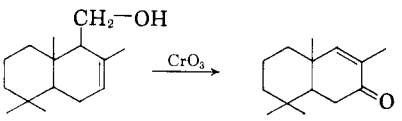
(10) A. Windaus, *Ber.*, **52**, 170 (1919).

(11) We would like to thank Professor C. W. Shoppee for kindly supplying us with an authentic sample of A-norcholest-5-en-3-one.

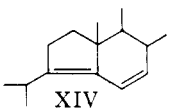
(12) F. M. Westheimer and N. Nicolaides, *J. Am. Chem. Soc.*, **71**, 25 (1949). This mechanism involves acid-catalyzed esterification of the alcohol followed by loss of a proton or rearrangement of a bond to a potentially electron deficient oxygen. Application of this mechanism to the chromic acid oxidation of III might involve the following steps.[13]



(13) A similar reaction was observed by C. J. W. Brooks and K. M. Overton [*Proc. Chem. Soc.*, 323, (1957)] in the oxidation of drimanol to nordriminone.



The pentane fraction obtained by chromatography of the reaction product was crystallized from acetone to yield material, m.p. 49–60°. Chromatography of this gave II, m.p. 78–80°, $[\alpha]_{D}^{22}$ −126.6° (C, 0.73), $\lambda_{max}^{CCl_4}$ 6.02 μ, λ_{max}^{EtOH} 242 mμ, e 13,900 sh, 238 mμ, e 13,200 sh, 250 mμ, e 10,560. Its analysis was correct for a diene isomeric with VI. This unknown diene was ozonized and the volatile carbonyl components were trapped by distillation into 2,4-dinitrophenylhydrazine sulfate solution. An equivalent of acetone corresponding to the presence of 44% isopropylidene grouping was obtained. From these results we are led to conlude that the diene obtained from the solvolysis is not a homogeneous material but probably is composed of two or more dienic molecules which have co-crystallized. This is a frequently encountered situation in the case of certain triterpenes and steroids where isomerism is due to the position of the double bonds in a conjugated system. The presence of VI is indicated by the ozonolysis data. A structure such as XIV might also contribute.



Structures corresponding to methyl group migration such as 3-methyl-4-methylenecholest-5-ene cannot be excluded but it is unlikely that they would co-crystallize with the A-ring contracted dienes due to their different molecular shapes.

A preliminary study of the rate of acetolysis of I was made. The first order rate constant in 0.02*M* glacial acetic acid at 50.00°k_1 = 1.58 × 10^{-3} sec.$^{-1}$ was about 10 times faster than that reported by Winstein and Adams[2d] for cholesteryl *p*-toluenesulfonate, k_1 = 1.3 × 10^{-4} sec.$^{-1}$. Further research is being directed towards measuring the solvolytic rate of the saturated 4,4-dimethylcholestanyl *p*-toluenesulfonate and other substituted cases in order to distinguish between homoallylic participation of the C_5–C_6 double bond and simple involvement of the C_4–C_5 bond.

The formation of 3-isopropanol-A-norcholest-5-ene and the dienic material corresponds to rearrangement by ring contraction. The concept of homoallylic participation essentially involves an emptying *p*-orbital resulting in a potential energy hole into which a neighboring orbital will extend. By means of semiempirical molecular orbital calculations Winstein and Simonetta have shown that considerable stabilization results from the interaction of the double bond in the cholesteryl ion with the cationic center at C_3 and that this stabilization depends upon the degree of orbital overlap.[14]

(14) S. Winstein and M. Simonetta, *J. Am. Chem. Soc.*, **76**, 18 (1954).

The total stabilization represents a compromise between best overlap and minimum strain due to angle deformation and nonbonded interactions. Since the degree of overlap depends upon the C_3–C_5 distance, substitution of a gem-dimethyl group at C_4 in place of the two hydrogens should result in a slight decrease in this distance and hence better overlap. We therefore believe that a homoallylic ion is formed which is attacked preferentially at C_4. 3,5-Cyclo-4,4-dimethylcholesterol is not formed due to the comparatively large amount of strain in this molecule which results from the groups at C_4, C_6, and C_{10} being axial and β-oriented. The formation of 4,4-dimethylcholesterol (IV) may be due to ionization of the toluenesulfonate ester by breaking the oxygen-sulfur bond rather than the alkyl-oxygen bond. The large amount of olefin formed, 70% compared to 15% obtained in cholesteryl *p*-toluenesulfonate, may be due to the inability of the solvent to solvate the ion effectively because of the two methyl groups at C_4. Instead of a solvated ion collapsing to the solvolytic product, the poorly solvated ion may stabilize itself by loss of a proton rather than forming a covalent bond with a solvent molecule.

Experimental[15]

4,4-Dimethylcholesteryl p-toluenesulfonate (I). To a solution of 2 g. of 4,4-dimethylcholesterol[4] in 4 ml. of dry pyridine, 2 g. of *p*-toluenesulfonyl chloride was added. This mixture was warmed on the steam bath for about 5 min. until solution was complete. The solution was then allowed to stand at room temperature overnight. At the end of this time, ice and water were added in succession to the resulting solid mass. The crystalline material was recrystallized twice from ether and yielded 1.7 g. of I, m.p. 94–95°[d], $[\alpha]_D^{22}$ −42.3°, (C, 2).

Anal. Calcd. for $C_{36}H_{56}O_4S$: C, 76.01; H, 9.92. Found: C, 76.17; H, 9.96.

Solvolysis of 4,4-dimethylcholesteryl p-toluenesulfonate (I). A solution of 2.58 g. of ester, 2.83 g. of potassium acetate, and 50 ml. of water in 75 ml. of acetone was kept at reflux for 15 hr. Then, most of the acetone was removed under reduced pressure. The remaining aqueous portion was extracted with ether. The combined extracts were dried and concentrated *in vacuo*. The residual oil was dried further under high vacuum resulting in a thick, clear semiviscous gum, 1.92 g. This product was dissolved in a small volume of ether and absorbed on a column of 100 g. of neutral alumina. Elution with 200 ml. of pentane yielded 1.37 g. of a clear viscous oil. Further elution with 8:2 ether-chloroform and 1:1 ether-chloroform yielded 540 mg. of crystalline material. The 1.37 g. of oil was crystallized from acetone at −78° to yield 1.0 g., m.p. 49–60°. This material was chromatographed on 30. g. of neutral alumina and fractional elution with *n*-pentane gave II 720 mg., m.p. 78–80°, $[\alpha]_D^{22}$ −126.6° (C, 0.73), $\lambda_{max}^{CCl_4}$ 6.02 μ, λ_{max}^{EtOH} 242 mμ, e 13,990 sh, 238 mμ, e 13,200 sh, 250 mμ e 10,560. The analytical sample prepared by repeated recrystallization from acetone had m.p. 84–86°.

Anal. Calcd. for $C_{29}H_{48}$: C, 87.80; H, 12.20. Found: C, 87.59; H, 12.50.

(15) All melting points were determined on a Kofler micro hotstage. The microanalyses were performed by George F. Robertson, Florham Park, N. J.

The 540 mg. of crystalline material was rechromatographed on 20 g. of acid-washed alumina. Elution with 1:1 pentane-ether gave III, 300 mg. m.p. 120–122°. The analytical sample prepared by recrystallization from acetone had m.p. 125–126°, $[\alpha]_D^{22}$ −21.90° (C, 2).

Anal. Calcd. for $C_{29}H_{50}O$: C, 84.00; H, 12.15. Found: C, 84.26; H, 12.45.

Further elution with pure ether gave 100 mg. of material m.p. 142–144° which was identified as 4,4-dimethylcholesterol (IV) by a mixed melting point determination and infrared absorption comparison with authentic IV.

A-Norcholest-5-en-3-one (IV). A solution of 100 mg. of III in 0.75 ml. of acetone was treated with 0.15 ml. of chromium trioxide in 8*N* sulfuric acid added dropwise at 35° over a period of 3 min.[9] An immediate green precipitate was formed. A solution of meta sodium bisulfite (2 ml.) was added followed by a solution of potassium carbonate (4 ml.). This mixture was extracted with ether and the ether solution was dried and concentrated under reduced pressure yielding a crystalline product which was purified by filtration over alumina. One recrystallization from acetone yielded 40 mg. of V, m.p. 96–97°. The analytical sample was prepared by recrystallization acetone, m.p. 99–100°. λ_{max}^{MeOH} 245 mμ, e 9,481. The oxime had m.p. 179–180°.

3-Isopropylidene-A-nor-cholest-5-ene (VI). To a solution of 200 mg. of III dissolved in 2 ml. of pyridine, 2 ml. of phosphorus oxychloride was added. After heating at reflux for 1 hr., the reaction mixture was cooled and ice water cautiously added. The reaction mixture was extracted with ether and the ethereal extracts were washed with cold dilute hydrochloric acid and a saturated solution of sodium bicarbonate, dried, and concentrated *in vacuo*. The resulting crystalline product, 180 mg., was recrystallized from acetone to yield 135 mg. of VI, m.p. 101–104°, $[\alpha]_D^{22}$ −168° (C, 2), λ_{max}^{EtOH} 249 mμ, e 12,590.

Anal. Calcd. for $C_{29}H_{48}$: C, 87.80; H, 12.20. Found: C, 88.10; H, 12.33.

Ozonolysis of (II). II (163 mg.) was dissolved in 5 ml. of chloroform. At 0°, ozone was swept through the solution for 0.5 hr. The chloroform was then removed *in vacuo*. Two ml. of methanol and 6 ml. of water were added. Most of this solution was distilled into a solution of 200 mg. of 2,4-dinitrophenylhydrazine in 0.4 ml. of sulfuric acid and 8 ml. of methanol. After standing at room temperature overnight, water was added followed by extraction with ether. The ether solution was concentrated to dryness, dissolved in benzene, and absorbed on a column of 10 g. of neutral alumina. Elution with ether gave 30 mg. of acetone-2,4-dinitrophenylhydrazone m.p. 125–126°, undepressed upon admixture with an authentic sample. To estimate the yield of acetone by this method, a control experiment was performed by distilling a mixtue of 24 mg. of acetone, 2 ml. of methanol, and 6 ml. of water into a solution of 2,4-dinitrophenylhydrazine sulfate prepared above. After extraction and chromatography 68 mg. of acetone 2,4-dinitrophenylhydrazone was obtained corresponding to a 70% yield. This 70% yield was reasonably well reproduced in 3 experiments. Acetone was proven to be absent from the solvents used by allowing a solution of water, methanol, sulfuric acid and 2,4-dinitrophenylhydrazine in the amount used above stand overnight. After the same procedure, extraction and chromatography, no acetone-2,4-dinitrophenylhydrazone was found. The 30 mg. of acetone-2,4-dinitrophenylhydrazone then indicate the presence of 44% of isopropylidene grouping present in II.

Attempted acid-catalyzed rearrangement of II. Fifty mg. of II was dissolved in 15 ml. of 50% aqueous acetone. Two drops of concentrated sulfuric acid were added and the solution maintained at reflux for 3 hr. The acetone was removed *in vacuo* and the aqueous part extracted with ether. The ether solution was dried and concentrated to dryness yielding 48 mg. of unchanged starting material m.p. 121–122°, undepressed by mixed melting with an authentic sample of II.

Determination of rate of acetolysis of I. The kinetic procedure used was essentially the same as that of Winstein and Adams.[2(d)]

Acknowledgment. The authors wish to thank J. Kent of Merck and Co. for the 4,4-dimethylcholestenone used in the synthesis of 4,4-dimethylcholesterol and Professor Paul Schleyer for helpful discussions in connection with the kinetic data presented.

PRINCETON, N. J.

[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE, WEIZMANN INSTITUTE OF SCIENCE]

Synthesis and Reactions of 3β-Acetoxy-20-ethynyl-5-pregnen-20-ol

FRANZ SONDHEIMER, NAFTALI DANIELI, AND YEHUDA MAZUR

Received March 13, 1959

The reaction between 3β-acetoxy-5-pregnen-20-one (Ia) and sodium acetylide in liquid ammonia is shown to yield the 20-ethynyl carbinol II mentioned in the title. Dehydration of the latter with phosphorus oxychloride in pyridine led to the 20-ethynyl-$\Delta^{20(21)}$-ethylene III. Hydration of II gave the keto-diol Va, which could be oxidized by the Oppenauer method to the corresponding Δ^4-3-ketone VI, a homolog of 17α-hydroxyprogesterone. Reaction of the keto-diol Va with sodium hypobromite and subsequent methylation yielded the bisnorcholanic acid derivative VII. 3β-Acetoxy-5,16-pregnadien-20-one (VIII) was found not to react with sodium or lithium acetylide in liquid ammonia, whereas the 16β-hydroxy-20-ketone Ib and the 16α-benzyloxy-20-ketone Ic were converted to the 16-dehydro-20-ketone VIII under these conditions.

Although the reaction of androstan-17-one derivatives with acetylene is well known and is of industrial importance,[1] the corresponding reaction of pregnan-20-ones with acetylene has not been reported previously. We were interested whether the latter type of reaction could be carried out successfully, since its extension to 16-dehydro- or 16-oxygenated-pregnan-20-ones might result in the synthesis of the steroidal sapogenins, while its application to 21-hydroxypregnan-20-one derivatives could lead to substances belonging to the bufo-scilla group of cardiac-active steroids.[2]

In practice, we have now found that the reaction between 3β-acetoxy-5-pregnen-20-one (pregnenolone acetate) (Ia) and sodium acetylide in liquid ammonia proceeds smoothly and after reacetylation gives 3β-acetoxy-20-ethynyl-5-pregnen-20-ol (II), m.p. 193°, in 70% yield. The structural assignment is based on the infrared spectrum (presence of a terminal acetylene, absence of a saturated ketone) and the elemental analysis. Although a new asymmetric center is introduced in the conversion of Ia to II, only one isomer of the latter was isolated. This is presumably the 20β-hydroxy isomer (convention of Fieser and Fieser[3]), since the reaction of pregnan-20-ones with lithium aluminum hydride[4] and with sodium borohydride[5] gives this isomer predominantly.

A number of transformations involving the 20-ethynyl-20-hydroxy grouping of II were carried out. Treatment with phosphorus oxychloride in hot pyridine resulted in dehydration[6] and yielded a conjugated vinyl-acetylene, m.p. 105°, the spectral properties of which indicated it to be the $\Delta^{20(21)}$-ethylene III rather than the $\Delta^{17(20)}$-ethylene IV. Thus in the ultraviolet, the substance showed a maximum at 223 mμ (ε 10,500); this is compatible with the monosubstituted vinyl-acetylene structure III (*cf. trans*-pent-2-en-4-yne, λ_{max} 223 mμ[7]; pent-2-en-4-yn-1-ol, λ_{max} 223 mμ[8]), but is at too low a wave length for the α,β,β-trisubstituted vinyl-acetylene IV (*cf.* the β,β-disubstituted vinyl-acetylene 2-methylpent-2-en-4-yn-1-ol, λ_{max} 226 mμ[9]). In the infrared, the product showed a band at 11.14 μ, the position to be expected of a disubstituted terminal acetylene.[10]

The acetylene grouping of the acetylenic carbinol II could readily be hydrated by means of a methanolic boron trifluoride–mercuric oxide–trichloroacetic acid catalyst,[6,11] a reaction which also caused saponification of the acetate grouping at C-3. The resulting 20-acetyl-5-pregnene-3β,20-diol (Va), m.p. 239°, thus obtained in over 70% yield, on acetyla-

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(2) *Cf.* F. Sondheimer, N. Stjernström, and D. Rosenthal, *J. Org. Chem.*, **24**, 1280 (1959).

(3) L. F. Fieser and M. Fieser, *Experientia*, **4**, 285 (1948).

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(8) L. J. Haynes, I. M. Heilbron, E. R. H. Jones, and F. Sondheimer, *J. Chem. Soc.*, 1583 (1947).

(9) R. Ahmad and B. C. L. Weedon, *J. Chem. Soc.*, 3286 (1953).

(10) *Cf.* N. Sheppard and D. M. Simpson, *Quart. Revs. (London)*, **6**, 1 (1952), Table 7. The starting material II showed a weaker band in the same region, so this evidence can be accepted only with some reserve.

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