Measurement of Ion Hydration by the Diffusion Method

BY A. HUNYAR

C. H. Hale and T. de Vries have recently reported[1] that the hydration of quaternary ammonium salts cannot be determined by the Nernst–Washburn method[2] because the reference substance as well as water is transported during electrolysis. This fact was previously demonstrated by T. Erdey-Gruz and A. Hunyar[3] using a modified form of the diffusion method developed by J. W. McBain and T. H. Liu.[4] They usually employed allyl alcohol of various concentrations as a reference substance and hydrochloric acid, potassium bromide, potassium chloride, lithium chloride, lithium acetate and tetramethylammonium chloride as electrolytes. They found that the concentration of the reference substance decreased, with one exception, in that part of the apparatus from which the electrolyte diffused and increased in that part into which it diffused.[5] The remarkable fact concerning these experiments was that the amount of allyl alcohol transported increased nearly linearly with the concentration of alcohol in the range 0.2 to 25% from 0.003 to 0.31 mole of allyl alcohol per mole of potassium chloride. The amount of alcohol transported decreased from 0.033 mole of allyl alcohol per mole of potassium chloride on the first day to 0.023 on the fourth day which was mathematically shown to be due to the back diffusion of the alcohol. The following results were obtained.

Electrolyte	Hydration numbers by Remy[6]	Mole of allyl alcohol per mole electrolyte
$LiC_2H_3O_2$	22.0	0.041
LiCl	15.6	.033
$N(CH_3)_4Cl$	7.6	.015
KCl	7.1	.031
KBr	6.2	.025
HCl	4.0	.005

Pogány[7] also observed that the electrolytes carried more reference substance than water, using the diffusion method. In the electrolysis of a solution of silver nitrate with pyridine as reference substance, Morgan and Kanolt[8] reported that a large proportion of the pyridine was combined with silver ions.

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(1) Hale and De Vries, THIS JOURNAL, **70**, 2473 (1948).

(2) Washburn, *ibid.*, **31**, 322 (1909); *Z. physik. Chem.*, **66**, 513 (1909).

(3) Ph.D. Dissertation of A. Hunyar, Budapest, 1937.

(4) McBain and Liu, THIS JOURNAL, **53**, 59 (1931).

(5) The exception was the case of arsenic trioxide as a reference substance with potassium chloride as electrolyte, when it was observed that more water than arsenic trioxide was transported. An average of 1.4 mole of water per mole of potassium chloride was carried.

(6) "Handbuch f. Exp. Phys.," Vol. XII, part 1, p. 293.

(7) Pogány, *Magyar Chém. Folyoirat*, **48**, 85 (1942); *C. A.*, **38**, 3186 (1942).

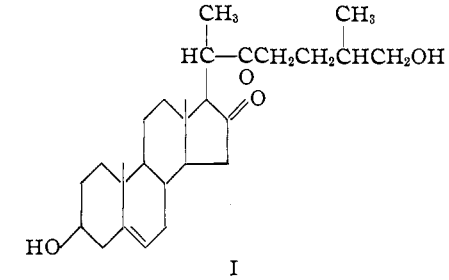
(8) Morgan and Kanolt, THIS JOURNAL, **28**, 572 (1906).

Steroidal Sapogenins. III. 16-Alkylsapogenins[1]

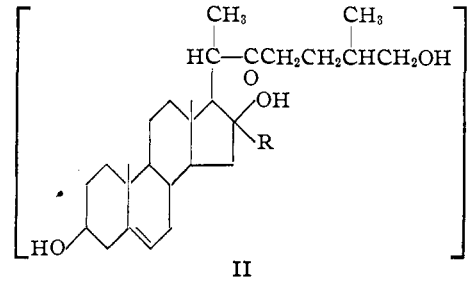
BY ST. KAUFMANN AND G. ROSENKRANZ

Through our recent work[1] it became evident that the two keto groups of the open-side-chain sapogenin, kryptogenin, possess different reactivity and that the conversion into sapogenins of the spiroketal form can easily be achieved as soon as the hydroxy group is introduced in the 16-position: we prepared[2] the 16-dihydrokryptogenin, a very unstable compound which can easily be transformed into diosgenin.

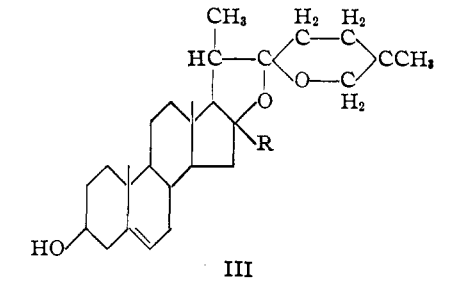
Based on this selective behavior of the 16-keto group we now reacted kryptogenin (I) with alkylmagnesium halides and obtained the respective 16-alkyldiosgenins (III) in good yield. The intermediate compound is very probably a 16-alkyl derivative of 16-dihydrokryptogenin (II)



I



II



III

The same reaction occurs with the esters of kryptogenin. If an excess of alkylmagnesium halide is used, the ester groups also react, thus yielding the free compounds.

In analogous manner, 5,6-dihydrokryptogenin or its esters can be transformed into the 16-alkyltigogenins. These latter compounds can be obtained also from the respective 16-alkyldiosgenins

(1) For Paper II in this series see Rosenkranz, Kaufmann, Landa, Corona and Olalde, THIS JOURNAL, **70**, 3518 (1948).

(2) Kaufmann and Rosenkranz, *ibid.*, **70**, 3502 (1948).

by catalytical hydrogenation with platinum oxide as catalyst.

Since it is known that the neosapogenins can be converted by acids into the corresponding normal side-chain sapogenins, while the compounds obtained with alkylmagnesium halide are stable against acids, we suggest that the normal side chain should be ascribed to the 16-alkylsapogenins described above.

The unsaturated 16-alkylsapogenins behave like diosgenin and the saturated like tigogenin inasmuch as they form mono-esters and as the 3-hydroxy group can easily be converted into a keto-group. The transformation and degradation of the side chain, as well as the resulting 16-alkylpregnane and androstane derivatives shall be dealt with in a forthcoming paper.

Experimental[3,4]

16-Methyldiosgenin.—To a solution of 10 g. (about 0.02 mole) of kryptogenin diacetate in 200 cc. of dry benzene, a diluted solution of 0.2 mole of methylmagnesium bromide in ether was added. The mixture was refluxed for three hours under anhydrous conditions, then poured into water and ice containing hydrochloric acid, and subsequently extracted with ether. After washing the ether solution with water until neutral it was dried and evaporated. After recrystallization from ether-methanol, about 7 g. of 16-methyldiosgenin was obtained m. p. 174–175°, $[\alpha]^{20}D$ −105° (in chloroform). *Anal.* Calcd. for $C_{28}H_{44}O_3$: C, 78.45; H, 10.34. Found: C, 78.46; H, 10.39.

The same product can be obtained from free kryptogenin, utilizing anhydrous dioxane instead of benzene as a solvent. After refluxing 16-methyldiosgenin with hydrochloric acid in alcoholic solution for ten hours, it can be recovered unaltered.

Acetate.—M. p. 171–172°, $[\alpha]^{20}D$ −100° (in chloroform). *Anal.* Calcd. for $C_{30}H_{46}O_4$: C, 76.55; H, 9.85. Found: C, 76.74; H, 9.75.

Benzoate.—M. p. 218–218.5°, $[\alpha]^{20}D$ −70° (in chloroform). *Anal.* Calcd. for $C_{35}H_{48}O_4$: C, 78.94; H, 9.02. Found: C, 78.89; H, 9.30.

16-Methyl-4,5-dehydrotigogenone.—16-Methyldiosgenin was oxidized with cyclohexanone and aluminum *t*-butylate to 16-methyl-4,5-dehydrotigogenone; m. p. 182.5–186°, $[\alpha]^{20}D$ −8° (in chloroform). *Anal.* Calcd. for $C_{28}H_{42}O_3$: C, 78.82; H, 9.92. Found: C, 78.78; H, 9.98.

16-Ethyldiosgenin.—The Grignard reaction with ethylmagnesium bromide led to 16-ethyldiosgenin; m. p. 171–172°, $[\alpha]^{20}D$ −107° (in chloroform). *Anal.* Calcd. for $C_{29}H_{46}O_3$: C, 78.68; H, 10.47. Found: C, 78.59; H, 10.51.

Acetate.—M. p. 176.5–177.5°, $[\alpha]^{20}D$ −105° (in chloroform). *Anal.* Calcd. for $C_{31}H_{48}O_4$: C, 76.81; H, 9.98. Found: C, 76.81; H, 9.91.

Benzoate.—M. p. 208–211°, $[\alpha]^{20}D$ −72° (in chloroform). *Anal.* Calcd. for $C_{36}H_{50}O_4$: C, 79.07; H, 9.21. Found: C, 79.12; H, 9.14.

16-Ethyl-4,5-dehydrotigogenone.—Prepared as the lower homolog, m. p. 171–173°, $[\alpha]^{20}D$ −7° (in chloroform). *Anal.* Calcd. for $C_{29}H_{44}O_3$: C, 78.86; H, 10.04. Found: C, 79.12; H, 10.01.

16-Methyltigogenin.—(a) This saturated compound was prepared from 5,6-dihydrokryptogenin-diacetate and methylmagnesium bromide under analogous conditions as described for 16-methyldiosgenin; m. p. 215–216.5°, $[\alpha]^{20}D$ −56° (in chloroform). *Anal.* Calcd. for $C_{28}H_{46}O_3$: C, 78.07; H, 10.76. Found: C, 78.08; H, 10.75.

(3) The microanalyses were carried out by Dr. Carl Tiedcke, New York, N. Y., and in our microanalytical laboratory under the direction of Miss Amparo Barba.

(4) All the melting points were determined on the Kofler micromelting point apparatus.

(b) The same product was obtained by catalytical hydrogenation of 16-methyldiosgenin in glacial acetic acid with platinum oxide as catalyst; m. p. 215–216.5°. The mixed m. p. with the 16-methyltigogenin obtained by method (a) showed no depression.

Acetate.—M. p. 186.5–189.5°, $[\alpha]^{20}D$ −65° (in chloroform). *Anal.* Calcd. for $C_{30}H_{48}O_4$: C, 76.22; H, 10.23. Found: C, 76.28; H, 9.98.

Benzoate.—M. p. 207–212°, $[\alpha]^{20}D$ −50° (in chloroform). *Anal.* Calcd. for $C_{35}H_{50}O_4$: C, 78.60; H, 9.42. Found: C, 78.50; H, 9.47.

16-Methyltigogenone.—It was prepared by oxidation of 16-methyltigogenin with chromic anhydride in glacial acetic acid; m. p. 175–178°, $[\alpha]^{20}D$ −45° (in chloroform). *Anal.* Calcd. for $C_{28}H_{44}O_3$: C, 78.45; H, 10.34. Found: C, 78.43; H, 10.52.

16-Ethyltigogenin.—The Grignard reaction of 5,6-dihydrokryptogenin with ethylmagnesium bromide led to 16-ethyltigogenin. The catalytical hydrogenation of 16-ethyldiosgenin with platinum oxide gave the same product; m. p. 194.5–197°, $[\alpha]^{20}D$ −60° (in chloroform). *Anal.* Calcd. for $C_{29}H_{48}O_3$: C, 78.32; H, 10.88. Found: C, 78.32; H, 10.86.

Acetate.—M. p. 197–199°, $[\alpha]^{20}D$ −62° (in chloroform). *Anal.* Calcd. for $C_{31}H_{50}O_4$: C, 76.47; H, 10.35. Found: C, 76.66; H, 10.29.

Benzoate.—M. p. 178.5–181°, $[\alpha]^{20}D$ −49° (in chloroform). *Anal.* Calcd. for $C_{36}H_{52}O_4$: C, 78.78; H, 9.55. Found: C, 78.59; H, 9.66.

16-Ethyltigogenone.—Prepared as the lower homolog; m. p. 169–173°, $[\alpha]^{20}D$ −44° (in chloroform). *Anal.* Calcd. for $C_{29}H_{46}O_3$: C, 76.68; H, 10.47. Found: C, 76.58; H, 10.59.

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The Exchange of Mercury(I) and Mercury(II) Ions

BY EDWARD L. KING

The exchange of mercury(I) and mercury(II) ions in solution is of interest because this involves breaking the bond in dimeric mercury(I) ion. Unpublished work[1a,b] indicates that this exchange proceeds rapidly at room temperature. It seemed desirable to carry out further experimental studies on this reaction using several techniques for separation of the two oxidation studies of mercury.

The separation of the two oxidation states has been effected by the precipitation of mercury(I) chloride, mercury(I) chromate and mercury(I) sulfate. In addition a partial separation has been effected by the diffusion technique[2] although no exchange experiments were run using this technique.

Experiments of three types were run using the precipitation of mercury(I) chloride and mercury(I) chromate. These differed in the order of addition of reagents: (a) the precipitating agent was added to a solution containing mercury(I) and mercury (II) perchlorates immediately after the two valence states had been brought together, (b) a solution containing mercury(II) perchlorate and the precipitating reagent was added to the solu-

(1) (a) Ruben and Nahinsky, reported by G. T. Seaborg in *Chem. Rev.*, **27**, 199 (1940); (b) Professor Arthur F. Scott, private communication.

(2) Van Alten and Rice, THIS JOURNAL, **70**, 883 (1948).