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°, $[\alpha]^{20}\mathrm{D}$ −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°, $[\alpha]^{20}\mathrm{D}$ −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°, $[\alpha]^{20}\mathrm{D}$ −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°, $[\alpha]^{20}\mathrm{D}$ −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°, $[\alpha]^{20}\mathrm{D}$ −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°, $[\alpha]^{20}\mathrm{D}$ −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°, $[\alpha]^{20}\mathrm{D}$ −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°, $[\alpha]^{20}\mathrm{D}$ −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°, $[\alpha]^{20}\mathrm{D}$ −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.

(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°, $[\alpha]^{20}\mathrm{D}$ −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°, $[\alpha]^{20}\mathrm{D}$ −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°, $[\alpha]^{20}\mathrm{D}$ −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°, $[\alpha]^{20}\mathrm{D}$ −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°, $[\alpha]^{20}\mathrm{D}$ −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°, $[\alpha]^{20}\mathrm{D}$ −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°, $[\alpha]^{20}\mathrm{D}$ −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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RECEIVED APRIL 5, 1949

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[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.

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-

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[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).

tion of mercury(I) perchlorate, and (c) the solution containing mercury(II) perchlorate was added to a slurry of the freshly precipitated mercury(I) compound. Using mercury(I) sulfate precipitation, the procedure corresponding to (a) was the only type experiment performed.

The results of experiments of type a and b are reported in Table I. It is seen that the exchange is essentially complete even in experiments of type (b).

TABLE I

EXCHANGE OF MERCURY(I) AND MERCURY(II) IONS

Exp. type	Ppt.	Composition (moles/liter) (Hg^{++})	(Hg_2^{++})	(H^+)	Extent of exchange
a	Hg_2Cl_2	0.0031	$0.0016^{\otimes a}$	0.5^b	94, 98
a	Hg_2Cl_2	$10^{-5 \otimes a}$	10^{-3}	0.5^b	>98
b	Hg_2Cl_2	$10^{-5 \otimes a}$	10^{-3}	0.5^b	97^c, 98^d
b	Hg_2Cl_2	$10^{-5 \otimes a}$	10^{-3}	3	$97–98^e$
a	$Hg_2CrO_4{}^f$	0.0044	$0.0069^{\otimes a}$	0.1	94, 98
b	$Hg_2CrO_4{}^f$	$0.0048^{\otimes a}$	0.0067	0.1	92, 102
a	$Hg_2SO_4{}^g$	0.0093	$0.0059^{\otimes a}$	0.16^h	~100%
a	$Hg_2SO_4{}^g$	$0.0136^{\otimes a}$	0.0064	0.16^h	

[a] ⊗ at concentration indicates activity started here. [b] Solutions also contain 3 *M* sodium perchlorate. [c] Two experiments. [d] Two experiments at 0°. [e] Three experiments; Cl^- concentration 0.04–0.06 *M*. [f] Composition of solid not established. [g] Precipitation incomplete; results of two experiments coupled lead to listed conclusion. [h] Not corrected for HSO_4^- formation.

The results of the experiments of type b involving mercury(I) chromate are consistent with a mechanism involving rapid homogeneous exchange and a rapid rate of recrystallization of the freshly precipitated solid. The concentration conditions in the chloride experiments are such that no conclusions may be drawn in this regard.

Experiments of type c are relevant to this question. The extent to which mercury(II) ion exchanges with precipitated mercury(I) chloride varies. The extent of exchange is approximately 30% if the mercury(II) is added within a few seconds after precipitation and then stirred with the precipitate for 2.5 minutes; it is 10% if the mercury(II) is added 7.5 minutes after precipitation and then stirred for 2.5 minutes. These represent extremes in the results of the seven experiments of this type performed. Contrasted with this are the results of this type experiment involving mercury(I) chromate. It was found that mercury(II), added in an amount comparable to the mercury(I), present as long as one minute after the precipitation of the mercury(I) chromate, exchanges completely with the precipitate upon stirring an additional two minutes. If, however, six minutes elapse between the time of precipitation and the addition of the mercury(II), essentially no exchange occurs upon stirring two minutes. This behavior, too, is consistent with a mechanism involving a rapid homogeneous exchange coupled with a relatively high recrystallization rate for freshly precipitated mercury(I) chromate and a much lower recrystallization rate for the coagulated solid. Visual observations reveal the change in the nature of the precipitate at times approximately one minute after precipitation. It was found that mercury(I) chromate precipitated under these conditions would dissolve completely in approximately thirty seconds upon treatment with excess iron(II) if only thirty seconds elapsed between the time of precipitation and addition of iron(II), while many minutes were required if this time interval was increased to three minutes.

This work doesn't discount the possibility that the exchange observed is in reality being induced during the precipitation. Under the conditions of these experiments it appears that the bond in dimeric mercury(I) is readily broken.

It has been shown that mercury(I) ion diffuses approximately 10% more rapidly than mercury(II) under certain concentration conditions. This observation is consistent with the relative diffusion coefficients determined by Kolthoff and Miller.[3] The condition under which this separation is achieved $((Hg_2^{++})_0/(Hg^{++})_0 = 0.5)$ is such that the counting rate of the diffusate would vary by only 5% depending upon whether the extent of exchange is 0% or 100%. The analytical and counting rate uncertainties are such that it does not appear worthwhile to use this technique in the exchange study.

Experimental

The radioactive mercury was prepared by the $Hg(n, \gamma)$ reaction in the Oak Ridge pile and allocated by the United States Atomic Energy Commission. The work was all performed after the Hg^{197} had decayed; thus the mercury isotope present was $Hg^{205,203}$. Solutions of active mercury(II) perchlorate were prepared by dissolving active mercury(II) oxide in perchloric acid. Solutions of active mercury(I) perchlorate were prepared by allowing a solution of mercury(I) perchlorate to exchange for several days with a small amount of active mercury(II) perchlorate. Other reagents were all analytical reagent grade and all solutions were prepared using doubly distilled water.

The mercury(I) fraction was generally counted in the form precipitated while the mercury(II) was counted as the oxide or a basic salt. The samples were mounted for counting on filter paper by suction filtering.

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[3] Kolthoff and Miller, THIS JOURNAL, **63**, 2732 (1941).

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RECEIVED MAY 31, 1949

β-Ketosulfides

BY FRANK KIPNIS[1] AND JOHN ORNFELT

In the course of studies on certain sulfur-containing ketones, it became desirable to prepare a series of β-ketosulfides. This type of compound had been synthesized previously,[2] but those com-

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[1] Present address: Oxford Products, Inc., Cleveland, Ohio.

[2] Ruhemann, *J. Chem. Soc.*, **87**, 461 (1905); Posner, *Ber.*, **35**, 809 (1905); Nicolet, THIS JOURNAL, **53**, 3066 (1931); **54**, 1998 (1932); **57**, 1098 (1935); Nicolet, *J. Biol. Chem.*, **95**, 389 (1932); Morgan and Friedman, *Biochem. J.*, **32**, 733 (1938); Fromm and Hubert, *Ann.*, **394**, 301 (1912); Frank and Smith, THIS JOURNAL, **68**, 2104 (1946).