tetrachloride essentially as has recently been described by Whitmore.[2] In many runs we found it practical to dissolve the silicon tetrachloride in either pure benzene or a mixture of dry ether and benzene (recovered from previous runs) rather than in pure ether. Yields were ordinarily 20–45%. Isopropylmagnesium bromide, however, gave 5–6% yield of the trichloride,[3] together with an equal weight of the dichloride (11% yield, based on the Grignard reagent).

For the preparation of diisobutylsilicon dichloride equimolar quantities of the Grignard reagent and isobutylsilicon trichloride (in benzene) were placed in reaction. The yield was about 20%.

Silicon tetrachloride was inert toward ethynylsodium, HC≡CNa, or ethynebis-(magnesium chloride), ClMgC≡CMgCl.

NEW COMPOUNDS, $RSiCl_3$ AND R_2SiCl_2

Substance	B. p. °C.	B. p. Mm.	d^{20}_4	Anal., Cl Calcd.	Anal., Cl Found	
p-$CH_3OC_6H_4SiCl_3$	128–130	13	1.46	44.04	43.62	44.32
p-$C_2H_5OC_6H_4SiCl_3$	137–138	13	1.36	41.62	41.42	41.18
$(i\text{-}C_3H_7)_2SiCl_2$	67–69	11	1.06	38.31	39.20	38.90
$(i\text{-}C_4H_9)_2SiCl_2$	93	16	1.00	33.26	33.26	33.17

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[2] Whitmore, *et al.*, THIS JOURNAL, **68**, 475 (1946).

[3] Booth and Spessard, *ibid.*, **68**, 2660 (1946).

COMMUNICATIONS TO THE EDITOR

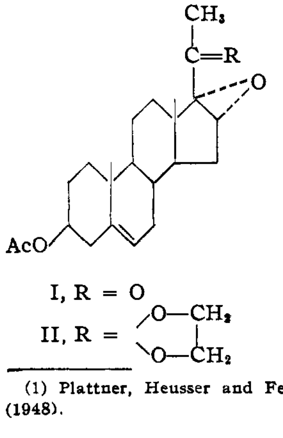
17α-HYDROXYSTEROIDS

Sir:

The recent communication by Plattner, Heusser and Feurer[1] impels us to record certain work on the reduction of steroid oxides which has been under way in these Laboratories for some time.

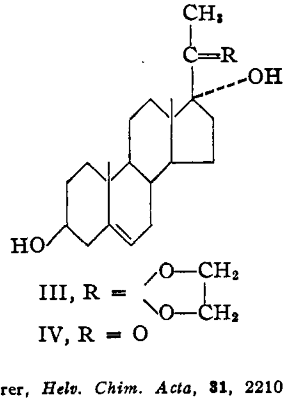
We have likewise prepared Reichstein's substances J and O by the reduction of 16,17-oxidoallopregnane-3β-ol-20-one acetate with lithium aluminum hydride. Furthermore, we have investigated the lithium aluminum hydride reduction of 16,17-oxido-5-pregnene-3β-ol-20-one acetate. The nature of the resulting 3,17,20-triol mixture was confirmed by oxidation with periodic acid to dehydroisoandrosterone (m. p. 148–149°; acetate, m. p. 166–168°).

We wish, particularly at this time, to report a novel procedure for the preparation of 17α-hydroxy steroids bearing a ketone group at position 20. The focal point in the facile preparation of these derivatives has been the protection of the 20-keto group through the formation of cyclic ketals. The 16,17-oxido-20-ketals undergo smooth reduction with lithium aluminum hydride and the resulting products are readily cleaved to the desired 17α-ol-20-ones.



I, R = O

II, R = O—CH₂, O—CH₂



III, R = O—CH₂, O—CH₂

IV, R = O

16,17-Oxido-5-pregnene-3β-ol-20-one Acetate (I).—Plates from methanol, m. p. 154–155°; $[\alpha]^{26}D$ −9.0° (chloroform). *Anal.* Calcd. for $C_{23}H_{32}O_4$: C, 74.16; H, 8.66. Found: C, 74.43; H, 8.72. It was prepared by the action of perbenzoic acid on derivatives of 5,16-pregnadiene-3β-ol-20-one.

Ketal of 16,17-Oxido-5-pregnene-3β-ol-20-one Acetate (II).—From the oxido-pregnene (I) and ethylene glycol by refluxing a benzene solution with *p*-toluenesulfonic acid monohydrate as catalyst as thick, needle-like prisms from benzene-methanol, m. p. 195–197°; $[\alpha]^{27}D$ −37.8° (chloroform). *Anal.* Calcd. for $C_{25}H_{36}O_5$: C, 72.07; H, 8.71. Found: C, 71.92; H, 8.67.

Ketal of 17α-Hydroxypregnenolone (III).—From the reduction of the ketal (II) with lithium aluminum hydride in benzene–ether solution as plate-like prisms from acetone, m. p. 185–187°; $[\alpha]^{26}D$ −44.8° (chloroform). *Anal.* Calcd. for $C_{23}H_{36}O_4$: C, 73.36; H, 9.64. Found: C, 73.63; H, 9.70.

17α-Hydroxypregnenolone (**5-Pregnene-3β,17α-diol-20-one**) (IV).—From the ketal (III) by cleavage with sulfuric acid in aqueous methanol as fine prisms from methanol, m. p. 265°[2]; $[\alpha]^{28}D$ −34.4° (2 parts ethanol–1 part dioxane). *Anal.* Calcd. for $C_{21}H_{32}O_3$: C, 75.86; H, 9.70. Found: C, 75.42; H, 9.84. Acetylation of the 17α-hydroxypregnenolone with acetic anhydride-pyridine gave the acetate, needles from benzene–petroleum ether (b. p. 35–60°), m. p. 232–234°.[2]

By the Oppenauer oxidation of 16,17-oxidopregnenolone (16,17-oxido-5-prenene-3β-ol-20-one) we have incidentally prepared 16,17-oxidoprogesterone (16,17-oxido-4-pregnene-3,20-dione) as fine prisms from aqueous methanol, m. p. 205–207°; $[\alpha]^{27}D$ +160.8° (chloroform). *Anal.* Calcd. for $C_{21}H_{28}O_3$: C, 76.79; H, 8.59. Found: C, 76.50; H, 8.68.

The investigations are being continued.

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[1] Plattner, Heusser and Feurer, *Helv. Chim. Acta*, **31**, 2210 (1948).

[2] *Cf.* Fuchs and Reichstein, *Helv. Chim. Acta*, **24**, 804 (1941) Hegner and Reichstein, *ibid.*, **24**, 828 (1941).