TABLE V

R

MERCAPTO-ACIDS, $HSCH_2CH_2CH(CH_2)_nCOOH$

R	n	Yield, %	B.p. °C.	B.p. Mm.	$n^{20}D$	d_{20}	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
CH_3	4	81.3	116	0.14	1.4802	1.016	$C_9H_{18}C_2S$	56.80	57.16	9.53	9.83	16.85	16.92
C_2H_5	4	75.3	133	.09	1.4813	1.013	$C_{10}H_{20}O_2S$	58.78	58.98	9.87	10.21	15.70	15.89
n-C_3H_7	4	54.6	140	.08	1.4809	0.995	$C_{11}H_{22}O_2S$	60.50	60.62	10.16	10.10	14.69	14.68
n-C_4H_7	4	74.4	141	.1	1.4810	.988	$C_{12}H_{24}O_2S$	62.02	62.22	10.41	10.13	13.80	14.10
i-C_4H_7	4	60.5	173	1.0	1.4810	.987	$C_{12}H_{24}O_2S$	62.02	62.40	10.41	10.44	13.80	13.34
C_2H_5	2	52.2	107	0.05	1.4839	1.044	$C_8H_{16}O_2S$	54.51	54.78	9.15	9.05	18.19	17.66
C_2H_5	3	74.6	148	.85	1.4842	1.031	$C_9H_{18}O_2S$	56.80	57.00	9.53	9.53	16.85	17.22
C_2H_5	5	54.8	142	.05	1.4823	1.004	$C_{11}H_{22}O_2S$	60.50	60.20	10.16	10.02	14.69	14.81
C_2H_5	6	37.2	145	.04	1.4812	0.993	$C_{12}H_{24}O_2S$	62.02	61.64	10.41	10.09	13.80	14.05

acidified and extracted with ether. After drying and removal of the ether, the residue was distilled at low pressure. Properties and analytical data are given in Table V.

Acknowledgments.—We are indebted to Mr. L. Brancone and staff for microanalytical determinations, to Mr. W. Fulmor and staff for infrared studies and to Mr. J. Sanjurjo for assistance in the high pressure operations.

PEARL RIVER, NEW YORK

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

Synthesis of Steroidal Methylene Compounds by the Wittig Reaction[1]

BY FRANZ SONDHEIMER AND RAPHAEL MECHOULAM

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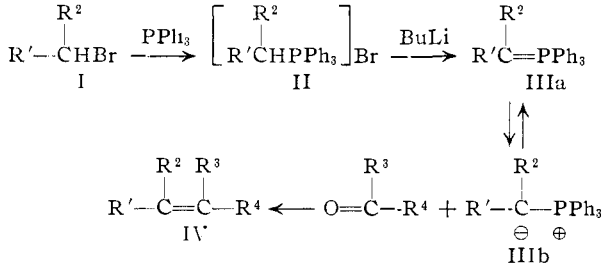
Different types of saturated and α,β-unsaturated steroidal ketones have been converted to the corresponding methylene compounds through reaction with triphenylphosphine-methylene. Such methylene compounds thereby became readily available. Steroidal hydroxy-ketones may be subjected to the reaction either directly or after protection of the hydroxyl group. Several methylene steroids described previously are shown to have been impure.

The recently discovered reaction between triphenylphosphine-alkylidenes of type III (obtained from the bromides I by the sequence shown) and carbonyl compounds to produce the corresponding ethylenes IV, the so-called Wittig reaction, has become one of wide scope and utility in synthetic chemistry.[2] We first became interested in the application of this reaction in the steroid field in



connection with a study we undertook to find new methods for constructing compounds containing sterol side chains from 17-keto and 20-keto steroids. This study led us to investigate the interaction between a variety of steroidal ketones with different triphenylphosphine-alkylidenes. It was found that the reaction proceeded most smoothly when triphenylphosphine-methylene (III, $R^1 = R^2 = H$) was employed and the present paper records the use of this reagent for the synthesis of various methylene-steroids (IV, $R^1 = R^2 = H$) from both saturated and α,β-unsaturated steroidal monoketones. We were not certain how successful the reaction would be with ketones containing other functions (hydroxy and acetoxy groups) which may react with triphenylphosphine-methylene, but in fact it was found that reasonably satisfactory results were obtained also with these polyfunctional substances. The methylene compounds thus obtained are often prepared only with difficulty and in some cases in impure form by other methods. On the other hand, the present route produces the methylene steroids simply and in a high state of purity.

The triphenylphosphine-methylene reagent was prepared in ether solution in the usual way[2] by treatment of methyltriphenylphosphonium bromide with butyllithium, and the reactions with the ketones were best carried out in refluxing tetrahydrofuran. The various steroidal ketones investigated are listed in Table I, together with the yields and properties of the products. The structures of the resulting methylene-steroids were confirmed by the elemental analyses, infrared spectra (disappearance of the carbonyl band and appearance of the terminal methylene bands at *ca.* 890 and 1650 $cm.^{-1}$)[3] and in some cases by comparison of the properties with those reported for the previously described compounds.

Cholestan-3-one (no. 1), a simple monofunctional compound containing the system Va, produced 3-

(1) Presented in part before the Organic Chemistry Division at the 131st Meeting of the American Chemical Society, Miami, Fla., April, 1957.

(2) *Cf.* G. Wittig, *Experientia*, **12**, 41 (1956); *Angew. Chem.*, **68**, 505 (1956), and earlier references cited there.

(3) *Cf.* N. Sheppard and D. M. Simpson, *Quart. Revs. (London)*, **6**, 1 (1952), Table 7.

methylene-cholestane (Vb)[4] in nearly 70% yield on treatment with 3 molar equivalents of the reagent. That a hydroxyl group may be present was shown by submitting androstan-17β-ol-3-one (no. 2) to the reaction under the same conditions, when 3-methylene-androstan-17β-ol was formed. The yield, however, was reduced to about 40%. Hecogenin acetate (no. 3), containing the 12-ketone system VIa, yielded 12-methylene-tigogenin (VIb) after saponification of the reaction mixture and this example shows that an acetoxy grouping may be present. Androstan-3β-ol-17-one (VII) (no. 4), a 17-ketone, produced 17-methylene-androstan-3β-ol (VIIIa). The yield of the latter was 32% when 3 molar equivalents of reagent was used, but was improved to 58% by employment of 5 molar equivalents (no. 5). This result, which was found toward the end of the investigation, indicates that with polyfunctional compounds the use of a very considerable excess of reagent is to be recommended for satisfactory yields. As can be seen from Table I, the 17-methylene-androstan-3β-ol (VIIIa) produced did not agree well either in m.p. or rotation with that obtained from 17α-methyl-androstan-17β-ol-3-one (IX) by dehydration at C-17 through distillation over copper sulfate to 17-methylene-androstan-3-one (VIIIb),[5] followed by Meerwein–Ponndorf reduction at C-3.[5] Oxidation of our 17-methylene-androstan-3β-ol (VIIIa) with the pyridine–chromium trioxide complex[6] yielded 17-methylene-androstan-3-one (VIIIb), which though now agreeing reasonably well in m.p. with that reported by the Swiss workers,[5] still showed a considerably lower rotation. That the explanation for this discrepancy is to be ascribed to the impure nature of the products VIIIa and VIIIb as obtained by the copper sulfate dehydration method[5] is indicated by the molecular rotation data (see below) and by carrying out the Wittig reaction with triphenylphosphine-methylene with the Δ⁵-compound, Δ⁵-androsten-3β-ol-17-one (Xa) (no. 6). In this case the product, 17-methylene-Δ⁵-androsten-3β-ol (XI), agreed very well in properties with those reported[7] for the substance obtained by the decarboxylation of $\Delta^{5,17(20)}$-pregnadien-3β-ol-21-oic acid (XII) and direct comparison confirmed identity.

In order to determine the effect of protecting the hydroxyl group, the yields given by Δ⁵-androsten-3β-ol-17-one (Xa) (no. 6), its acetate (Xb) (no. 7) and its tetrahydropyranyl ether (Xc) (no. 8)[8] with 3 molar equivalents of the reagent were compared.[9] The ester (after saponification of the product) was found to give a somewhat poorer yield (27%) than did the ketol (36%), whereas the ether (after acid treatment) gave a rather better yield (44%). Since, however, the formation of the tetrahydropyranyl ether of steroidal keto-alcohols is usually not quantitative, it is recommended that the free ketol be used in general in the Wittig reaction, especially in view of the finding with free androstan-3β-ol-17-one (VII) that the employment of a great excess of reagent materially increases the yield. The 20-ketone, Δ⁵-pregnen-3β-ol-20-one (XIIIa) (no. 9), reacted normally to give 20-methylene-Δ⁵-pregnen-3β-ol-20-one (XIIIb).

Three different types of steroidal α,β-unsaturated ketones were subjected to the reaction with triphenylphosphine-methylene. Δ⁴-Cholesten-3-one (XIVa) (no. 10) produced 3-methylene-Δ⁴-cholestene (XVIa), m.p. 73°, $[\alpha]_D$ +140°, $\lambda_{max}^{isooctane}$ 239 mμ, in 80% yield. This substance has been reported to be formed by dehydration of 3-methyl-Δ⁴-cholesten-3-ol (XV) (from Δ⁴-cholesten-3-one and methylmagnesium iodide) by means of *p*-toluenesulfonyl chloride and pyridine and to exhibit m.p. 64°, $[\alpha]_D$ +50.5° (benzene), $\lambda_{max}^{cyclohexane}$ 233 and 239 mμ.[10] The structural assignment rested upon the formation of formaldehyde in 6% yield on ozonolysis and on its isomerization with acids to 3-methyl-Δ³,⁵-cholestadiene (XVIIa), m.p. 79.5°, $[\alpha]_D$ −129°, $\lambda_{max}^{cyclohexane}$ 231 and 239 mμ. This same isomerization product with very similar properties was obtained by ourselves in almost quantitative yield by treating 3-methylene-Δ⁴-cholestene (XIVa) from the Wittig reaction with acid, the rearrangement being accompanied by the disappearance of the methylene bands at 882 and 1634 cm.⁻¹ in the infrared. It appeared that Musgrave's dehydration product was a mixture of the dienes XVIa and XVIIa, and this was confirmed when we repeated his experiment and compared the infrared spectrum of the diene thus obtained with the spectra of the pure dienes XVIa and XVIIa.[11] 3-Methylene-Δ⁴-cholestene (XVIa) is rather unstable due to its ready isomerization; both the m.p. and the rotation of an analytical sample were considerably lowered after being stored in the dark for some weeks.

The Wittig reaction of a Δ⁴-3-ketone may also be carried out in the presence of a hydroxyl group, as evidenced by the conversion of testosterone (XIVb) to 3-methylene-Δ⁴-androsten-17β-ol (XVIb) (no. 11). As in the cholesterol series, this substance is rather unstable and on treatment with acids is readily rearranged to 3-methyl-Δ³,⁵-androstadien-17β-ol (XVIIb). The Δ⁵-7-ketone, 7-ketocholesteryl acetate (XVIIIa) (no. 12), on treatment with

(4) D. H. R. Barton, A. S. Campos-Neves and R. C. Cookson (*J. Chem. Soc.*, 3500 (1956)) have now described the obtention of the same compound by this method.

(5) L. Ruzicka, P. Meister and V. Prelog, *Helv. Chim. Acta*, **30**, 867 (1947).

(6) G. I. Poos, G. E. Arth, R. E. Beyler and L. H. Sarett, THIS JOURNAL, **75**, 422 (1953).

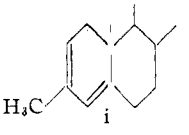
(7) F. Sondheimer, O. Mancera, M. Urquiza and G. Rosenkranz, *ibid.*, **77**, 4145 (1955).

(8) C. W. Greenhalgh, H. B. Henbest and E. R. H. Jones, *J. Chem. Soc.*, 1190 (1951); A. C. Ott, M. F. Murray and R. L. Pederson, THIS JOURNAL, **74**, 1239 (1952).

(9) H. H. Inhoffen, *et al.*, have now reported the reaction of triphenylphosphine-methylene with a keto-alcohol in the vitamin D series in which the alcohol function was protected as the tetrahydropyranyl ether (H. H. Inhoffen, J. F. Kath and K. Brückner, *Angew. Chem.*, **67**, 276 (1955)) or as the acetate (H. H. Inhoffen, G. Quinkert and H. J. Hess, *Naturwissenschaften*, **44**, 11 (1957)).

(10) O. C. Musgrave, *J. Chem. Soc.*, 3121 (1951).

(11) N. F. Kucherova and M. I. Ushakov (*Zhur. Obshchei Khim.*, **23**, 319 (1953); *C. A.*, **48**, 2744 (1954)) have reported that decomposition of the mixture obtained from Δ⁴-cholesten-3-one and methylmagnesium iodide with aqueous ammonium chloride solution at room temperature resulted in 86% of a substance, m.p. 68–69°, $[\alpha]_D$ −12° (CCl_4), to which the 3-methyl-Δ²,⁴-cholestadiene structure (i) was assigned. Unfortunately no ultraviolet data were presented (which would have distinguished i from XVIa and XVIIa), and this product is very probably also a mixture of the 3-methylene-Δ⁴-compound XVIa and the 3-methyl-Δ³,⁵-diene XVIIa.

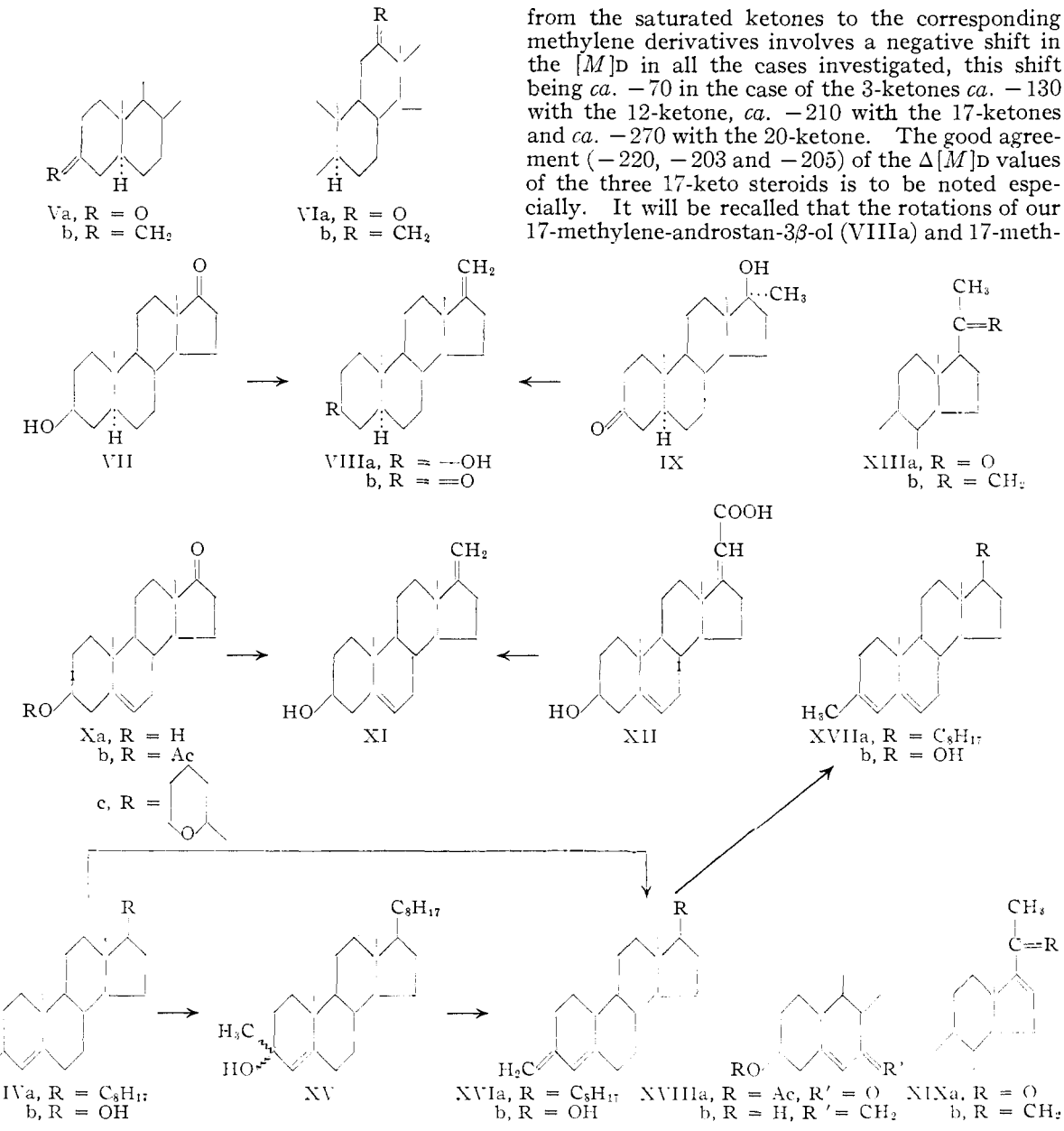


i

TABLE I

No.	Starting material	Moles reagent	Product	Yield, %	Physical properties[a]	Analysis, or reported properties[a]
1	Cholestan-3-one (Va)	3	3-Methylene-cholestane (Vb)	69	M.p. 64–65° from methanol, $[\alpha]D$ +24°, ν_{max} 886 and 1647 cm.$^{-1}$	M.p. 65–66°, $[\alpha]D$ +23° (CCl_4)[4]
2	Androstan-17β-ol-3-one (Va)	3	3-Methylene-androstan-17β-ol (Vb)	38	M.p. 149–150° from methanol, $[\alpha]D$ +8°, ν_{max} 889 and 1647 cm.$^{-1}$	Calcd. for $C_{20}H_{32}O$: C, 83.27; H, 11.18. Found: C, 83.47; H, 11.24
3	Hecogenin acetate (VIa)	7.5	12-Methylene-tigogenin (VIb)	51	M.p. 234–235° from acetone, $[\alpha]D$ −20°, ν_{max} 897 and 1642 cm.$^{-1}$	Calcd. for $C_{28}H_{44}O_3$: C, 78.45; H, 10.35. Found: C, 78.56; H, 10.27
4	Androstan-3β-ol-17-one (VII)	3	17-Methylene-androstan-3β-ol (VIIIa)	32	M.p. 144–145° from methanol, $[\alpha]D$ +12°, ν_{max} 882 and 1649 cm.$^{-1}$	M.p. 131–133°, $[\alpha]D$ +27°[5]
5	Androstan-3β-ol-17-one (VII)	5	17-Methylene-androstan-3β-ol (VIIIa)	58	.....	.....
6	Δ^5-Androsten-3β-ol-17-one (Xa)	3	17-Methylene-Δ^5-androsten-3β-ol (XI)	36	M.p. 132–133° from methanol, $[\alpha]D$ −66°, ν_{max} 882 and 1653 cm.$^{-1}$	M.p. 133–134°, $[\alpha]D$ −65°[7]
7	Δ^5-Androsten-3β-ol-17-one acetate (Xb)	3	17-Methylene-Δ^5-androsten-3β-ol (XI)	27	.....	.....
8	Δ^5-Androsten-3β-ol-17-one 3-tetrahydropyranyl ether (Xc)	3	17-Methylene-Δ^5-androsten-3β-ol (XI)	44	.....	.....
9	Δ^5-Pregnen-3β-ol-20-one (XIIIa)	4	20-Methylene-Δ^5-pregnen-3β-ol (XIIIb)	35	M.p. 133–134° from methanol, $[\alpha]D$ −59°, ν_{max} 893 and 1640 cm.$^{-1}$	Calcd. for $C_{22}H_{34}O$: C, 84.02; H, 10.90. Found: C, 83.91; H, 10.82
10	Δ^4-Cholesten-3-one (XIVa)	5	3-Methylene-Δ^4-cholestene (XVIa)	80	M.p. 72–73° from acetone, $[\alpha]D$ +140°, ν_{max} 882 and 1634 cm.$^{-1}$, λ_{max} 239 mμ (log ϵ 4.36) (isooctane)	Calcd. for $C_{28}H_{46}$: C, 87.88; H, 12.12. Found: C, 87.64; H, 11.98
11	Testosterone (XIVb)	5	3-Methylene-Δ^4-androsten-17β-ol (XVIb)	57	M.p. 137–138° from methanol, $[\alpha]D$ +163°, ν_{max} 882 and 1640 cm.$^{-1}$, λ_{max} 239 mμ (log ϵ 4.36) (isooctane)	Calcd. for $C_{20}H_{30}O$: C, 83.86; H, 10.56. Found: C, 83.72; H, 10.45
12	7-Ketocholesteryl acetate (XVIIIa)	5	7-Methylenecholesterol (XVIIIb)	40	M.p. 83–84° from ethanol, $[\alpha]D$ −188°, ν_{max} 893 and 1660 cm.$^{-1}$, λ_{max} 237 mμ (log ϵ 4.34) (isooctane)	M.p. 85°, $[\alpha]D$ −191°, λ_{max} 236 mμ (log ϵ 4.3)[12]
13	$\Delta^{5,16}$-Pregnadien-3β-ol-20-one acetate (XIXa)	5	20-Methylene-$\Delta^{5,16}$-pregnadien-3β-ol acetate (XIXb)	48	M.p. 124.5–126° from methanol, $[\alpha]D$ −76°, ν_{max} 886 and 1625 cm.$^{-1}$, λ_{max} 239 mμ (log ϵ 4.21) (isooctane)	Calcd. for $C_{24}H_{34}O_2$: C, 81.31; H, 9.67. Found: C, 81.31; H, 9.42.

[a] See footnote 13.



triphenylphosphine-methylene produced 7-methylene-cholesterol (XVIIIb), agreeing well in properties with the previously described substance of this structure.[12] In this case it was determined that the ester grouping had been completely saponified by the reagent during the course of the reaction. Finally the Δ^{16}-20-ketone, $\Delta^{5,16}$-pregnadien-3β-ol-20-one acetate (XIXa) (the degradation product of diosgenin), was subjected to the Wittig reaction (no. 13) and after acetylation yielded 20-methylene-$\Delta^{5,16}$-pregnadien-3β-ol acetate (XIXb).

In Table II the molecular rotations ($[M]_D$) of various ketones are compared with those ($[M]_D^{CH_2}$) of the corresponding compounds in which the ketone group has been replaced by methylene, described in this paper. It can be seen that passing from the saturated ketones to the corresponding methylene derivatives involves a negative shift in the $[M]_D$ in all the cases investigated, this shift being *ca.* −70 in the case of the 3-ketones *ca.* −130 with the 12-ketone, *ca.* −210 with the 17-ketones and *ca.* −270 with the 20-ketone. The good agreement (−220, −203 and −205) of the $\Delta[M]_D$ values of the three 17-keto steroids is to be noted especially. It will be recalled that the rotations of our 17-methylene-androstan-3β-ol (VIIIa) and 17-methylene-androstan-3-one (VIIIb) did not agree with the published figures[5]; the $\Delta[M]_D$ values of the three 17-ketones are −177, −143 and −202 if the published figures are used for the calculations, and this consideration confirms the view that our compounds are pure. In the case of the α,β-unsaturated ketones, passing from a Δ^5-7-ketone and a Δ^{16}-20-ketone to the corresponding methylene compounds also involves a negative shift in the molecular rotation (*ca.* −330 and *ca.* −140, respectively), whereas in the Δ^4-3-ketone series a positive shift of *ca.* +180 is observed. It is of interest to note that the isomerization of a 3-methylene-Δ^4-compound to the corresponding 3-methyl-$\Delta^{3,5}$-diene both in the cholesterol and in the testosterone series (XVIa → XVIIa and XVIb → XVIIb) is accompanied by a very large negative shift in $[M]_D$, the $\Delta[M]_D$ being −1039 and −981 in the two series.

(12) B. Bann, I. M. Heilbron and F. S. Spring, *J. Chem. Soc.*, 1274 (1936); S. Weinhouse and M. S. Kharasch, *J. Org. Chem.*, **1**, 490 (1936).

Other aspects of the Wittig reaction in the steroid field are now being investigated and will be reported later.

Acknowledgments.—We are indebted to Dr. G. Rosenkranz of Syntex S. A., Mexico City, for generously providing the various steroidal starting materials.

Experimental[13]

Typical Procedure for the Reaction of Steroidal Ketones with Triphenylphosphine-methylene.—A 1 *N* ethereal solution of butyllithium (9 cc.) was added to a suspension of 3.57 g. (10 millimoles) of methyltriphenylphosphonium bromide (prepared from methyl bromide and triphenylphosphine)[14] in 50 cc. of ether with swirling, under nitrogen. The mixture was shaken in nitrogen for 2 hr., the steroid dissolved in 50–100 cc. (or more if necessary) of ether was added, the mixture was shaken for a further 4 hr. and then allowed to stand overnight. Ether was distilled off at the same time as tetrahydrofuran was added until most of the ether had been replaced. The mixture was refluxed for 6 hr., cooled, diluted with water and extracted with ether. The organic extract was washed with water, dilute hydrochloric acid (the acid washing was omitted in experiments no. 10 and 11, where the acid-labile 3-methylene-Δ^4-steroids are formed) and water, dried and evaporated. The residue was either crystallized directly or more commonly chromatographed on alumina. In addition to the methylene compounds, the chromatograms yielded triphenylphosphine oxide and other phosphorus-containing compounds which were not further investigated.

17-Methylene-androstan-3-one (VIIIb) by Oxidation of 17-Methylene-androstan-3β-ol (VIIIa).—Chromium trioxide (0.1 g.) was added carefully to 3 cc. of dry pyridine. A solution of 0.1 g. of 17-methylene-androstan-3β-ol (from experiment no. 4) in 3 cc. of pyridine was added dropwise, and the mixture was allowed to stand at room temperature overnight. Water and then equal parts of benzene and ether were added, the mixture was filtered through Celite and the organic layer was washed with water, dried and evaporated. Crystallization from methanol furnished 17-methylene-androstan-3-one, m.p. 130–131.5°, $[\alpha]_D$ +41°; ν_{max} 882, 1653 and 1706 cm.$^{-1}$; reported[5]: m.p. 127–128°, $[\alpha]_D$ +62°.

Anal. Calcd. for $C_{20}H_{30}O$: C, 83.86; H, 10.56. Found: C, 83.64; H, 10.37.

3-Methyl-$\Delta^{3,5}$-cholestadiene (XVIIa) from 3-Methylene-Δ^4-cholestene (XVIa).—Concentrated hydrochloric acid (1 cc.) was added to 0.15 g. of 3-methylene-Δ^4-cholestene (from experiment no. 10) dissolved in 35 cc. of ethanol, and the solution was refluxed for 2 hr. Isolation with ether and crystallization from acetone–methanol yielded 0.13 g. of 3-methyl-$\Delta^{3,5}$-cholestadiene, m.p. 75–77°, which on further purification showed m.p. 79–80°, $[\alpha]_D$ −132°, $\lambda_{max}^{cyclooctane}$ 232 mμ (log ϵ 4.30) and 239 mμ (log ϵ 4.32); reported[10]: m.p. 79–79.5°, $[\alpha]_D$ −129°, $\lambda_{max}^{cyclohexane}$ 231 mμ (log ϵ 4.33) and 239 mμ (log ϵ 4.36).

Repetition of the dehydration of 3-methyl-Δ^4-cholesten-3-ol (XV) with *p*-toluenesulfonyl chloride and pyridine according to Musgrave[10] gave a diene with m.p. 61–63°, $[\alpha]_D$ +55°; reported[10]: m.p. 63–64°, $[\alpha]_D$ +50° (benzene). The infrared spectrum of this material clearly showed it to be a mixture of the two isomers XVIa and XVIIa by comparison with the spectra of the pure isomers.

3-Methyl-$\Delta^{3,5}$-androstadien-17β-ol (XVIIb).—This substance was obtained in *ca.* 70% yield by boiling 3-methylene-Δ^4-androsten-17β-ol (XVIb) (from experiment 11) with hydrochloric acid in ethanol, as described above in the cholesterol series. It crystallized from methanol and showed m.p. 128–130°, $[\alpha]_D$ −175°, $\lambda_{max}^{ethanol}$ 233 mμ (log ϵ 4.28) and 239 mμ (log ϵ 4.33).

Anal. Calcd. for $C_{20}H_{30}O$: C, 83.86; H, 10.56. Found: C, 83.56; H, 10.46.

Table II

Molecular Rotation Data of Methylene Steroids[a]

	$[M]_D$	$[M]_D$ CH_2	$\Delta[M]_D$
Cholestan-3-one (Va)	+158[b]	+ 92	− 66
Androstan-17β-ol-3-one (Va)	+ 94 (EtOH)[c]	+ 23	− 71
Hecogenin (VIa)	+ 43[d]	− 86	−129
Androstan-3β-ol-17-one (VII)	+255[e]	+ 35	−220
Androstane-3,17-dione	+320[b]	+117	−203
Δ^5-Androsten-3β-ol-17-one (Xa)	+ 16[f]	−189	−205
Δ^5-Pregnen-3β-ol-20-one (XIIIa)	+ 88 (EtOH)[g]	−185	−273
Δ^4-Cholesten-3-one (XIVa)	+342[h]	+535	+193
Testosterone (XIVb)	+314[i]	+480	+166
7-Ketocholesterol (XVIIIa)	−416[j]	−748	−332
$\Delta^{5,16}$-Pregnadien-3β-ol-17-one acetate (XIXa)	−125[k]	−269	−144

[a] See footnote 13. [b] D. H. R. Barton, *J. Chem. Soc.*, 813 (1945). [c] A. Butenandt, K. Tscherning and G. Hanish, *Ber.*, **68**, 2097 (1935). [d] M. E. Wall, M. M. Krider, E. S. Rothman and C. R. Eddy, *J. Biol. Chem.*, **198**, 533 (1952). [e] Determined in these Laboratories. [f] G. Rosenkranz, O. Mancera, F. Sondheimer and C. Djerassi, *J. Org. Chem.*, **21**, 520 (1956). [g] A. Butenandt and G. Fleischer, *Ber.*, **70**, 96 (1937). [h] L. F. Fieser, THIS JOURNAL, **75**, 4377 (1953). [i] F. Sondheimer, S. Kaufmann, J. Romo, H. Martinez and G. Rosenkranz, *ibid.*, **75**, 4712 (1953). [j] S. Bergström and O. Wintersteiner, *J. Biol. Chem.*, **141**, 597 (1941). [k] M. E. Wall, H. E. Kenney and E. S. Rothman, THIS JOURNAL, **77**, 5665 (1955).

(13) Melting points are uncorrected. Rotations were determined at 20–25° in chloroform solution unless specified otherwise. Ultraviolet spectra were measured on a Unicam Model S.P. 500 spectrophotometer and infrared spectra (in chloroform solution) on a Perkin–Elmer model 12 C single beam spectrophotometer with sodium chloride prism. Analyses were carried out in our microanalytical department under the direction of Mr. Erich Meier.

(14) G. Wittig and U. Schöllkopf, *Ber.*, **87**, 1318 (1954).

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