[JOINT CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND OF BIOCHEMISTRY, STANFORD UNIVERSITY]

Optical Rotatory Dispersion Studies. LXV.[1] Differentiation of Epimeric Steroidal Alcohols by Anomalous Rotatory Dispersion. Some Observations on the Nitrite Chromophore[2]

CARL DJERASSI, I. T. HARRISON, OLGA ZAGNEETKO,[3] AND A. L. NUSSBAUM

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Steroidal 20α- and 20β-hydroxy derivatives can be distinguished readily through the Cotton effects of their xanthate derivatives. In view of the difficulty in preparing xanthates of certain poly-substituted steroids, attention was directed towards the use of the readily prepared nitrite esters. These show multiple Cotton effects in a convenient spectral region and their rotatory dispersion curves can be employed for purposes of differentiation between epimeric pairs of alcohols even in the presence of the Δ^4-3-keto moiety.

Jones and Klyne[4] have recorded the plain rotatory dispersion curves of the epimeric 5α-pregnan-20α-(Ia) and 20β-ols(IIa) as well as of their acetates and benzoates. Of these six substances, five showed plain positive curves and only in the case of the benzoates was there noted a difference, in that the 20α-benzoate Ib exhibited a plain positive curve, while that of the 20β-benzoate IIb was negative. In connection with our studies[5] on the development of "chromophoric" derivatives (possessing anomalous rotatory dispersion curves) for some of the more common "nonchromophoric" functional groups, which exhibit only plain dispersion curves through the presently accessible spectral range, we have paid particular attention to the rotatory dispersion behavior of epimeric steroidal alcohols (*e.f.* Ia *vs.* IIa) and their derivatives.

The observation of Jones and Klyne[4] that the C-20 epimeric benzoates Ib and IIb possess plain dispersion curves of opposite sign was interesting, since the 20β-benzoate IIb was the only derivative exhibiting a negative curve (see Fig. 1). We have now been able to show that this is due to the 230 mμ absorption band of the benzoate,[6] since complete hydrogenation to the hexahydrobenzoate IId again restores the typical positive plain curve (Fig. 1) associated with the parent alcohol IIa and its acetate. In particular, this experiment eliminates the possibility that the steric requirements of the benzoate grouping as compared to the alcohol or acetate might favor another free-rotational rotomer composition, which is responsible for the negative sign of the curve. If this were the case, then the even more bulky hexahydrobenzoate IId should exhibit the same phenomenon.

The intrinsic disadvantage of plain rotatory dispersion curves[7] over anomalous ones has prompted us to look for "chromophoric" derivatives of such epimeric alcohols, where the sign of the Cotton effect might be employed for purposes of stereochemical assignment. Attention was first directed at xanthate derivatives since these have proved to be very useful with α-hydroxy acids[5a] and other alcohols.[8] Indeed, as shown in Fig. 1, the methyl xanthate (Ic) of 5α-pregnan-20α-ol exhibited a negative Cotton effect centered around the low-intensity, long wave-length xanthate absorption band at 354 mμ (ϵ 53), while the 20β-xanthate IIc showed an equally strong positive Cotton effect.

The xanthate derivative offer, therefore, an excellent means of differentiating between simple 20α- and 20β-ols, but they suffer from the practical disadvantage that the presence of other functional groups, such as the Δ^4-3-keto moiety, interferes in the method of preparation.

Attention has been called[5d,9] already to the fact that nitrites may represent useful "chromophoric" derivatives for alcohols, since Kuhn[10] had demon-

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[1] Paper LXIV, C. Djerassi, E. Lund, and A. A. Akhrem, *J. Am. Chem. Soc.*, *in press.*

[2] Supported in part by Grant No. CRTY-5061 from the National Cancer Institute of the National Institutes of Health, U.S. Public Health Service.

[3] Schering Corp., Bloomfield, N. J.

[4] P. M. Jones and W. Klyne, *J. Chem. Soc.*, 871 (1960).

[5] B. Sjöberg, A. Fredga, and C. Djerassi, *J. Am. Chem. Soc.*, **81**, 5002 (1959); (b) C. Djerassi and K. Undheim, *J. Am. Chem. Soc.*, **82**, 5755 (1960); (c) E. Bunnenberg and C. Djerassi, *J. Am. Chem. Soc.*, **82**, 5953 (1960); (d) C. Djerassi, E. Lund, E. Bunnenberg, and B. Sjöberg, *J. Am. Chem. Soc.*, **83**, 2307 (1961); (e) C. Djerassi, K. Undheim, R. C. Sheppard, W. G. Terry, and B. Sjöberg, *Acta Chem. Scand.*, **15**, 903 (1961); (f) C. Djerassi, E. Lund, E. Bunnenberg, and J. C. Sheehan, *J. Org. Chem.*, **26**, 4509 (1961).

[6] Crude calculations (ref. 4) had already indicated that this was the case and that the 273 mμ band is optically inactive. This latter conclusion has now been confirmed experimentally by our rotation measurements (Fig. 1) through the region of the first benzoate absorption maximum.

[7] See C. Djerassi, "Optical Rotatory Dispersion: Applications to Organic Chemistry," McGraw-Hill Book Co., New York, 1960, chap. 16.

[8] B. Sjöberg, L. Wolf, and C. Djerassi, unpublished observation; T. M. Lowry and H. Hudson, *Phil. Trans. Roy. Soc. London*, Ser. A, **232**, 117 (1933).

[9] Ref. 7, pp. 195-196.

[10] W. Kuhn and H. L. Lehmann, *Z. physik. Chem.*, **B18**, 32 (1932); W. Kuhn and H. Biller, *Z. physik. Chem.*, **B29**, 1 (1935).

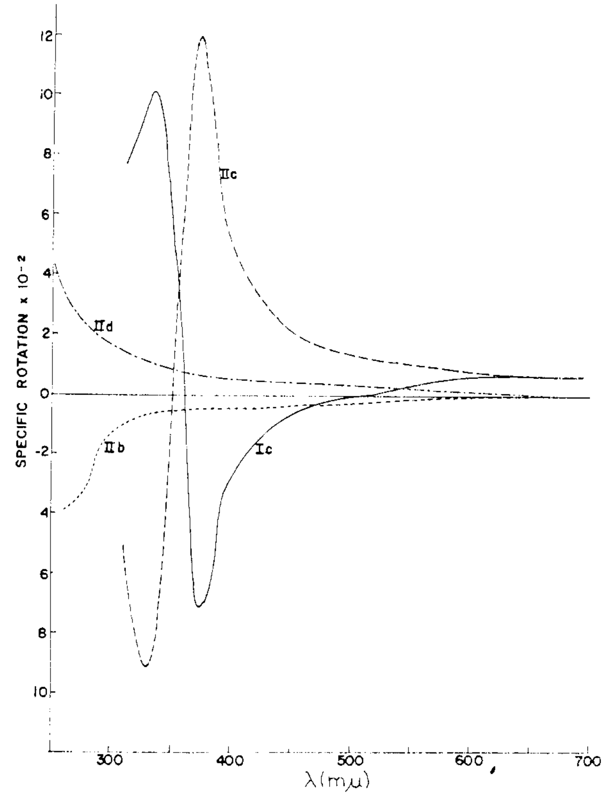

Fig. 1. Optical rotatory dispersion curves of 5α-pregnan-20α-ol methyl xanthate (Ic) (isoöctane), 5α-pregnan-20β-ol methyl xanthate (IIc) (isoöctane), 5α-pregnan-20β-ol benzoate (IIb) (methanol), and 5α-pregnan-20β-ol hexahydrobenzoate (IId) (methanol)

strated a multiple Cotton effect in some simple alkyl nitrites, which, however, were very labile. Recent photochemical studies with steroidal nitrites[11] showed that such higher molecular weight nitrites may be quite stable and in the present paper we record rotatory dispersion studies with a number of such crystalline nitrites. It may also be pertinent to mention at this time that photolysis of the xanthate Ic, under conditions[11] where 20-nitrites readily yield the angular aldoximes, proved to be very unsatisfactory. Most of the material was recovered unchanged and saponification of the crude irradiation product yielded only traces of acidic material (see Experimental) indicating that only minimal attack of the C-18 angular methyl group had occurred.

In Fig. 2 are collected the rotatory dispersion curves of a pair of C-20 epimeric nitrites, 5α-pregnane-3β,20α-diol 3-acetate 20-nitrite (III) and 5α-pregnane-3β,20β-diol 3-acetate 20-nitrite (IV). The former shows a series of positive Cotton effects, the fine structure corresponding to the various ultraviolet absorption maxima (see Fig. 5) of the —ON=O chromophore between 390–325 mμ,[12] while the dispersion curve of the 20β-nitrite IV is characterized by a series of negative Cotton effects; the same situation was also encountered with the Δ^4-analogs (see Experimental).

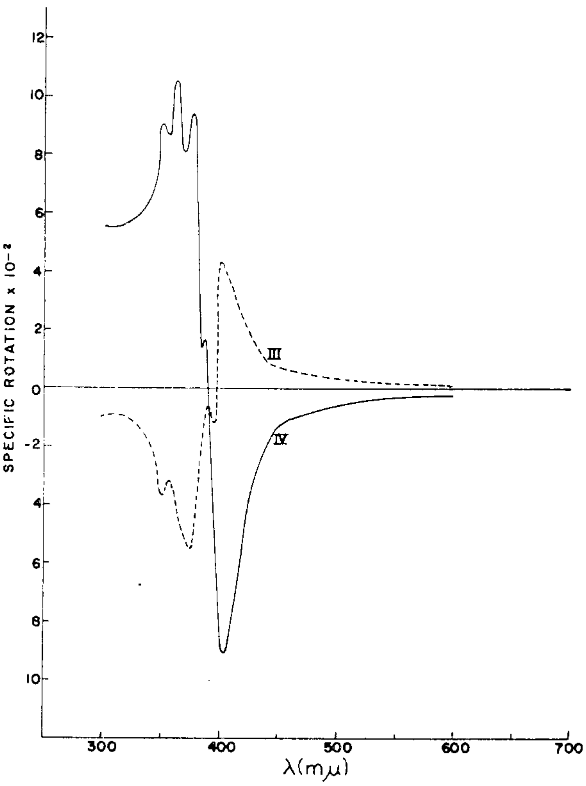

Fig. 2. Optical rotatory dispersion curves (dioxane) of 5α-pregnane-3β, 20α-(III) and 20β-(IV) diol 3-acetate 20-nitrite

The C-20 epimeric Δ^4-pregnen-20-ol-3-ones (Va, VIa)[13] possess nearly identical rotatory dispersion curves, that of the 20α-isomer Va being reproduced in Fig. 3. The multiple Cotton effect in the 350 mμ region is typical[14] of Δ^4-3-keto steroids and would not be expected to be affected to any extent by the type of C-20 isomerism observed in Va and VIa. It was now of interest to determine whether the characteristic rotatory dispersion features (Fig. 2) associated with the isolated 20α-(III) and 20β-(IV) nitrites would still be recognizable in the presence of the Δ^4-3-keto chromophore since its own multiple Cotton effect (Va, Fig. 3) over-

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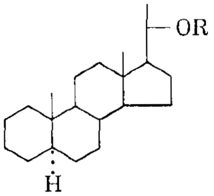
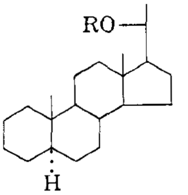
(11) D. H. R. Barton, J. M. Beaton, L. E. Geller, and M. M. Pechet, *J. Am. Chem. Soc.*, **82**, 2640 (1960); D. H. R. Barton and J. M. Beaton, *J. Am. Chem. Soc.*, **82**, 2641 (1960); A. L. Nussbaum, F. E. Carlon, E. P. Oliveto, E. Townley, P. Kabasakalian, and D. H. R. Barton, *J. Am. Chem. Soc.*, **82**, 2973 (1960); C. H. Robinson, O. Gnoj, A. Mitchell, R. Wayne, E. Townley, P. Kabasakalian, E. P. Oliveto, and D. H. R. Barton, *J. Am. Chem. Soc.*, **83**, 1771 (1961); A. L. Nussbaum, C. H. Robinson, E. P. Oliveto, and D. H. R. Barton, *J. Am. Chem. Soc.*, **83**, 2400 (1961). For complete review of this subject see A. L. Nussbaum and C. H. Robinson, *Tetrahedron, in press.*

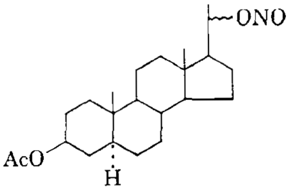
(12) *N*-Nitrosoamides (ref. 5d) show similar fine structure, which is displaced somewhat towards longer wave length.

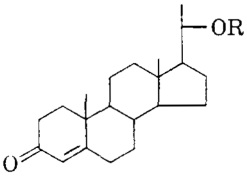
(13) For preparation see P. Wieland and K. Miescher, *Helv. Chim. Acta*, **32**, 1922 (1949).

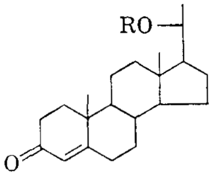
(14) E. W. Foltz, A. E. Lippman, and C. Djerassi, *J. Am. Chem. Soc.*, **77**, 4359 (1955); C. Djerassi, R. Riniker, and B. Riniker, *J. Am. Chem. Soc.*, **78**, 6377 (1956)

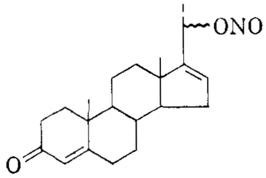

Ia. R = H
b. R = C_6H_5CO
c. R = $CH_3S\underset{\overset{\|}{S}}{C}$

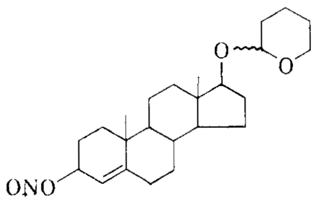

IIa. R = H
b. R = C_6H_5CO
c. R = $CH_3S\underset{\overset{\|}{S}}{C}$
d. R = $C_6H_{11}CO$

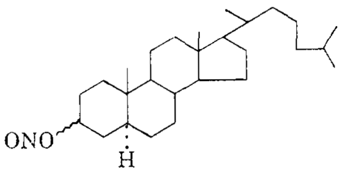

III. 20α
IV. 20β

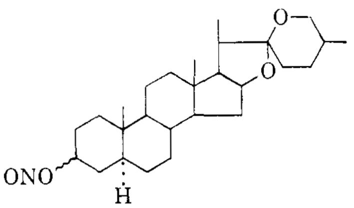

Va. R = H
b. R = NO


VIa. R = H
b. R = NO


VII. 20α
VIII. 20β


IX


X. 3α
XI. 3β


XII. 3α
XIII. 3β

laps with the lower wave length region of the nitrite's anomalous dispersion pattern. Both epimeric nitrites Vb and VIb can be prepared readily,[11] the Δ^4-3-keto grouping not interfering, in contrast to the situation existing with the corresponding xanthates, and their rotatory dispersion curves (Fig. 3) still permit the recognition of the sign of the first and most characteristic Cotton effect associated with the nitrite chromophore, that of the 20α-epimer Vb being positive and of VIb, negative.

The nitrites of the corresponding Δ^{16}-unsaturated analogs, 20α-(VIII) and 20β-(VIII)[15] hydroxy-$\Delta^{4,16}$-pregnadien-3-one, also show the expected multiple Cotton effect curves (Fig. 4), but it should be noted that in this instance the allylic 20α-nitrate VII exhibits an initial negative Cotton effect and its 20β-epimer VIII a positive one—in contrast to the situation existing (Fig. 3) with the ring-D saturated 20-nitrites (V, VI). We shall comment below on this point.

In order to study some ring-A epimeric nitrites, there were measured the rotatory dispersion curves (Fig. 5) of two such pairs, one of them in the cholestane (X *vs.* XI) and the other in the 5α-

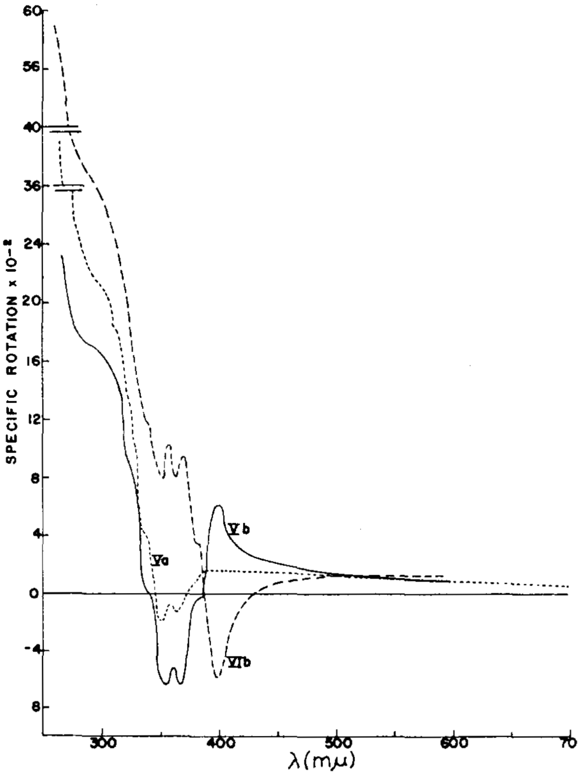


Fig. 3. Optical rotatory dispersion curves (dioxane) of Δ^4-pregnen-20α-ol-3-one (Va), Δ^4-pregnen-20α-ol-3-one nitrite (Vb), and Δ^4-pregnen-20β-ol-3-one nitrite (VIb)

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[15] The stereochemistry at C-20 of these allylic alcohols is known, since the 20α-ol was synthesized by microbiological oxidation of the corresponding $\Delta^{5,16}$-pregnadiene-3,20-diol (E. L. Shapiro, D. Gould, and E. B. Hershberg, *J. Am. Chem. Soc.*, **77**, 2912 (1955).

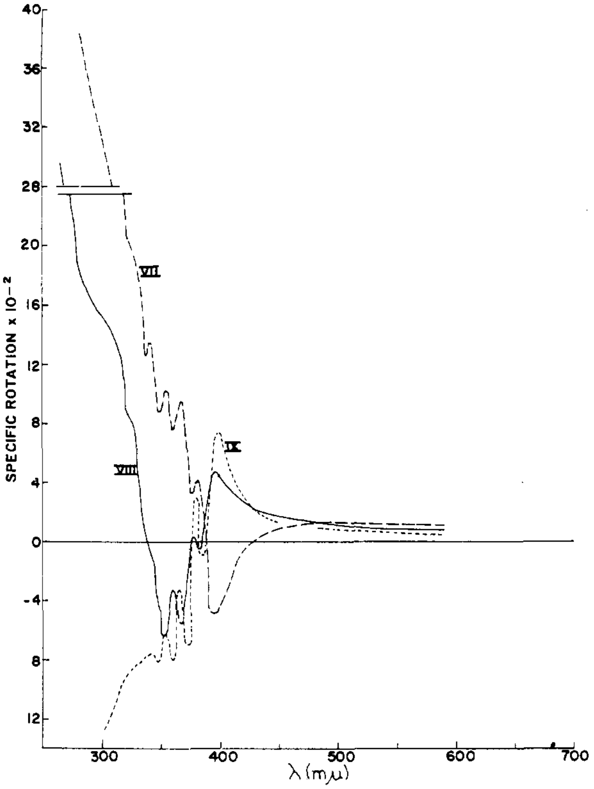

Fig. 4. Optical rotatory dispersion curves (dioxane) of $\Delta^{4,16}$-pregnadien-20α-ol-3-one nitrite (VII), $\Delta^{4,16}$-pregnadien-20β-ol-3-one nitrite (VIII), and Δ^4-androstene-3β,17β-diol 3-nitrite 17-tetrahydropyranyl ether (IX)

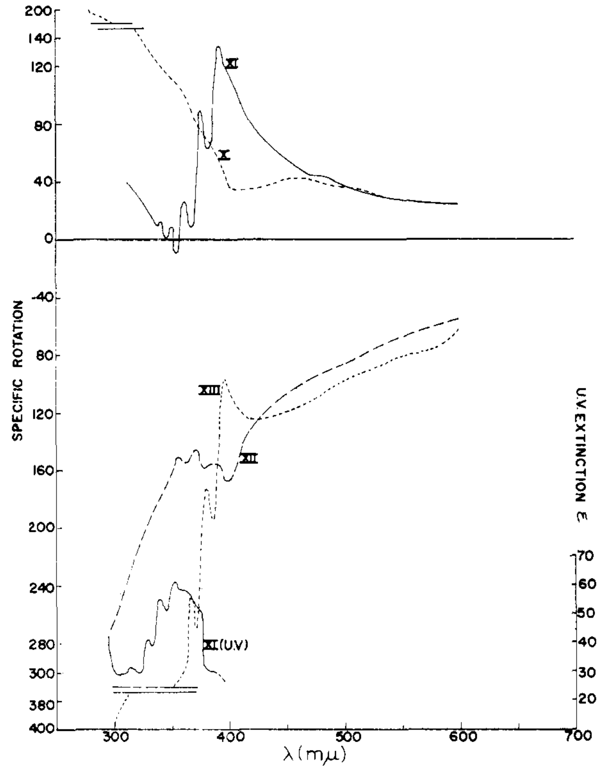

Fig. 5. Optical rotatory dispersion curves (dioxane) of cholestan-3α-ol nitrite (X), cholestan-3β-ol nitrite (XI), epitigogenin nitrite (XII), tigogenin nitrite (XIII), and ultraviolet absorption spectrum (dioxane) of cholestan-3β-ol nitrite (XI)

spirostan (XII *vs.* XIII) series. Cholestan-3β-ol nitrite (XI) exhibits a multiple positive Cotton effect—the fine structure occurring in the expected spectral region—of very low amplitude, when compared with the C-20 nitrites (Figs. 2–4) or when contrasted with an allylic nitrite such as Δ^4-androstene-3β,17β-diol 3-nitrite 17-tetrahydropyranyl ether (IX, Fig. 4). The corresponding epimer, cholestan-3α-ol nitrite (X) shows a series of barely discernible negative Cotton effects superimposed upon a positive background curve. In view of the weak amplitude of these Cotton effects, the background rotation of the steroid skeleton makes itself felt in a pronounced fashion, which is particularly noticeable in the dispersion curves (Fig. 5) of tigogenin (XIII) and epitigogenin (XII) nitrites. The steroidal spirostan system possesses a strong, negative plain dispersion curve[16] and the rather weak multiple Cotton effect of the ring-A saturated 3-nitrite function is superimposed on it. Nevertheless, it is easy to discern from Fig. 5 that the 3α-isomer, epitigogenin nitrate (XII), exhibits a negative multiple Cotton effect (as did the corresponding cholestane derivative X), while the 3β-epimer, tigogenin nitrite (XI), possesses a positive one superimposed upon the negative background curve of the 5α-spirostan nucleus.

In conclusion, it can be stated that nitrites should be considered seriously as suitable "chromophoric" derivatives for alcohols and that their multiple Cotton effects can be used for purposes of differentiation between epimeric pairs of alcohols. It should be noted, however, that each given stereochemical situation should be considered as *sui generis,* since the responsible nitroso chromophore is not fixed in space—as is the case with the cyclohexanones resulting in consequent generalizations incorporated in the octant rule[17]—but rather is subject to free rotation. The multiple Cotton effect, therefore, is typical of a given rotomer composition of the nitrite and this, in turn, will depend upon its immediate stereochemical environment. At the present time, it is only permissible to generalize within these relatively narrow limits and it is necessary to have available some suitable reference compound in which the nitrite occupies a known stereochemistry. The present paper, therefore, contains reference curves for nitrites of saturated 20-alcohols, Δ^{16}-unsaturated 20-alcohols, saturated C-3 alcohols of the 5α series and the corresponding allylic Δ^4-3-ols,[18] and these can now be employed in

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(16) C. Djerassi and R. Ehrlich, *J. Am. Chem. Soc.*, **78,** 440 (1956).

(17) W. Moffitt, R. B. Woodward, A. Moscowitz, W. Klyne, and C. Djerassi, *J. Am. Chem. Soc.*, **83,** 4013 (1961).

(18) We had available only one member of such a pair, the Δ^4-3β-nitrite IX. However, since it exhibited a multiple positive Cotton effect (Fig. 4), the 3α-epimer can be predicted to possess a negative one.

stereochemical studies of unknown steroidal alcohols (or their bicyclic analogs) where the relevant hydroxyl group is located in a similar environment. A relevant example would be the direct applicability of the present data to the determination of the C-20 stereochemistry in some of the steroidal alkaloids (*e.g.* funtumidine).[19]

EXPERIMENTAL[20]

5α-Pregnan-20α-ol methyl xanthate (Ic). To 195 mg. of 5α-pregnan-20α-ol (Ia)[21] in 15 cc. of dry benzene was added 120 mg. of a 50% emulsion of sodium hydride in mineral oil, the solution was heated under reflux overnight, 0.3 cc. of carbon disulfide was added and heating continued for 24 hr. Finally, 2 cc. of methyl iodide was added and the mixture heated under reflux for a further 24 hr., all operations being conducted with the complete exclusion of moisture. The benzene solution was washed with water, dried, evaporated, and the residue was filtered in hexane solution through 2 g. of grade III neutral alumina. Recrystallization from acetone gave 112 mg. of large prisms, m.p. 156–157°, $\lambda_{\max}^{\text{isooct}}$ 276 and 354 mμ, ε 10,800 and 53; R. D. (Fig. 1) in isoöctane (*c*, 0.094): $[\alpha]_{589}$ +44°, $[\alpha]_{372.5}$ −725°, $[\alpha]_{332.5}$ +1000°, $[\alpha]_{310}$ +751.

Anal. Calcd. for $C_{23}H_{38}OS_2$: C, 70.04; H, 9.64; O, 4.06; S, 16.27. Found: C, 70.41; H, 9.41; O, 4.59; S, 15.64.

A sample of this xanthate (257 mg.) in 400 cc. of dry, thiophene-free benzene was irradiated for 9 hr. in a Vycor tube (water-cooled) in a continuous current of nitrogen using a Hanovia mercury arc lamp with reflector situated two inches away from the reaction vessel. Over 70% of unchanged xanthate was recovered, the remainder representing a mixture of at least six components as determined by thin-layer chromatography. In 95% ethanol solution, more extensive changes seem to occur (thin-layer chromatography) and in order to see whether any of the expected photolysis product (angular thioacetic ester at position 13) was formed, the total crude product was hydrolyzed with 5% ethanolic sodium hydroxide, whereupon only 5% of an acidic oil was isolated.

5α-Pregnan-20β-ol methyl xanthate (IIc). An identical sequence was employed to convert 5α-pregnan-20β-ol (IIa) into its xanthate IIc, m.p. 123–125°; R. D. (Fig. 1) in isooctane (*c*, 0.10): $[\alpha]_{589}$ +78°, $[\alpha]_{372.5}$ +1188°, $[\alpha]_{330}$ −921°, $[\alpha]_{310}$ −508°.

Anal. Found: C, 69.39; H, 9.75; O, 4.53; S, 15.70.

5α-Pregnan-20β-ol hexahydrobenzoate (IId).[22] 5α-Pregnan-20β-ol benzoate (IIb)[4] (79 mg.) was hydrogenated in 60 cc. of glacial acetic acid at room temperature and atmospheric pressure using 100 mg. of pre-reduced platinum oxide catalyst. Hydrogen uptake was complete within 1 hr., whereupon the catalyst was filtered, the solvent evaporated, and the residue crystallized from methanol to provide colorless needles of IId, m.p. 97–99°; R. D. (Fig. 1) in methanol (*c*, 0.10): $[\alpha]_{650}$ +10°, $[\alpha]_{589}$ +16°, $[\alpha]_{250}$ +456°.

Anal. Calcd. for $C_{28}H_{46}O_2$: C, 81.10; H, 11.19. Found: C, 81.16; H, 11.01.

5α-Pregnane-3β,20α-diol 3-acetate 20-nitrite (III). R. D. (Fig. 2) in dioxane (*c*, 0.026): $[\alpha]_{589}$ +10°, $[\alpha]_{405}$ +432°, $[\alpha]_{396}$ −123°, $[\alpha]_{392}$ −62°, $[\alpha]_{364}$ −555°, $[\alpha]_{358}$ −308°, $[\alpha]_{350}$ −370°, $[\alpha]_{300}$ −100°.

5α-Pregnane-3β,20β-diol 3-acetate 20-nitrite (IV). R. D., (Fig. 2) in dioxane (*c*, 0.13): $[\alpha]_{589}$ −30°, $[\alpha]_{405}$ −910° $[\alpha]_{389}$ +155°, $[\alpha]_{388}$ +135°, $[\alpha]_{379}$ +935°, $[\alpha]_{370}$ +800°, $[\alpha]_{364}$ +1045°, $[\alpha]_{358}$ +861, $[\alpha]_{350}$ +897°, $[\alpha]_{320}$ +565°, $[\alpha]_{295}$ +652°.

Δ⁵-Pregnene-3β,20α-diol 3-acetate 20-nitrite. R. D. in dioxane (*c*, 0.10): $[\alpha]_{589}$ −39°, $[\alpha]_{405}$ +370°, $[\alpha]_{390}$ −300°, $[\alpha]_{386}$ −252°, $[\alpha]_{376}$ −790°, $[\alpha]_{370}$ −482°, $[\alpha]_{364}$ −810°, $[\alpha]_{357}$ −570°, $[\alpha]_{352}$ −645°, $[\alpha]_{345}$ −515°, $[\alpha]_{342}$ −527, $[\alpha]_{337}$ −475°, $[\alpha]_{320}$ −500°.

Δ⁵-Pregnene-3β,20β-diol 3-acetate 20-nitrite. R. D. in dioxane (*c*, 0.05): $[\alpha]_{589}$ −104°, $[\alpha]_{405}$ −1080°, $[\alpha]_{390}$ −48°, $[\alpha]_{388}$ −72°, $[\alpha]_{377}$ +712°, $[\alpha]_{372}$ +568°, $[\alpha]_{365}$ +800°, $[\alpha]_{358}$ +600°, $[\alpha]_{355}$ +625°, $[\alpha]_{300}$ +192°.

Δ⁴-Pregnen-20α-ol-3-one (Va). R. D. (Fig. 3) in dioxane (*c*, 0.11): $[\alpha]_{589}$ +81°, $[\alpha]_{400}$ +163°, $[\alpha]_{362.5}$ −117°, $[\alpha]_{358}$ −90°, $[\alpha]_{350}$ −185°, $[\alpha]_{340}$ +400° (infl.), $[\alpha]_{305}$ +2045° (infl.), $[\alpha]_{265}$ +3885°.

Δ⁴-Pregnen-20β-ol-3-one (VIa). R. D. in dioxane (*c*, 0.13) +73°, $[\alpha]_{400}$ +142°, $[\alpha]_{363}$ −214°, $[\alpha]_{357}$ −132°, $[\alpha]_{350}$ −237°, $[\alpha]_{340}$ +300° (infl.), $[\alpha]_{323}$ +1200° (infl.), $[\alpha]_{305}$ +1960° (infl.), $[\alpha]_{270}$ +3140°.

Δ⁴-Pregnen-20α-ol-3-one nitrite (Vb). R. D. (Fig. 3) in dioxane (*c*, 0.116): $[\alpha]_{589}$ +107°, $[\alpha]_{399}$ +607°, $[\alpha]_{383}$ −35°, $[\alpha]_{380}$ −26°, $[\alpha]_{370}$ −665°, $[\alpha]_{363}$ −501°, $[\alpha]_{356}$ −665°, $[\alpha]_{338}$ +55° (infl.), $[\alpha]_{290}$ +1710° (shoulder), $[\alpha]_{265}$ +2330°.

Δ⁴-Pregnen-20β-ol-3-one nitrite (VIb). R. D. (Fig. 3) in dioxane (*c*, 0.13): $[\alpha]_{589}$ +126.5°, $[\alpha]_{398}$ −580°, $[\alpha]_{384}$ +350° (infl.), $[\alpha]_{370}$ +930°, $[\alpha]_{364}$ +803°, $[\alpha]_{357}$ +1025°, $[\alpha]_{352}$ +797°, $[\alpha]_{338}$ +1185° (infl.), $[\alpha]_{323}$ +1905° (infl.), $[\alpha]_{260}$ +5900°.

Δ⁴,¹⁶-Pregnadien-20α-ol-3-one nitrite (VII). R. D. (Fig. 4) in dioxane (*c*, 0.11): $[\alpha]_{589}$ +107°, $[\alpha]_{395}$ −533°, $[\alpha]_{381}$ +440°, $[\alpha]_{375}$ +308°, $[\alpha]_{367}$ +972°, $[\alpha]_{360}$ +753°, $[\alpha]_{354}$, +1040°, $[\alpha]_{348}$ +870°, $[\alpha]_{341}$ +1370°, $[\alpha]_{337}$ +1280°, $[\alpha]_{325}$ +2000°, $[\alpha]_{280}$ +3840°.

Δ⁴,¹⁶-Pregnadien-20β-ol-3-one nitrite (VIII). R. D. (Fig. 4) in dioxane (*c*, 0.12): $[\alpha]_{589}$ +80°, $[\alpha]_{395}$ +482°, $[\alpha]_{382}$ −80°, $[\alpha]_{371}$ +39°, $[\alpha]_{366}$ −576°, $[\alpha]_{360}$ −306°, $[\alpha]_{352}$ −631°, $[\alpha]_{340}$ −51° (infl.), $[\alpha]_{325}$ +797° (infl.), $[\alpha]_{300}$ +1510°, $[\alpha]_{265}$ +2965°.

Δ⁴-Androstene-3β,17β-diol 3-nitrite 17-tetrahydropyranyl ether (IX). R. D. (Fig. 4) in dioxane (*c*, 0.11): $[\alpha]_{589}$ +50°, $[\alpha]_{398}$ +745°, $[\alpha]_{387}$ −106°, $[\alpha]_{380}$ +284°, $[\alpha]_{373}$ −710°, $[\alpha]_{366}$ −320°, $[\alpha]_{360}$ −815°, $[\alpha]_{354}$ −640°, $[\alpha]_{347}$ −810°, $[\alpha]_{342}$ −745°, $[\alpha]_{292}$ −1290°.

Cholestan-3α-ol nitrite (X). R. D. (Fig. 5) in dioxane (*c*, 0.10): $[\alpha]_{589}$ +24°, $[\alpha]_{400}$ +36°, $[\alpha]_{388}$ +62° (infl.), $[\alpha]_{377}$ +72 (infl.), $[\alpha]_{374}$ +89°, $[\alpha]_{280}$ +200°.

Cholestan-3β-ol nitrite (XI). R. D. (Fig. 5) in dioxane (*c*, 0.10): $[\alpha]_{589}$ +24°, $[\alpha]_{392}$ +134°, $[\alpha]_{383}$ +62° $[\alpha]_{377}$ +90°, $[\alpha]_{368}$ +7°, $[\alpha]_{362}$ +28°, $[\alpha]_{355}$ −11°, $[\alpha]_{350}$ +10°, $[\alpha]_{345}$ 0°, $[\alpha]_{340}$ +14°, $[\alpha]_{337}$ +10°, $[\alpha]_{310}$ +41°.

Epitigogenin nitrite (XII). R. D. (Fig. 5) in dioxane (*c*, 0.12): $[\alpha]_{589}$ −57°, $[\alpha]_{397}$ −167°, $[\alpha]_{385}$ −154°, $[\alpha]_{377}$ −157°, $[\alpha]_{370}$ −144°, $[\alpha]_{360}$ −154°, $[\alpha]_{355}$ −150°, $[\alpha]_{297}$ −270°.

Tigogenin nitrite (XIII). R. D. (Fig. 5) in dioxane (*c*, 0.11): $[\alpha]_{589}$ −70°, $[\alpha]_{420}$ −123°, $[\alpha]_{396}$ −96°, $[\alpha]_{386}$ −194°, $[\alpha]_{380}$ −172°, $[\alpha]_{370}$ −269°, $[\alpha]_{367}$ −246°, $[\alpha]_{360}$ −300° (infl.), $[\alpha]_{300}$ −398°.

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(19) R. Goutarel, *Tetrahedron*, **14**, 126 (1961).

(20) All of the rotatory dispersion curves were measured by Mrs. Ruth Records with an automatically recording spectropolarimeter. The synthesis of these nitrites, which have not already been described (ref. 11), will be reported elsewhere in connection with photochemical experiments.

(21) R. E. Marker, *J. Am. Chem. Soc.*, **61**, 852 (1939).

(22) This experiment was performed by Miss Ann-Marie Weidler.