

*Anal.* Calcd. for  $C_{29}H_{22}S$ ; C, 86.52; H, 5.51; S, 7.97. Found: C, 86.34, 86.83; H, 6.03, 5.86; S, 8.25.

Oxidation of IV with hydrogen peroxide in acetic acid converted this to its sulfone (VI), colorless crystals from ethanol, m.p. 192–193°, showing very strong sulfone bands at 7.70 and 8.82  $\mu$ . *Anal.* Calcd. for  $C_{29}H_{22}O_2S$ : C, 80.15; H, 5.10. Found: C, 80.04; H, 5.18. These transformations may be summarized by the scheme shown. Further work involving changing all four phenyl groups and also replacing sulfur by phosphorus is under way.

DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF PENNSYLVANIA  
PHILADELPHIA 4, PENNSYLVANIA

GEORGE SULD  
CHARLES C. PRICE

RECEIVED DECEMBER 30, 1960

### THE PHOTOLYSIS OF ORGANIC NITRITES. II. SYNTHESIS OF STEROIDAL HYDROXAMIC ACIDS

Sir:

The recent syntheses of aldosterone<sup>1</sup> and of 18-nitroprogesterone,<sup>2</sup> via photochemical rearrangement of nitrite esters at positions C-11 and C-20 of the steroid nucleus, have demonstrated the power of this synthetic method.

We wish to report here the preparation of a new class of nitrogen containing steroids, formed by photolytic rearrangement of C-17 $\beta$ -nitrite esters.

Reaction of 5 $\alpha$ -androstane-3 $\alpha$ ,17 $\beta$ -diol 3 $\alpha$ -acetate<sup>3</sup> with nitrosyl chloride in pyridine gave the 17 $\beta$ -nitrite (I; m.p. 177–180°;  $[\alpha]_D -33^\circ$  (all rotations in dioxane unless otherwise stated));  $\lambda_{max}^{Nujol}$  5.76, 6.10, 6.25, 7.94  $\mu$ ) which was photolyzed in benzene<sup>5</sup> to give the hydroxamic acid (II, R = OH, R<sup>1</sup> = CH<sub>3</sub>CO; m.p. 229–233°;  $[\alpha]_D -2^\circ$ ;  $\lambda_{max}^{Nujol}$  3.28, 5.77, 6.12  $\mu$ ; instant color with ferric chloride), isolated by direct crystallization. Acetylation of II with acetic anhydride gave the N-acetoxy derivative (II, R = CH<sub>3</sub>CO<sub>2</sub>; R<sup>1</sup> = CH<sub>3</sub>CO; m.p. 173–176°;  $[\alpha]_D +16^\circ$ ;  $\lambda_{max}^{Nujol}$  5.58, 5.75, 5.9, 8.05, 8.12  $\mu$ ). Our formulation of the photolysis product (II, R = OH) as 17a-aza-D-homo-5 $\alpha$ -androstane-3 $\alpha$ ,17a-diol-17-one 3 $\alpha$ -acetate is substantiated by the reduction of (II, R = OH) to 17a-aza-D-homo-5 $\alpha$ -androstane-3 $\alpha$ -ol-17-one 3 $\alpha$ -acetate (II, R = H; R<sup>1</sup> = CH<sub>3</sub>CO; m.p. 280–284°;  $[\alpha]_D +18^\circ$ ;  $\lambda_{max}^{Nujol}$  3.12, 3.24, 5.76, 5.96, 6.22, 7.95  $\mu$ ) with zinc and acetic acid,<sup>6</sup> and to 17a-aza-D-homo-5 $\alpha$ -androstane-3 $\alpha$ -ol-17-one (II, R = R<sup>1</sup> = H; m.p. 341–346°;  $[\alpha]_D +25^\circ$  (CH<sub>3</sub>OH);  $\lambda_{max}^{Nujol}$  3.05, 3.22, 6.05  $\mu$ ) by reduction with hydrazine<sup>7</sup> in ethylene glycol. The lactam (II,

(1) 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, *ibid.*, **82**, 2641 (1960).

(2) A. L. Nussbaum, F. E. Carlon, E. P. Oliveto, E. Towmley, P. Kabasakalian and D. H. R. Barton, *ibid.*, **82**, 2973 (1960).

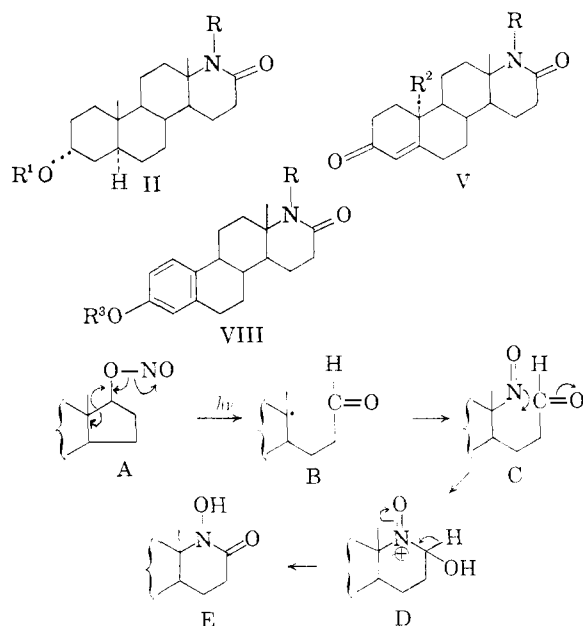
(3) K. Miescher, H. Kagi, C. Scholz, A. Wettstein and E. Tschopp, *Biochem. Z.*, **294**, 39 (1937).

(4) Satisfactory analyses were obtained for all the compounds described in this communication.

(5) We thank Mr. R. Armswood for his assistance with the photolyses.

(6) Cf. J. D. Dutcher and O. Wintersteiner, *J. Biol. Chem.*, **155**, 359 (1944); see also J. A. Moore and J. Binkert, *J. Am. Chem. Soc.*, **81**, 6029 (1959).

(7) Cf. D. W. C. Ramsay and F. S. Spring, *J. Chem. Soc.*, 3409 (1950).



R = H, R<sup>1</sup> = CH<sub>3</sub>CO) was prepared independently from 17-oximino-5 $\alpha$ -androstane-3 $\alpha$ -ol-3-acetate<sup>8</sup> by Beckmann rearrangement, using thionyl chloride in dioxane,<sup>9</sup> and authentic II (R = R<sup>1</sup> = H) then was secured by hydrolysis of the Beckmann product with methanolic potassium hydroxide. Similarly, testosterone 17 $\beta$ -nitrite (III; m.p. ca. 100° dec;  $[\alpha]_D +69^\circ$ ;  $\lambda_{max}^{MeOH}$  239  $\mu$  (17,700);  $\lambda_{max}^{Nujol}$  5.98, 6.05, 6.20  $\mu$ ) and 19-nortestosterone 17 $\beta$ -nitrite (IV; m.p. 83–87° dec;  $[\alpha]_D +9^\circ$ ;  $\lambda_{max}^{MeOH}$  238  $\mu$  (17,800);  $\lambda_{max}^{Nujol}$  6.0, 6.14  $\mu$ ) furnished, respectively, when photolyzed in benzene, 17a-aza-D-homo-4-androstene-17a-ol-3,17-dione (V, R = OH, R<sup>2</sup> = CH<sub>3</sub>; m.p. 220–223°;  $[\alpha]_D +67^\circ$ ;  $\lambda_{max}^{MeOH}$  238  $\mu$  (17,900);  $\lambda_{max}^{Nujol}$  3.05, 5.98, 6.20  $\mu$ ) and the 19-nor analog (V, R = OH, R<sup>2</sup> = H; m.p. 227–235°;  $[\alpha]_D +21^\circ$ ;  $\lambda_{max}^{MeOH}$  237  $\mu$  (17,900);  $\lambda_{max}^{Nujol}$  3.25, 6.04, 6.14  $\mu$ ). Acetylation gave the N-acetoxy derivatives (V, R = CH<sub>3</sub>CO<sub>2</sub>, R<sup>2</sup> = CH<sub>3</sub>; m.p. 172–174°  $[\alpha]_D +80^\circ$ ;  $\lambda_{max}^{MeOH}$  239  $\mu$  (17,000);  $\lambda_{max}^{Nujol}$  5.58, 5.95, 6.18, 8.45  $\mu$ ) and (V, R = CH<sub>3</sub>CO<sub>2</sub>, R<sup>2</sup> = H; m.p. 185–188°;  $[\alpha]_D +39^\circ$ ;  $\lambda_{max}^{MeOH}$  237  $\mu$  (18,200);  $\lambda_{max}^{Nujol}$  5.60, 5.90, 6.04, 6.18, 8.45  $\mu$ ).

Reduction of V (R = OH, R<sup>2</sup> = CH<sub>3</sub>) with zinc-acetic acid gave the known<sup>9,10,11</sup> lactam (V, R = H, R<sup>2</sup> = CH<sub>3</sub>).

Photolysis in benzene solution of estradiol 3-benzoate 17 $\beta$ -nitrite (VI; m.p. 165–167° dec;  $[\alpha]_D +8^\circ$ ;  $\lambda_{max}^{MeOH}$  229  $\mu$  (21,700);  $\lambda_{max}^{Nujol}$  5.74, 6.1, 6.24, 6.30, 7.90  $\mu$ ) and estradiol 3-methyl ether 17 $\beta$ -nitrite (VII; m.p. 143–145° dec;  $[\alpha]_D -11^\circ$ ;  $\lambda_{max}^{MeOH}$  276  $\mu$  (2,000), 285  $\mu$  (1,800);  $\lambda_{max}^{Nujol}$  6.12, 6.18, 6.22, 8.0, 8.1  $\mu$ ) gave the hydroxamic acids (VIII, R = OH, R<sup>3</sup> = C<sub>6</sub>H<sub>5</sub>CO; m.p. 227–232° dec,  $[\alpha]_D +62^\circ$ ;  $\lambda_{max}^{MeOH}$  229  $\mu$

(8) A. Butenandt and K. Tscherning, *Z. physiol. Chem.*, **229**, 185 (1934).

(9) Cf. B. M. Regan and F. N. Hayes, *J. Am. Chem. Soc.*, **78**, 639 (1956).

(10) B. Kaufmann, *ibid.*, **73**, 1779 (1951).

(11) We are indebted to Dr. B. M. Regan for his kindness in supplying an authentic specimen of the lactam V (R = H, R<sup>2</sup> = CH<sub>3</sub>) for comparison purposes.

(21,300);  $\lambda_{\max}^{\text{Nujol}}$  3.25, 5.78, 6.12, 6.30, 6.70, 7.96, 8.24 $\mu$ ) and (VIII, R = OH, R<sup>3</sup> = CH<sub>3</sub>; m.p. 186–191°;  $[\alpha]_D^{+80}$ ;  $\lambda_{\max}^{\text{MeOH}}$  276 m $\mu$  (2,000), 285 m $\mu$  (1,800);  $\lambda_{\max}^{\text{Nujol}}$  3.25, 6.10, 6.21, 6.35, 6.67, 7.99  $\mu$ ), respectively. Reduction of VIII (R = OH, R<sup>3</sup> = C<sub>6</sub>H<sub>5</sub>CO) and VIII (R = OH, R<sup>3</sup> = CH<sub>3</sub>) to the known<sup>9,10</sup> lactams VIII (R = H, R<sup>3</sup> = C<sub>6</sub>H<sub>5</sub>CO) and VIII (R = H, R<sup>3</sup> = CH<sub>3</sub>) was accomplished using zinc-acetic acid and hydrazine, respectively.

The photolysis mixtures from VI and VII also gave, in each case, another hydroxamic acid. These products (IX; m.p. 205–210° dec.,  $[\alpha]_D^{-3}$ ;  $\lambda_{\max}^{\text{MeOH}}$  230 m $\mu$  (20,000);  $\lambda_{\max}^{\text{Nujol}}$  3.28, 5.75, 6.12, 6.24, 6.30, 6.68, 7.92  $\mu$ ) and (X; m.p. 205–207°;  $[\alpha]_D^0$ ;  $\lambda_{\max}^{\text{MeOH}}$  276 m $\mu$  (2,000), 285 m $\mu$  (1,800);  $\lambda_{\max}^{\text{Nujol}}$  3.28, 6.12, 6.22, 6.34, 6.68, 8.0  $\mu$ ) correspond, respectively, to isomers of (VIII, R = OH, R<sup>3</sup> = C<sub>6</sub>H<sub>5</sub>CO) and (VIII, R = OH, R<sup>3</sup> = CH<sub>3</sub>).

This difference most probably is due to isomerism at C-13, rather than to the presence of the alternative 17-aza-17a-keto system.<sup>12</sup>

A plausible mechanism (partial structures A-E) can be invoked to account for these photolytic rearrangements. Initial fission of the O-NO bond can lead to the intermediate C-13 nitroso intermediate(s) (C). The formation of the hydroxamic acid (E) from (C) may then follow the path C → D → E (or equivalent process).

(12) The known 18-isoestrone 3-methyl ether (A. Butenandt, A. Wolff and P. Karlson, *Ber.*, **74**, 1308 (1941)) has been converted, via the 17-oxime, to a 13-isolactam identical with the lactam derived from X. This evidence together with other corroborating data will be discussed in a later, detailed publication.

C. H. ROBINSON  
O. GNOJ  
A. MITCHELL  
R. WAYNE  
E. TOWNLEY  
P. KABASAKALIAN  
E. P. OLIVETO

SCHERING CORPORATION  
BLOOMFIELD, NEW JERSEY

RESEARCH INSTITUTE FOR  
MEDICINE AND CHEMISTRY  
49 AMHERST STREET  
CAMBRIDGE, MASSACHUSETTS

D. H. R. BARTON

RECEIVED FEBRUARY 18, 1961

#### THE HYDROGEN VIBRATIONS IN COBALT CARBONYL HYDRIDE. BONDING CONSIDERATIONS.<sup>1</sup>

Sir:

The determination of the frequencies and the character of the hydrogen vibrations in HCo(CO)<sub>4</sub> would be important in establishing the nature of the bonding in this interesting molecule. Previous work has shown that the infrared bands at 703<sup>2-4</sup> and 331<sup>4</sup> cm.<sup>-1</sup> arise from vibrations which involve substantial motion of the hydrogen atom. Since the C and/or O atoms also participate substantially in these modes in the hydride and/or deuteride,<sup>4</sup> a salient question is whether the 703 cm.<sup>-1</sup> vibration involves Co-H bending motion<sup>4</sup>

(1) This work was supported by the Atomic Energy Commission under contract AT(11-1)-164.

(2) W. F. Edgell, C. Magee and G. Gallup, *J. Am. Chem. Soc.*, **78**, 4185 (1956).

(3) F. A. Cotton and G. Wilkinson, *Chem. and Ind.*, 1305 (1956).

(4) W. F. Edgell, G. Asato, W. Wilson and C. Angell, *J. Am. Chem. Soc.*, **81**, 2022 (1959).

or Co-H stretching motion.<sup>3,5</sup> If the former were true, one would expect at least one hydrogen vibration at a frequency much greater than 703 cm.<sup>-1</sup>. This question has been investigated previously by examining the infrared spectrum of films of HCo(CO)<sub>4</sub> and DCo(CO)<sub>4</sub> on a silver chloride window at -196°.<sup>3</sup> It was reported that no bands were observed in the region of ~1400 cm.<sup>-1</sup> in the deuteride.<sup>3</sup> Now, if there were no fundamental in the deuteride at ~1400 cm.<sup>-1</sup>, there could be no "pure" Co-H stretching vibration in the hydride near ~1950 cm.<sup>-1</sup>, where bands have been observed.<sup>2,8</sup>

This question now has been reexamined by studying the infrared spectrum of gaseous HCo(CO)<sub>4</sub> and DCo(CO)<sub>4</sub> at pressures up to 20 mm. in cells with effective path lengths as great as 5 meters. Special attention was paid to the region between 1000 and 2000 cm.<sup>-1</sup>. Among the bands observed in this region for HCo(CO)<sub>4</sub> is one with easily resolvable PQR structure at 1934 cm.<sup>-1</sup> (previously reported<sup>2,8</sup>) and a weaker, somewhat broad, band at 1400 cm.<sup>-1</sup>. The samples of DCo(CO)<sub>4</sub> had 80–90% of the H atoms replaced by D atoms. The hydride band at 1934 cm.<sup>-1</sup> almost completely disappears in our deuteride spectra and the band at 1400 cm.<sup>-1</sup> is replaced by a sharper band at 1396 cm.<sup>-1</sup>. In addition a number of new bands were found in the deuteride spectra including ones at 1193, 1691, 1787 and 1850 cm.<sup>-1</sup>.

The following interpretation is placed on these results. The hydride band at 1400 cm.<sup>-1</sup> is the overtone of 703 cm.<sup>-1</sup>. The latter frequency shifts to 600 cm.<sup>-1</sup> in the deuteride where its overtone now gives rise to the band found at 1193 cm.<sup>-1</sup>. The hydride band at 1934 cm.<sup>-1</sup> is reasonably understood as the Co-H stretching frequency! The Co-D stretching vibration is the band at 1396 cm.<sup>-1</sup>. The deuteride bands at 1691, 1787 and 1850 cm.<sup>-1</sup> arise from combinations of the 1396 cm.<sup>-1</sup> fundamental with the previously observed<sup>4</sup> deuteride fundamentals at 296, 393 and 458 cm.<sup>-1</sup>.

These results form a most convincing argument for the presence of a Co-H bond in HCo(CO)<sub>4</sub>. They, together with the earlier spectra,<sup>2-4</sup> are consistent with the C<sub>3v</sub> configuration previously proposed.<sup>2</sup> They show that the C and/or O atoms do not participate significantly in the hydrogen stretching motion and hence the bonding of the hydrogen atom is like that recently found for HMn(CO)<sub>5</sub>.<sup>4,5</sup> It is now possible to give a more advanced discussion of the molecular vibrations and the frequency assignment in HCo(CO)<sub>4</sub> and DCo(CO)<sub>4</sub>. These, as well as the experimental details of this and recent work<sup>4</sup> on these molecules, will be given in a forthcoming paper which will discuss their relation to the various models for the bonding of the hydrogen atom.

The force constant for the Co-H bond is found to be ca. 2.22 md./A. Thus this bond is stronger than the Mn-H bond in HMn(CO)<sub>5</sub><sup>4</sup> despite contrary expectations<sup>5</sup> based on thermal and chemical stabilities.

The fact that the hydrogen vibrations are similar in HCo(CO)<sub>4</sub> and HMn(CO)<sub>5</sub> strengthens the be-

(5) F. A. Cotton, J. L. Down and G. Wilkinson, *J. Chem. Soc.*, 833 (1959).