T. E. Gier

COMMUNIC

compounds and, in fact, m./e. peaks assignable to both HC^+ and HP^+ were observed.

The infrared spectrum of solid HCP monomer at -196° is wholly consistent with the HCP structure. The fundamentals are given below and compared with those found for solid HCN at the same temperature. There is also a band in

	ν (cm. ⁻¹)	Assignment	K (dynes/cm. 10 ⁵)
HCP	3180	C–H str.	5.4
HCN	3120	C–H str.	5.4
HCP	1265	C-P str.	8.7
HCN	2120	C-N str.	16.2
HCP	671	C-H bend	
HCN	8306	C-H bend	

the HCP spectrum at 1354 cm.⁻¹ which appears to be the first overtone of the C–H bending vibration and a weak broad band at 812 cm.^{-1} that could be a combination band of the C–H bending with a lattice vibration. There is no absorption in the 2350–2440 cm.⁻¹ region characteristic of P–H stretch.

Further support for the HC \equiv P structure was obtained from the reaction of the monomer with excess anhydrous HCl at -110° Under these conditions, CH₃PCl₂ was the sole product.

(6) The value for HCN(g) is 712 cm.⁻¹. The marked shift to higher wave numbers suggests strong hydrogen bonding in solid HCN.

Contribution No. 661

CENTRAL RESEARCH DEPARTMENT

EXPERIMENTAL STATION E. I. DU PONT DE NEMOURS AND COMPANY

WILMINGTON, DELAWARE

Received January 19, 1961

THIABENZENE. I. 1,2,4,6-TETRAPHENYLTHIABENZENE, A NEW CONJUGATED RING SYSTEM

Sir:

2,4,6-Triphenylthiopyrylium perchlorate¹ (I, 2.5 g.) suspended in 100 ml. of ether under an atmosphere of nitrogen was treated with 3.5 equivalents of phenyllithium in ether. Solid I disappeared rapidly giving a deep red-violet solution. After 5 min., aqueous ammonium chloride was added, the ethereal layer then was washed with water and dried over potassium carbonate. After adding 50-75 ml. of purified petroleum ether (b.p. $30-60^{\circ}$) and chilling in Dry Ice-acetone, the violet solution was decanted from ca. 0.2 g. of lightcolored solid and evaporated to dryness in vacuo. The residual violet resin was redissolved in 30 ml. of ether and poured into 250 ml. of petroleum ether cooled in a Dry Ice-acetone bath. The finely divided amorphous violet thiabenzene (II), m.p. ca. 45-48°, weighed 0.7 g.

Anal. Calcd. for $C_{29}H_{22}S$: C. 86.51; H, 5.52; S, 7.96; mol. wt., 402. Calcd. for $C_{29}H_{22}S \cdot 1/2$ Et₂O: C, 84.70; H, 6.19; S, 7.29. Found: C, 85.26, 84.94; H, 5.80, 5.70; S, 7.06; mol. wt., 380 (cryos., benzene).

Analysis indicated the retention of some ether. Purification was obstructed by the chemical reactivity and the non-crystalline character of the product. The principal ultraviolet maxima occurred at 244 and 524 m μ (ethanol), the major in-

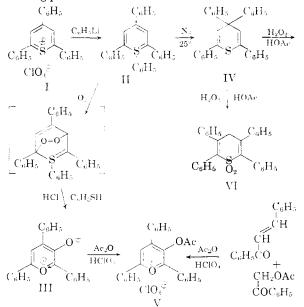
(1) R. Wizinger and P. Ulrich, Helv. chim. acta, 39, 207 (1956).

frared bands at 6.28, 6.70, 6.95, 7.05, 8.05 and 14.40 $\mu.$

An ethereal solution of II, prepared from 10 g. of I, after washing with aqueous ammonium chloride and water, was treated with oxygen for 30 min. The violet color faded to orange-yellow. On bubbling dry hydrogen chloride into the solution, the odor of thiophenol immediately became evident² and a deep orange precipitate settled from solution. The solid was dissolved in acetone, precipitated by water and recrystallized as dark red needles (III) from acetone, 4.45 g. (60%), m.p. 193.5–195°.

Anal. Calcd. for $C_{23}H_{16}O_2$: C, 85.20; H, 4.96. Found: C, 85.19; H, 5.09. From the mother liquors, small amounts of two colorless compounds $C_{23}H_{16}O_3$, m.p. 181° (0.7 g.) and 280° (0.25 g.) and 0.4 g. of 2,4,4,6-tetraphenylthiapyran (IV) m.p. 156–157°, were obtained.

The red compound III (0.4 g.) was dissolved in 15 ml. of acetic anhydride containing 6 drops of sulfuric acid and refluxed for 4 hr. After cooling, the reaction mixture was poured into 150 ml. of ice-cold 20% perchloric acid. The microcrystalline yellow product was recrystallized from glacial acetic acid as canary-yellow platelets of 3-acetoxy-2,4,6-triphenylpyrylium perchlorate (V), 0.3 g. (60%), m.p. 230-231.5°. Anal. Calcd. for C₂₅-H₁₉ClO₇: C, 64.31; H, 4.10; Cl, 7.60. Found: C, 64.09; H, 4.16; Cl, 7.83. The same product was obtained by the reaction of benzalacetophenone with phenacyl acetate in acetic anhydride containing perchloric acid. The infrared spectra were identical and there was no depression of mixture melting point.



II lost its violet color slowly on standing under nitrogen, in bulk or in solution. When 200 mg. was sealed under nitrogen and kept for 20 days, a pale yellow resin resulted. Recrystallization from methanol gave 50 mg. of IV, m.p. 155–156°.

(2) The thiophenol was characterized further by conversion to 2,4dinitrodiphenyl sulfide, m.p. 119-120° (R. W. Bost, J. O. Turner and R. D. Norton, J. Am. Chem. Soc., 54, 1985 (1932)). 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. $192-193^{\circ}$, showing very strong sulfone bands at 7.70 and 8.82 μ . Anal. Calcd. for C₂₉H₂₂O₂S: 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	George Suld
UNIVERSITY OF PENNSYLVANIA	CHARLES C. PRICE
Philadelphia 4, Pennsylvania	

Received December 30, 1960

THE PHOTOLYSIS OF ORGANIC NITRITES. II. SYNTHESIS OF STEROIDAL HYDROXAMIC ACIDS Sir:

The recent syntheses of aldosterone¹ and of 18nitriloprogesterone,² 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 β -nitrite esters.

Reaction of 5α -androstane- 3α , 17 β -diol 3α -acetate³ with nitrosyl chloride in pyridine gave the 17β -nitrite (I; m.p. 177-180°; $[\alpha]p - 33°$ (all rotations in dioxane unless otherwise stated.)4; $\lambda_{\max}^{N_{ujol}}$ 5.76, 6.10, 6.25, 7.94 μ) which was photolyzed in benzene⁵ to give the hydroxamic acid (II, R = OH, R¹ = CH₃CO; m.p. 229–233°; [α]D -2°; λ_{max}^{Nujol} 3.28, 5.77, 6.12 μ; instant color with ferric chloride), isolated by direct crystallization. Acetylation of II with acetic anhydride gave the Nacetoxy derivative (II, $R = CH_3CO_2$; $R^1 = CH_3$ -CO; m.p. 173–176°; $[\alpha]_{D}$ +16°; λ_{max}^{Nujol} 5.58, 5.75, 5.9, 8.05, 8.12 μ). Our formulation of the photolysis product (II, R = OH) as 17a-aza-Dhomo- 5α -androstane- 3α , 17a-diol-17-one 3α -acetate is substantiated by the reduction of (II, R = OH) to 17a-aza-D-homo-5 α -androstan-3 α -ol-17-one 3 α acetate (II, R = H; R¹ = CH₃CO; m.p. 280–284°; $[\alpha]_D$ +18°; λ_{max}^{Nujol} 3.12, 3.24, 5.76, 5.96, 6.22, 7.95 μ) with zinc and acetic acid,⁶ and to 17aaza-D-homo-5 α -androstan-3 α -ol-17-one. (II, R = $R^1 = H; m.p. 341-346^\circ; [\alpha]_D + 25^\circ (CH_3OH);$ $\lambda_{max}^{Nujol} 3.05, 3.22, 6.05 \mu)$ by reduction with hydrazine⁷ in ethylene glycol. The lactam (II, (1) D. H. R. Barton, J. M. Beaton, L. E. Geller and M. M. Pechet,

(1) D. M. R. Barton, J. M. Beaton, D. B. Gener 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. Townley, P. Kabasakalian and D. H. R. Barton, *ibid.*, **82**, 2973 (1960).

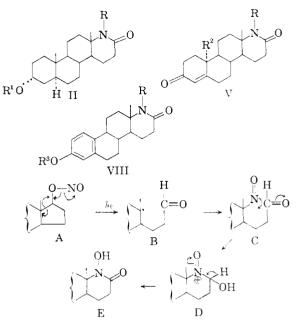
(3) K. Miescher, H. Kagi, C. Scholz, A. Wettstein and E. Tschopp, Biochem. Z., 294, 39 (1937).

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

 $(\bar{\mathfrak{o}})$ 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).



 $R = H, R^1 = CH_3CO)$ was prepared independently from 17-oximino- 5α -androstan- 3α -ol-3-acetate⁸ by Beckmann rearrangement, using thionyl chloride in dioxane,⁹ and authentic II ($R = R^1 =$ H) then was secured by hydrolysis of the Beckmann product with methanolic potassium hy-Similarly, testosterone 17β -nitrite (III; droxide. m.p. ca. 100° dec; $[\alpha]_{D}$ +69°; λ_{max}^{MeOH} 239 m μ (17,700); λ_{max}^{Nujol} 5.98, 6.05, 6.20 μ) and 19-nortestosterone 17*β*-nitrite (IV; m.p. 83-87° dec; $[\alpha]_{\rm D} + 9^{\circ}; \lambda_{\rm max}^{\rm MeOH} 238 \, {\rm m}\mu \, (17,800); \, \lambda_{\rm max}^{\rm Nujol} 6.0,$ μ) furnished, respectively, when photo-6.14lyzed in benzene, 17a-aza-D-homo-4-androsten-17a-ol-3,17-dione (V, R = OH R² = CH₃; m.p. 220-223°; $[\alpha]_{\text{D}} + 67^{\circ}; \lambda_{\text{max}}^{\text{MoOH}} 238 \text{ m}\mu (17,900);$ $\lambda_{\max}^{\text{Nu}\text{iol}}$ 3.05, 5.98, 6.20 μ) and the 19-nor analog (V, R = OH, R² = H; m.p. 227-235°, [α]D +21°, $\lambda_{\max}^{\text{MeoH}}$ 237 m μ (17,900), $\lambda_{\max}^{\text{Nu}\text{iol}}$ 3.25, 6.04, 6.14 μ). Acetylation gave the N-acetoxy deriva-0.14 μ). Acceptation gave the N-acetoxy defivi-tives (V, R = CH₃CO₂, R² = CH₃; m.p. 172–174° [α]p +80°, $\lambda_{max}^{\text{meoH}}$ 239 mμ (17,000), $\lambda_{max}^{\text{Nujol}}$ 5.58, 5.95, 6.18, 8.45 μ) and (V, R = CH₃CO₂, R² = H; m.p. 185–188°, [α]p +39°, $\lambda_{max}^{\text{meoH}}$ 237 mμ (18,200); $\lambda_{max}^{\text{Nujol}}$ 5.60, 5.90, 6.04, 6.18, 8.45 μ).

Reduction of V (R = OH, $R^2 = CH_3$) with zinc-acetic acid gave the known^{9,10,11} lactam (V, R = H, $R^2 = CH_3$).

Photolysis in benzene solution of estradiol 3benzoate 17β -nitrite (VI; m.p. $165-167^{\circ}$ dec.; $[\alpha]_{D} + 8^{\circ}; \lambda_{max}^{M \circ 0H} 229 \text{ m}\mu (21,700); \lambda_{max}^{Nujol} 5.74, 6.1, 6.24, 6.30, 7.90 <math>\mu$) and estradiol 3-methyl ether 17β -nitrite (VII; m.p. $143-145^{\circ}$ dec; $[\alpha]_{D} -11^{\circ}; \lambda_{max}^{M \circ 0H} 276 \text{ m}\mu (2,000), 285 \text{ m}\mu (1,800); \lambda_{max}^{Nujol} 6.12, 6.18, 6.22, 8.0, 8.1 <math>\mu$) gave the hydroxamic acids (VIII, R = OH, R³ = C_6H_5CO; m.p. 227-232° dec., $[\alpha]_{D} + 62^{\circ}; \lambda_{max}^{M \circ 0H} 229 \text{ m}\mu$

(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 ($R = H, R^{\dagger} = CH_{3}$) for comparison purposes.