washed with water and dried to yield 1.7 g. of 2-amino-6-purinethiol, identified by its ultraviolet absorption data.[11]

Preparation of Guanine from 2-Amino-6-chloropurine (XII).—2-Amino-6-chloropurine (0.5 g.) was added to 100 ml. of 1 *N* hydrochloric acid. The solution was refluxed for 1 hr. and allowed to cool. The precipitate was filtered, washed with water, and dried to give 0.4 g. of guanine hydrochloride.

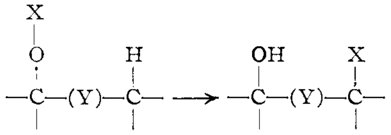
TEMPE, ARIZ.

COMMUNICATIONS TO THE EDITOR

A NEW PHOTOCHEMICAL REACTION

Sir:

It was conceived by one of us (D.H.R.B.) that the exchange process [(I) → (II)], where Y represents a chain of atoms so disposed as to bring $(-\overset{|}{\underset{|}{C}}-O-X)$ and the non-activated $(-\overset{|}{\underset{|}{C}}-H)$ bond into close (or potentially close) juxtaposition, might be feasible especially if photochemically induced. Such an exchange for (—O—X) bonds is without precedent, although other methods of attacking unactivated $(-\overset{|}{\underset{|}{C}}-H)$ intramolecularly already are known.[1,2] Of the various systems possible (*e.g.*, X = halogen, $-NO_2$, —NO, —OR, *etc.*) the nitrites appear to be most suitable. The exchange reaction [(I) → (II) (X = NO)]



$$-\underset{|}{\overset{\overset{X}{|}}{\overset{O}{\overset{|}{C}}}}-(Y)-\underset{|}{\overset{H}{\overset{|}{C}}}- \longrightarrow -\underset{|}{\overset{OH}{\overset{|}{C}}}-(Y)-\underset{|}{\overset{X}{\overset{|}{C}}}-$$

(I) (II)

cannot be induced in good yield thermally but acceptable and, in some cases, high yields can be secured by irradiation with ultraviolet light. The following are two illustrations for the case where $(Y) = -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$.

3β-Acetoxy-5α-pregnan-20β-ol (III) in dry pyridine at −20 to −30°, treated with nitrosyl chloride in slight excess, gave the 20β-nitrite[3] (94%), m.p. (from methanol) 162–164.5°, $[\alpha]^{25°}\text{D}$ −16° (*c*, 1.1, all rotations in $CHCl_3$ unless stated otherwise). Photolysis of this nitrite (10.0 g.) in a Pyrex vessel in dry benzene (200 ml.) at 10° under pure nitrogen for 2–5 hr. (disappearance of nitrite bands in the infrared) using a 200-watt Hanovia high pressure mercury arc lamp with a Pyrex filter sleeve gave on chromatography (III) (0.27 g.) and 18-oximino-5α-pregnane-Cβ,20β-diol 3-acetate (IV, R = Ac) (3.42 g., 34.2%), m.p. (needles from acetone–hexane) 192–195°, $[\alpha]^{25°}\text{D}$ + 19° (*c*, 0.7), $\nu_{\max}^{\text{KBr}}$ at 1635 cm.$^{-1}$ (oxime).

With acetone-H_2O (5:1) containing approx. 2% of concd. HCl at room temperature for 18 hr. the oxime afforded the masked aldehyde (V, R = Ac) (78%), m.p. (from methylene dichloride-methanol) 171–179°, $[\alpha]^{22°}\text{D}$ +17° (*c*, 1.1), no aldehyde absorption in the infrared. Wolff-Kishner reduction of (V, R = Ac) gave 5α-pregnane-3β, 20β-diol (m.p., mixed m.p., rotation and infrared spectrum) in high yield (93%).

The oxime (IV, R = Ac) with pyridine-Ac_2O on the steam-bath for 15 min. and then with Ac_2O-AcONa at reflux for 30 min. gave 3β,20β-diacetoxy-5α-pregnane-18-nitrile (VI, R = Ac), m.p. (from hexane) 131–132°, $[\alpha]^{25°}\text{D}$ +5° (*c*, 1.0), $\nu_{\max}^{\text{KBr}}$ at 2250 (nitrile) and 1740 and 1250 cm.$^{-1}$ (acetate). The corresponding diol (VI, R = H) had m.p. (from methylene dichloride–hexane) 229.5–231.5°, $[\alpha]^{25°}\text{D}$ −2° (*c*, 1.0), $\nu_{\max}^{\text{CHCl}_3}$ at 2250 cm.$^{-1}$ (nitrile).

Treatment of (VI, R = H) with 4:1 EtOH-concd. HCl under reflux for 15 min. gave the iminolactone (VII, X = NH, R = H) (89%), m.p. 171–174°, $[\alpha]^{26°}\text{D}$ +3° (*c*, 1.0), $\nu_{\max}^{\text{CHCl}_3}$ at 1670 cm.$^{-1}$ (C=N), which on heating with 2 *N* hydrochloric acid on the steam-bath for 24 hr. furnished the lactone (VII, X = O, R = H), m.p. 217–218°, $[\alpha]^{25}\text{D}$ +12° (*c*, 1.0 in Me_2CO), $\nu_{\max}^{\text{CHCl}_3}$ at 1750 cm.$^{-1}$ (γ-lactone). The corresponding acetate[2] (VII, X = O, R = Ac), prepared with pyridine-Ac_2O, had m.p. (from acetone–hexane) 207–209°, $[\alpha]^{24°}\text{D}$ −9° (*c*, 1.0), $\nu_{\max}^{\text{CCl}_4}$ at 1765 (γ-lactone) and at 1745 and 1240 cm.$^{-1}$ (acetate). This acetate (VII, X = O, R = Ac) also was obtained (m.p., mixed m.p. and infrared spectrum) by oxidation of (V, R = Ac) with pyridine-CrO_3.

Similarly the nitrite of 6β-hydroxycholestanyl acetate (VIII, R = NO, X = H_2), m.p. (from methanol) 153–154°, $[\alpha]\text{D}$ −31° (*c*, 0.56) (32.2 g.), irradiated in toluene (700 ml.), gave a crystalline precipitate of the nitroso-dimer (16.5 g.) corresponding to the oxime (VIII, R = H, X = NOH). Refluxing the dimer in 2-propanol furnished this

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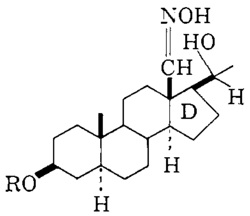
(1) *Inter alia*, A. W. Hofmann, *Ber.*, **18**, 5, 109 (1885); K. Loeffler and C. Freytag, *ibid.*, **42**, 3427 (1909); K. Loeffler, *ibid.*, **43**, 2035 (1910); G. H. Coleman and G. E. Goheen, THIS JOURNAL, **60**, 730 (1938); S. Wawzonek and P. J. Thelen, *ibid.*, **72**, 2118 (1950); S. Wawzonek, M. F. Nelson and P. J. Thelen, *ibid.*, **73**, 2806 (1951); S. Wawzonek and T. P. Culbertson, *ibid.*, **81**, 3367 (1959); P. Buchschacher, J. Kalvoda, D. Arigoni and O. Jeger, *ibid.*, **80**, 2905 (1958); F. Greuter, J. Kalvoda and O. Jeger, *Proc. Chem. Soc.*, 349 (1958); E. J. Corey and W. R. Hertler, THIS JOURNAL, **80**, 2903 (1958), **81**, 5209 (1959); E. J. Corey and R. W. White, *ibid.*, **80**, 6686 (1958); P. Buchschacher, M. Cereghetti, H. Wehrli, K. Schaffner and O. Jeger, *Helv. Chim. Acta*, **42**, 2122 (1959); M. Cereghetti, H. Wehrli, K. Schaffner and O. Jeger, *ibid.*, **43**, 354 (1960); H. Wehrli, M. Cereghetti, K. Schaffner and O. Jeger, *ibid.*, **43**, 367 (1960).

(2) G. Cainelli, M. L. Mihailović, D. Arigoni and O. Jeger, *ibid.*, **42**, 1124 (1959); B. Kamber, G. Cainelli, D. Arigoni and O. Jeger, *ibid.*, **43**, 347 (1960).

(3) Satisfactory analytical data have been secured for all compounds described in this communication.



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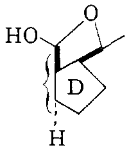

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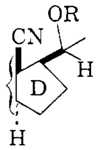

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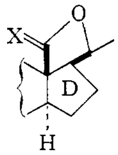
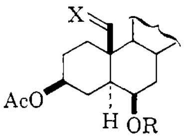


VII



VIII

oxime, m.p. (from methanol) 184-185°, $[\alpha]_D$ $-17°$ (c, 0.71) (15.2 g.). The structure of the oxime was proved by a series of transformations analogous to those described above for the first example of the reaction.

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M. M. PECHET

RECEIVED APRIL 7, 1960

A SYNTHESIS OF ALDOSTERONE ACETATE

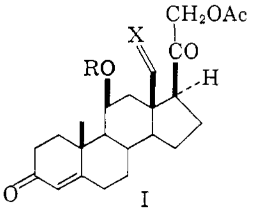
Sir:

We wish to report a convenient three step partial synthesis of aldosterone acetate[1] using the new photochemical reaction reported in the preceding communication.[2] Corticosterone acetate (I, R = H, X = H_2) in dry pyridine was treated with excess nitrosyl chloride at room temperature to give corticosterone acetate nitrite (I, R = NO, X = H_2), m.p. 174-176°, $[\alpha]_D$ $+316°$ (c, 1.1; all rotations in $CHCl_3$). This nitrite (4.0 g.) in toluene (200 ml.) was irradiated at 32° under pure nitrogen for 75 min. as described.[2] The crystalline solid which had separated was removed (885 mg., 21.2%) and identified as aldosterone acetate oxime (I, R = H, X = NOH). Recrystallized from benzene this had m.p. 175-194°, $[\alpha]_D$ $+198°$ (c, 1.3), λ_{max} 240 mμ (ϵ = 16,500), $\nu_{max}^{CHCl_3}$ 3550, 3350, 1740, 1665 and 1615 cm.$^{-1}$. Treatment with pyridine-acetic anhydride at 100° for 5 min. gave the oxime acetate (I, R = N, X = NOAc), m.p. (from ethyl acetate) 183-187°, $\nu_{max}^{CHCl_3}$ 3650, 1780, 1750, 1675 and 1625 cm.$^{-1}$. Aldosterone acetate oxime (505 mg.) was added at 10° to a mixture of acetic acid (8 ml.) and aqueous sodium nitrite (5%, 4 ml.) and kept with agitation for 5 min. Extraction with methylene chloride gave, on crystallization from ethyl acetate, aldosterone 21-acetate (II) (320 mg.), identified by m.p., rotation, analysis, ultraviolet and infrared spectra (comparison with authentic racemate) and by paper chromatography.

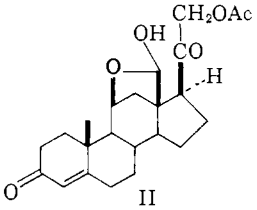
On melting, or on refluxing in methanol for 1 hr., aldosterone acetate oxime was converted into the nitrone (III), m.p. 194-197°, $[\alpha]_D$ $+119°$ (c, 1.0), λ_{max} 239 mμ (ϵ = 27,400), ν_{max}^{KBr} 1735, 1660 and 1600 cm.$^{-1}$. The usual infrared band for a 20-ketone was absent. We shall discuss the mechanism of the nitrite photolyses reported here and in the preceding communication[2] in our complete paper.

Very recently an alternative partial synthesis of aldosterone has been reported involving about 20 steps from 3α-acetoxypregnane-11,20-dione.[3]

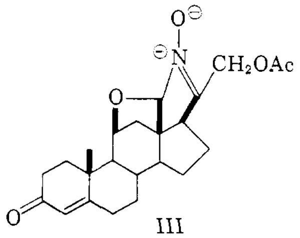
It is a pleasure to acknowledge the encouragement and help that we have at all times received from Dr. M. M. Pechet. Skillful technical assistance was provided by Mrs. M. A. Golub, Misses R. A. Holland and M. A. Kennedy and by Mr. P. C. Ludwig for the work described in this and in the preceding Communication.



I



II



III

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[1] S. A. Simpson, T. F. Tait, A. Wettstein, R. Neher, J. V. Euw, O. Schindler and T. Reichstein, *Helv. Chim. Acta*, **37**, 1163, 1200 (1954).

[2] D. H. R. Barton, J. M. Beaton, L. E. Geller and M. M. Pechet, THIS JOURNAL, **82**, 2640 (1960).

[3] K. Heusler, J. Kalvoda, C. Meystre, P. Wieland, G. Anner, A. Wettstein, G. Cainelli, D. Arigoni and O. Jeger, *Experientia*, **16**, 21 (1960). See also L. Velluz, G. Muller, R. Bardoneschi and A. Poittevin, *Compt. rend.*, 725 (1960).

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RECEIVED APRIL 7, 1960

STRUCTURE OF O,O'-DIETHYL METHYLPHOSPHONOTHIOATE AND CONJUGATIVE PROPERTIES OF THE P=S BOND

Sir:

In connection with more comprehensive studies on the nature of heteroörganic bonds, we have examined recently the structure of O,O'-diethyl methylphosphonothioate, $CH_3P(S)(OCH_2CH_3)_2$, and have ascertained a novel structural feature which has important implications for reaction mechanisms involving this and analogous organic phosphorus systems. Employing high-resolution nuclear resonance equipment,[1] we have obtained fine details of both the H^1 and P^{31} spin-resonance transitions of this compound in an extremely homogeneous magnetic field of 14,092 gauss. Two fixed-frequency oscillators were used successively to irradiate the sample. The material was especially purified for this and other studies.

In the H^1 trace, the two expected higher-field band patterns stand out clearly: an equal inten-

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[1] Varian Associates V4300-2.