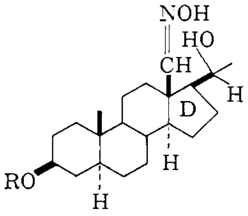
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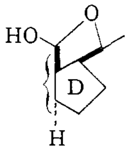
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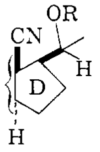
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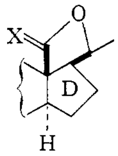
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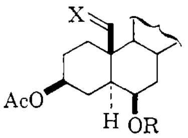
VIII

oxime, m.p. (from methanol) 184-185°, [α]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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RECEIVED APRIL 7, 1960

A SYNTHESIS OF ALDOSTERONE ACETATE

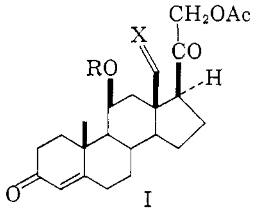
Sir:

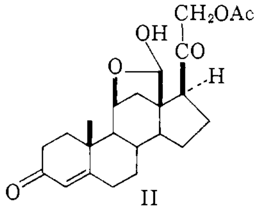
We wish to report a convenient three step partial synthesis of aldosterone acetate[1] using the new photochemical reaction reported in the preceding communication.[2] Corticosterone acetate (I, R = H, X = H_2) in dry pyridine was treated with excess nitrosyl chloride at room temperature to give corticosterone acetate nitrite (I, R = NO, X = H_2), m.p. 174-176°, [α]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°, [α]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°, [α]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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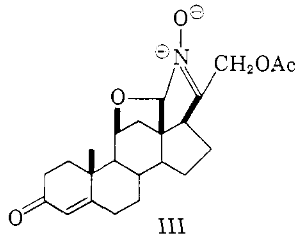
III

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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.