The initial yield of H_2 from oxygen saturated water containing KBr, which prohibits removal of H_2 through secondary reaction with OH, was 0.41 ± 0.01. The observed initial yield of H_2 from oxygen saturated water was 0.20 ± 0.02. Thus the H_2 yield was lowered by 0.21 through secondary reaction of H_2 with OH. With oxygen sweeping through the solution during irradiation to remove the H_2 produced, the initial yield of H_2O_2 was 1.10. The initial yield of H_2O_2 in oxygen saturated water in closed vessels was 1.31. Thus, the H_2O_2 formed through secondary reaction of the H_2 was equivalent to the H_2 used up, 0.21. Within experimental error, the initial yields were the same at *p*H 7 and at *p*H 2 (H_2SO_4).

These results, combined with results from studies of potassium bromide solutions by Sworski[3] indicate that the mechanism proposed by Allen[2] can be applied to oxygen swept solutions. Our value of 1.10 for the initial H_2O_2 yield corresponds to F + 2E in the Allen terminology, and agrees with the value 1.08 obtained by Sworski by extrapolation to zero potassium bromide concentration. Taking 3.2 as the initial H_2O_2 yield in solutions of hydrogen plus oxygen in which every radical is converted to H_2O_2,[4] the yields of H, OH, H_2 and H_2O_2 from the decomposition of oxygen saturated water by cobalt gamma rays are 2.8, 2.1, 0.41 and 0.76 respectively.

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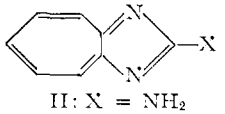
RECEIVED MAY 10, 1954

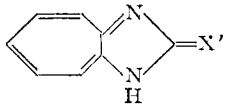
1,3-DIAZAZULENE

Sir:

We had previously obtained a compound which was assumed to be 2-amino-1,3-diazazulene (II) or its tautomer (II′) by the condensation of tropolone methyl ether (I) and guanidine.[1] 6-Amino-1,3-diazazulene or its tautomer had also been obtained from 2,5-diaminotroponimine and formic acid.[2] Recently, we obtained 1,3-diazazulene itself and examined its properties. A brief summary of this study is given here.



II: X = NH_2
III: X = SH
IV: X = OH
V: X = H



II′: X′ = NH
III′: X′ = S
IV′: X′ = O

Reaction of I and one mole equiv. of thiourea in absolute ethanol, in the presence of sodium ethoxide, results in the formation of yellow needles, m.p. 68–70°, in 80% yield. This is a sodium salt and its treatment with acetic acid gives 2-mercapto-1,3-diazazulene (III or III′) as orange crystals, m.p. > 300° (Calcd. for $C_8H_6N_2S$: C, 59.19; H, 3.73; N, 17.33. Found: C, 59.52; H, 4.07; N, 17.56). III is sparingly soluble in water and in organic solvents and forms insoluble silver, copper, and iron salts. Hydrochloride, m.p. > 310° (Found: N, 13.80); picrate, m.p. 262° (dec.) (Found: N, 18.22); methyl thioether (on treatment with diazomethane), m.p. 102° (Found: C, 61.01; H, 4.82; N, 16.67); disulfide, m.p. 218° (dec.) (Found: C, 59.12; H, 3.47; N, 17.42).

Refluxing of III with mercuric oxide in acetic acid or heating of II in a sealed tube at 160–170° with concd. hydrochloric acid, or barium hydroxide results in the formation of 2-hydroxy-1,3-diazazulene (IV or IV′) as pale yellow needles, m.p. 245° (Calcd. for $C_8H_6ON_2$: C, 65.75; H, 4.11; N, 19.17; Found: C, 66.14; H, 4.34; N, 18.75). Hydrochloride, m.p. > 300° (Found: N, 15.64); picrate, m.p. 254° (decomp.) (Found: N, 18.56); acetyl compound, m.p. 187° (dec.) (Found: N, 15.26); methylated compound (on treatment with diazomethane), m.p. 186.5° (Found: N, 17.97); 2,4-dinitrophenylhydrazone, m.p. 234° (decomp.) (Found: N, 25.23).

When III is heated on a water-bath for a half hour with 10% nitric acid, it undergoes oxidation and hydrolysis to give 1,3-diazazulene (V) as yellow needles, m.p. 120° (anhydrous, recrystallized from petroleum ether and benzene), in 60% yield. (Calcd. for $C_8H_6N_2$: C, 73.83; H, 4.65; N, 21.54. Found: C, 73.66; H, 4.56; N, 21.58.[3] Dipole moment, 4.03 *D* (25°, benzene) (measured by Mr. Y. Kurita, Nagoya University). V is soluble in water, alcohol, benzene and chloroform. It easily absorbs 1 mole of water of crystallization and gives pale yellow crystals melting at about 60° (Found: C, 64.65; H, 5.44; H_2O, 11.92). Ultraviolet absorption maximum of the hydrate in methanol[4]: 218 mμ (log ε = 4.28), 250 (4.61), 295 (3.76), 303 (3.78), and 390 (2.97). Infrared absorption maximum of the hydrate in Nujol (5–8 μ region): 6.10 μ (m), 6.27 (m), 7.06 (s), 7.56 (s), and 7.76 (w). V is stable to acids but labile in alkalies. Picrate, m.p. 207° (dec.) (Found: C, 46.95; H, 2.86; N, 19.17); dihydrochloride, darkens at 175° (Found: N, 13.98); methiodide, m.p. 167° (decomp.) (Found: N, 10.68); silver nitrate double compound, m.p. 280° (decomp.) (Found: Ag, 35.27).

Oxidation of V with chromic acid mixture gives imidazole-4,5-dicarboxylic acid,[5] m.p. 285° (dec.), which is easily decarboxylated to imidazole, m.p. 90°. This fact supports the structures assumed for the above compounds. V does not undergo electrophilic substitution, such as azo coupling, nitrosation, and sulfonation, by the ordinary method. Bromination of V in chloroform gives an insoluble red-colored complex, decomposing at *ca.* 115°, and yellow crystals, decomposing at *ca.* 145° (Found: C, 22.10; H, 2.19; N, 6.03). The former contains an active bromine and its reductive decomposition (with potassium iodide followed by sodium thiosulfate) results in the recovery of V. From the ultraviolet absorption spectrum of the yellow crystals (only one max. in methanol at 247 mμ: log ε =

(1) T. Nozoe, T. Mukai, K. Takase, I. Murata and K. Matsumoto, *Proc. Japan Acad.*, **28**, 452 (1953).

(2) T. Nozoe, M. Sato, S. Ito, K. Matsui, and T. Matsuda, *ibid.*, **29**, 565 (1953).

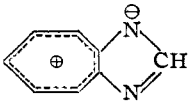
(3) Analyzed sample dried over phosphorus pentoxide in vacuum at room temperature for 48 hours.

(4) The ultraviolet spectral curve in benzene or carbon tetrachloride solution is similar to that of methanol solution but that in cyclohexane is widely different, showing absorption in a longer wave length range than 500 mμ.

(5) H. R. Snyder, R. G. Hendrick and L. A. Brooks, *Org. Syntheses*, **22**, 65 (1942).

3.85), it seems not to be the bromine substitution product, but rather the bromine addition product.

These reactions indicate the large contribution of the structures of the type shown below for 1,3-diazazulene and the fact can also be explained by the large dipole moment.



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SENDAI, JAPAN

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TOSHIO MUKAI
ICHIRO MURATA

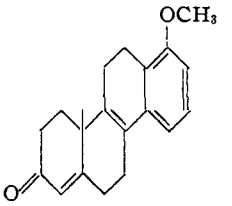
RECEIVED MARCH 10, 1954

TOTAL SYNTHESIS OF AN 11-OXYGENATED STEROID

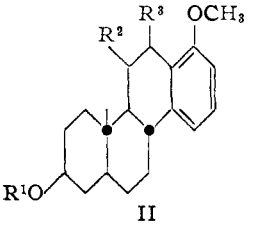
Sir:

We announce hereby the total synthesis of 3β,-11β-dihydroxyandrostane-17-one (VII), a substance which has been isolated from beef adrenal glands[1] and has recently been found in human urine as a metabolite of compound "F."[2]

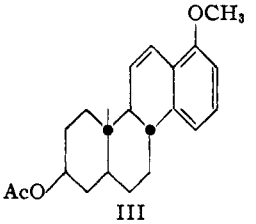
We have obtained *dl*-VII from the readily available tetracyclic ketone I, the conversion of which to *dl*-epiandrosterone has already been described.[3] Reduction of I with lithium[4] and alcohol (10%) in ammonia yielded the tetrahydro carbinol II (R^1 = R^2 = R^3 = H) isolated as the acetate II (R^1 = Ac, R^2 = R^3 = H), m.p. 151.3–152.3° (C, 76.8; H, 8.82), which upon treatment with lead tetraacetate in acetic acid was converted in good yield to the 12-acetoxy compound II (R^1 = Ac, R^2 = H, R^3 = OAc),[5] m.p. 206–212° (dec.) (C, 71.9; H, 8.04). On warming in acetic acid the 12-acetoxy group was readily eliminated[5] affording the 11,12-olefin III, m.p. 157.2–159° (C, 77.4; H, 8.36). Hydroxylation of the olefinic bond with peracid[6] (preferably performic acid) yielded a mixture of esters of stereoisomeric triols II (R^1 = H, R^2 = R^3 = OH) from which homogeneous components have been isolated, but which could be reduced directly by vigorous treatment with lithium and alcohol (40%) in ammonia[3] to simultaneously hydrogenolyze the substituent at C_{12}[7] and reduce the aromatic nucleus. After acid hydrolysis of the enol ether, a mixture of the 13,14- and 16,17-dehydroketones—IV(C=C at 13,14), m.p. 276–277°, λ_{max} 248 mμ (log ε 4.14) (C, 74.8; H, 9.52); and IV (C=C at 16,17), diacetate, m.p. 204–205°, λ_{max} 224.7 mμ (log ε 3.94) (C 71.1; H, 8.23)—crystallized readily in good yield. As in the 11-desoxy series[3] this mixture on hydrogenation over palladium in the presence of a trace of potassium hydroxide gave a single product, *dl*-3β,11β-dihydroxy-D-homo-18-nor-androstane-17a-one (IV), m.p. 256–257° (C, 74.3; H, 9.92).



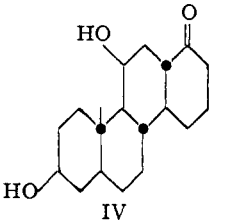
I



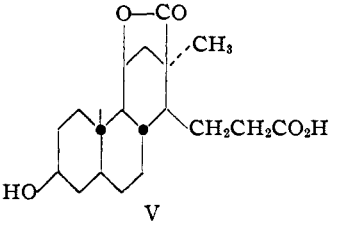
II



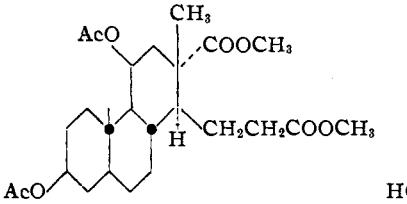
III



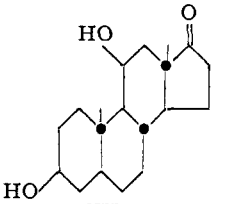
IV



V



VI



VII

The remaining steps were similar to those employed in the 11-desoxy series.[3] Conversion of IV to the fufurylidene derivative (diacetate, m.p. 246–248°, C, 71.6; H, 7.73) followed by methylation and acetylation gave *dl*-3β,11β-diacetoxy-17-furfurylidene-D-homoandrostane-17a-one, m.p. 256–258° (C, 72.5; H, 8.02) along with the 13-iso (preponderant) compound, m.p. 242–243° (C, 72.0; H, 7.68). These angularly methylated C_{13} epimers were ozonized, and the resulting dibasic acids esterified with diazomethane to give respectively *dl*-dimethyl 3β,11β-diacetoxyetioallohomobilianate (VI), m.p. 131.5–133° (C, 64.7; H, 8.12) and the 13-iso compound, m.p. 143.5–144.5° (C, 65.3; H, 8.56). The infrared spectrum of the former epimer was identical with that of authentic *d*-diester (oil, C, 65.3; H, 8.30), which was prepared by opening ring D[8] of *d*-VII produced from *allo*preg-

(1) T. Reichstein and J. Von Euw, *Helv. Chim. Acta*, **21**, 1197 (1938); **24**, 879 (1941).

(2) A. D. Kemp, A. Kappas, I. I. Salamon, F. Herling and T. F. Gallagher, *J. Biol. Chem.*, in press.

(3) W. S. Johnson, B. Bannister, B. M. Bloom, A. D. Kemp, R. Pappo, E. R. Rogier and J. Szmuszkovicz, THIS JOURNAL, **75**, 2275 (1953).

(4) *Cf.* A. L. Wilds and N. A. Nelson, *ibid.*, **75**, 5360 (1953).

(5) *Cf.* The acetoxylation and elimination reactions in a model series, W. S. Johnson, J. M. Anderson and W. E. Shelberg, THIS JOURNAL, **66**, 218 (1944).

(6) We are deeply indebted to Professor Gilbert Stork of Columbia University for encouraging us to exploit and helping us to properly apply this scheme for introducing the 11-oxygen via the 11,12-olefin. We wish to thank him particularly for giving us abundant unpublished information from his laboratory on methods of oxidizing the methoxydihydronaphthalene system.

(7) Under the milder (10% alcohol) conditions reduction stops at this stage affording after acetylation II (R^1 = Ac, R^2 = OAc, R^3 = H), m.p. 197.5–199° (C, 72.1; H, 8.14).

(8) By the method used in the estrone series, W. S. Johnson, D. K. Bannerjee, W. P. Schneider, C. D. Gutsche, W. E. Shelberg and L. J. Chinn, THIS JOURNAL, **74**, 2832 (1952).