$\Delta^{4,9(11)}$-Pregnadiene-3,20-dione ($\Delta^{9(11)}$-Dehydroprogesterone) (XIII).—11α-Hydroxyprogesterone p-toluenesulfonate (0.50 g.) dissolved in 10 cc. of collidine was refluxed for 30 minutes, and the cooled mixture was then diluted with water. Isolation with ether yielded a solid product (0.33 g.), which was chromatographed on 20 g. of ethyl acetate washed alumina. The fractions eluted with hexane–benzene and benzene were crystallized from acetone–hexane, and yielded 0.24 g. (74%) of $\Delta^{9(11)}$-dehydroprogesterone, m.p. 127–128°, $[\alpha]^{20}D$ +171° (chloroform), +155° (acetone), λ_{max} 240 mμ, log ϵ 4.22, $\nu_{max}^{CHCl_3}$ 1700 and 1666 cm.$^{-1}$, no free hydroxyl band.

Anal. Calcd. for $C_{21}H_{28}O_2$: C, 80.73; H, 9.03. Found: C, 80.79; H, 9.15.

The dehydration of 11β-hydroxyprogesterone (XIV) with boiling concentrated hydrochloric acid and acetic acid, following Shoppee and Reichstein,[7a] was also carried out. After careful chromatography on alumina, material with m.p. 115–118° was obtained [Shoppee and Reichstein[7a] give m.p. 120–122°, $[\alpha]^{18}D$ +145 ± 5° (acetone)], which was undepressed in m.p. on admixture with the pure $\Delta^{9(11)}$-dehydroprogesterone described above; moreover the infrared spectra were very similar. Paper chromatography[20] of this material showed that it consisted of two compounds of closely similar polarities. The major constituent proved to be identical (mixed paper chromatogram, sulfuric acid curve comparison) with the above $\Delta^{9(11)}$-dehydroprogesterone. The minor constituent, which was not further investigated, may be the Δ^{11}-isomer.

(20) We are indebted to Dr. A. Zaffaroni for this analysis.

MEXICO CITY 17, D. F.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF SYNTEX, S. A.]

Steroidal Sapogenins. XXXIII.[1] Aromatization Experiments in the Diosgenin Series

BY FRANZ SONDHEIMER, F. NEUMANN, H. J. RINGOLD AND G. ROSENKRANZ

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$\Delta^{1,4,6}$-22a-Spirostatrien-3-one (II) in mineral oil solution on vapor phase aromatization furnished 19-nor-$\Delta^{1,3,5(10),6}$-22a-spirostatetraen-3-ol (IIIa), hydrogenation of which led to the phenol IVa. The 3-methyl ether IVb of the latter on side chain degradation afforded 3-methoxy-17-acetyl-$\Delta^{1,3,5(10),16}$-estratetraene (Vb), a valuable intermediate for the synthesis of 19-nor hormone analogs. The structure of the degradation product Vb was confirmed through hydrogenation to the known 3-methoxy-17β-acetyl-$\Delta^{1,3,5(10)}$-estratriene (VIb). The "dienone phenol" rearrangement of $\Delta^{1,4,6}$-22a-spirostatrien-3-one (II) could be carried out, without attack of the side chain, by means of p-toluenesulfonic acid in acetic anhydride at room temperature. The resulting 1-methyl-19-nor-$\Delta^{1,3,5(10),6}$-22a-spirostatetraen-3-ol acetate (IX) was hydrogenated to the 1-methyl phenol acetate X.

3-Hydroxy-17-acetyl-$\Delta^{1,3,5(10),16}$-estratetraene (Va) and the 3-methyl ether Vb, as well as 3-hydroxy-17β-acetyl-$\Delta^{1,3,5(10)}$-estratriene (VIa) and the ether VIb, are important intermediates for the synthesis of the interesting 19-nor analogs of the C-21 steroidal hormones. Thus, the conversion of these ring A aromatic substances to the highly active progestational hormone 19-norprogesterone has recently been announced from these laboratories.[2] The $\Delta^{1,3,5(10),16}$-tetraenes Va and Vb are of especial utility, since the presence of the Δ^{16}-double bond in these compounds makes possible the application of the convenient Julian bromohydrin procedure[3] for producing the corresponding 17α-hydroxy-20-ketones, from which the 19-nor analogs of the more complex adrenal hormones may be prepared. The phenol Va has been prepared previously from estrone acetate (XI) through hydrogen cyanide addition, dehydration and Grignard reaction,[4] and also from allopregnane-3,20-dione (VII) through successive tribromination and dehydrobromination to $\Delta^{1,4,16}$-pregnatriene-3,20-dione(VIII),[5] followed by pyrolytic aromatization.[6] Neither of these routes is satisfactory in detail and therefore an alternative path to the $\Delta^{1,3,5(10),16}$ tetraene V was sought. An attractive possibility involved the aromatization of ring A of a polyenone containing the intact diosgenin (22a-spirostan) side chain, since degradation of the latter should then lead directly to a ring A aromatic pregnane derivative containing the desired Δ^{16}-20-one system (type V). In this paper we record the accomplishment of this type of transformation.

The conversion of Δ^4-22-spirosten-3-one (I) (the Oppenauer oxidation product of diosgenin[7]) by successive bromination and dehydrobromination to $\Delta^{1,4,6}$-22a-spirostatrien-3-one (II) has been reported previously.[8] It has been shown that steroidal $\Delta^{1,4,6}$-trien-3-ones on vapor phase aromatization at 600° in mineral oil[9] or in tetralin[10] solution furnish the corresponding 3-hydroxy-$\Delta^{1,3,5(10),6}$-tetraenes with the C-19 methyl group eliminated (type III). The trienone II dissolved in mineral oil was therefore subjected to the pyrolysis procedure, but in contrast to the previous cases studied,[9a,9b] the product could not be made to crystallize by chilling the resulting solution. A convenient isolation procedure involved removal of the mineral oil by passage through alumina and elution with hexane, after which the steroidal products could be obtained by the usual chro-

(1) Paper XXXII, G. Rosenkranz, O. Mancera and F. Sondheimer, THIS JOURNAL, **76**, 2227 (1954).

(2) L. Miramontes, G. Rosenkranz and C. Djerassi, *ibid.*, **73**, 3540 (1951); C. Djerassi, L. Miramontes and G. Rosenkranz, *ibid.*, **75**, 4440 (1953).

(3) P. L. Julian, E. W. Meyer, W. J. Karpel and I. Ryden Waller, *ibid.*, **71**, 3574 (1949); **72**, 5145 (1950); F. B. Colton, W. R. Nes, D. A. v. Dorp, H. L. Mason and E. C. Kendall, *J. Biol. Chem.*, **194**, 235 (1952).

(4) L. Velluz and G. Muller, *Bull. soc. chim. France*, 166 (1950).

(5) M. Rubin, H. Wishinsky and F. Bompard, THIS JOURNAL, **73**, 2338 (1951).

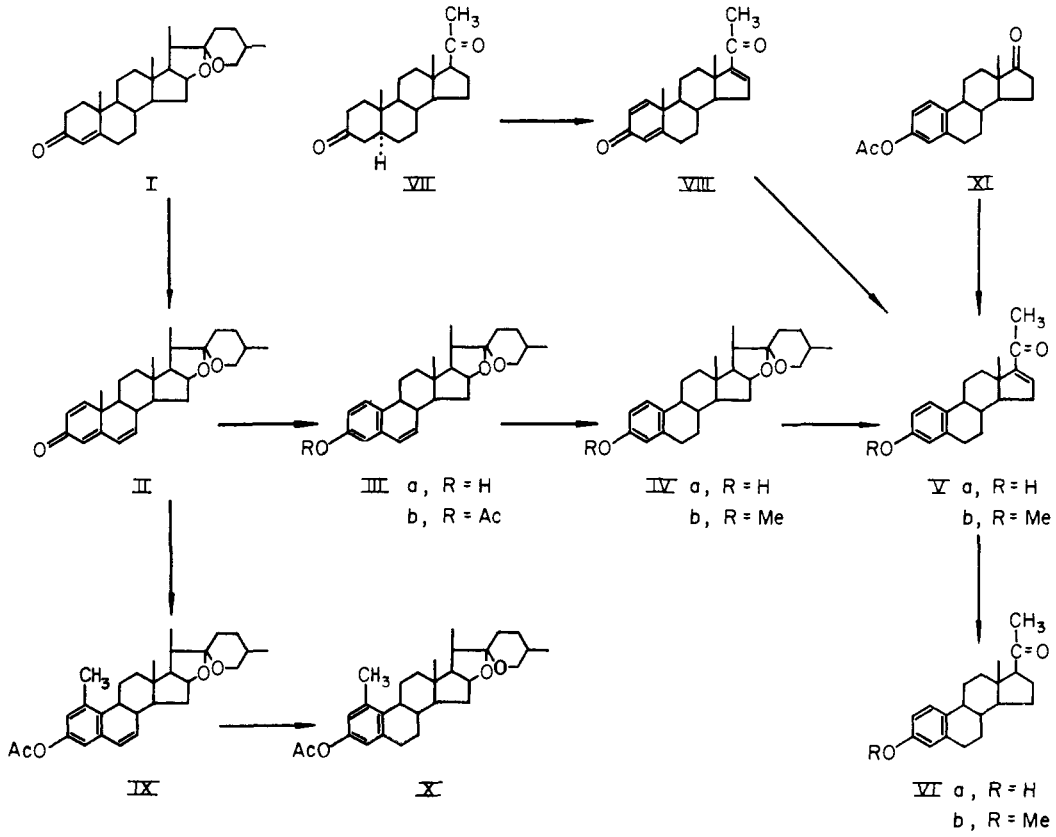
(6) C. Djerassi, G. Rosenkranz, J. Iriarte, J. Berlin and J. Romo, *ibid.*, **73**, 1523 (1951).

(7) R. E. Marker, T. Tsukamoto and D. L. Turner, *ibid.*, **62**, 2525 (1940).

(8) R. Yashin, G. Rosenkranz and C. Djerassi, *ibid.*, **73**, 4654 (1951).

(9) (a) S. Kaufmann, J. Pataki, G. Rosenkranz, J. Romo and C. Djerassi, *ibid.*, **72**, 4531 (1950); (b) C. Djerassi, G. Rosenkranz, J. Romo, S. Kaufmann and J. Pataki, *ibid.*, **72**, 4534 (1950); *cf.* (c) E. B. Hershberg, M. Rubin and E. Schwenk, *J. Org. Chem.*, **15**, 292 (1950).

(10) J. Romo, G. Rosenkranz and C. Djerassi, *ibid.*, **15**, 1289 (1950).



matographic technique. In this way a crystalline substance was isolated which must clearly be the required 6-dehydro phenol IIIa, since it exhibited a triple maximum in the ultraviolet at 222 mμ, 262 mμ and 304 mμ typical for this type of tetraene,[9a,9b,10] and showed a hydroxyl band but no carbonyl bands in the infrared. Hydrogenation of the $\Delta^{1,3,5(10),6}$-tetraene IIIa over a 5% palladium-on-charcoal catalyst proceeded readily to yield the $\Delta^{1,3,5(10)}$-triene IVa, with its expected medium-intensity ultraviolet maximum at 280 mμ.[11] This substance showed very favorable crystallization properties, and in practice it was found advisable not to crystallize the 6-dehydro phenol IIIa, but to carry out the hydrogenation step on the incompletely purified aromatization product.

The phenol IVa was next methylated with methyl sulfate to the ether IVb, and the latter was subjected to the usual side chain degradation process (heating with acetic anhydride to a "furosten," oxidation with chromium trioxide to a "diosone" and finally treatment with sodium bicarbonate). The 3-hydroxy group was protected as the methyl ether, since eventually a phenol methyl ether was required for Birch reduction to 19-nor compounds. The degradation, in which no attempt was made to characterize the intermediates, furnished the required 3-methoxy-17-acetyl-$\Delta^{1,3,5(10),16}$-estratetraene (Vb). This compound, like the known corresponding free phenol Va,[4,6] showed maxima in the ultraviolet at 230 mμ (high intensity) due essentially to the Δ^{16}-20-keto grouping and at 278 mμ (medium intensity) due to the phenol grouping. Its structure was confirmed through hydrogenation to the $\Delta^{1,3,5(10)}$-triene methyl ether VIb, a substance prepared previously by methylation[6] of the free phenol VIa (obtained by the routes XI → Va → VIa[4] and VII → VIII → Va → VIa[5,6]) and from the corresponding etianic acid derivative[12] by conversion to the acid chloride and reaction with dimethylcadmium.[6]

In addition to the above described pyrolytic aromatization involving the loss of the C-19 methyl group, the $\Delta^{1,4,6}$-trien-3-one II also was subjected to the acid-catalyzed dienone phenol rearrangement, a reaction which is known[6,13] to yield 1-methyl-6-dehydro phenol acetates of type IX. It has been found,[14] however, that the 22a-spirostan side chain present in the trienone II is converted at least in part to the "furosten" when heated with *p*-toluenesulfonic acid in acetic anhydride, the conditions usually employed[6,13] for effecting the rearrangement. Doubtlessly it is for this reason that a mixture of products was obtained under the aforementioned conditions. On the other hand, the reaction proceeded more smoothly when the $\Delta^{1,4,6}$-trien-3-one II was treated with *p*-toluenesulfonic acid and acetic anhydride at room temperature, and the 1-methyl-6-dehydrophenol acetate IX could be isolated in *ca.* 30%

(11) *Cf.* L. Dorfman, *Chem. Revs.*, **53**, 47 (1953), Table 19.

(12) C. Djerassi and C. R. Scholz, THIS JOURNAL, **71**, 3962 (1949).

(13) (a) C. Djerassi, G. Rosenkranz, J. Romo, J. Pataki and S. Kaufmann, *ibid.*, **72**, 4540 (1950); (b) A. Sandoval, L. Miramontes, G. Rosenkranz and C. Djerassi, *ibid.*, **73**, 990 (1951); (c) J. Romo, C. Djerassi and G. Rosenkranz, *J. Org. Chem.*, **15**, 896 (1950).

(14) D. H. Gould, H. Staendle and E. B. Hershberg, THIS JOURNAL, **74**, 3685 (1952), and independent observations from our laboratories.

yield. The presence of the 1-methyl-3-acetoxy-$\Delta^{1,3,5(10),6}$-tetraene chromophore in this substance was confirmed by its ultraviolet spectrum (maxima at 224 mμ and 266 mμ[13]) and infrared spectrum whereas the retention of the intact spiroketal side chain was demonstrated by the elemental analysis and molecular rotation (*vide infra*). The tetraen-ol acetate IX was hydrogenated over a palladium-on-charcoal catalyst and yielded the 1-methyl-3-acetoxy-$\Delta^{1,3,5(10)}$-triene X.

In Table I are set out the molecular rotation values of ring A aromatic steroids of several series, including the compounds of the 22a-spirostan series described in this paper. The difference in the molecular rotation as compared with that of the corresponding 3β-acetoxy-5α saturated compound ($[M]^{sat.}_D$), chosen as a convenient standard, has been calculated in each case. It is apparent that reasonably good agreement exists among the various series for the $\Delta[M]_D$ values of the 19-nor phenols (type IVa), the 1-methyl-19-nor-6-dehydro phenol acetates (type IX) and the 1-methyl-19-nor phenol acetates (type X). In particular, the fact that the $\Delta[M]_D$ values of compounds IX and X in the 22a-spirostan series are of the expected magnitude provides confirmation that these substances still contain the spiro-ketal side chain, for degradation to structures with the "furosten" side chain would have involved a considerable positive shift (*ca.* +400°)[15] in the molecular rotation.

It is of interest to note that although passage from the saturated 3β-acetoxy-5α structure ($[M]^{sat.}_D$) to the 19-nor-$\Delta^{1,3,5(10),6}$-phenol system ($[M]^{IIIa}_D$) involves in all cases a considerable negative shift in the molecular rotation, this varies from −276 in the cholestane to −624 in the androstan-17β-ol acetate series. It is evident that altering the nature of the side chain in compounds of type IIIa produces different changes in the molecular rotation than in the other types discussed.

Experimental[16,17]

19-Nor-$\Delta^{1,3,5(10),6}$-22a-spirostatetraen-3-ol (IIIa).—A solution of $\Delta^{1,4,6}$-22a-spirostatrien-3-one (II)[8] (136 g.) in mineral oil (8 l.) was dropped at a rate of *ca.* 2 cc./sec. through a glass tube (32 × 3.0 cm.) filled with Pyrex helices and heated to 600°.[18] The resulting cloudy dark yellow solution deposited no appreciable precipitate on being chilled. It was therefore passed through a column containing 2.6 kg. of ethyl acetate washed alumina, and the mineral oil was washed out with hexane (6 l.). Elution with hexane–benzene and benzene yielded 4.8 g. of recovered starting material (m.p. 205–208°), whereas further elution with benzene–ether and ether furnished a total of 82.8 g. of semi-solid fractions. These on crystallization from acetone–hexane, followed by recrystallization of the solid product (21.4 g., m.p. 209–212°) from acetone, gave 16.2 g. of the $\Delta^{1,3,5(10),6}$-tetraene IIIa, m.p. 221–224°, and 66.4 g. of oily mother liquors. The analytical sample of IIIa was obtained as colorless needles from acetone, m.p. 231–233°, $[\alpha]_D$ −202°, λ_{max} 222 mμ (log ϵ 4.50), 262 mμ (log ϵ 4.00) and 304 mμ (log ϵ 3.44), $\nu_{max}^{CHCl_3}$ free hydroxyl band only.

Anal. Calcd. for $C_{26}H_{34}O_2$: C, 79.15; H, 8.69. Found: C, 78.63; H, 8.61.

An aliquot of the above mother liquors on re-chromatography gave only small amounts of crystalline product, and they were employed directly for hydrogenation (*vide infra*), in view of the greater ease of crystallization of the $\Delta^{1,3,5(10)}$-triene IVa.

The acetate IIIb was prepared from the crystalline tetraene in the usual manner (acetic anhydride–pyridine, steam-bath, 1 hour) and after crystallization from methanol–chloroform formed needles, m.p. 202–204°, $[\alpha]_D$ −186°, λ_{max} 262 mμ (log ϵ 4.02), $\nu_{max}^{CHCl_3}$ 1744 cm.$^{-1}$, no free hydroxyl band.

Anal. Calcd. for $C_{28}H_{36}O_4$: C, 77.03; H, 8.31. Found: C, 77.03; H, 8.04.

19-Nor-$\Delta^{1,3,5(10)}$-22a-spirostatrien-3-ol (IVa).—The $\Delta^{1,3,5(10),6}$-tetraene IIIa (1.0 g., m.p. 221–224°) dissolved in 50 cc. of ethyl acetate was hydrogenated overnight in the presence of 0.3 g. of a 5% palladium-on-charcoal catalyst at atmospheric pressure and room temperature. Removal of catalyst and solvent and crystallization of the residue from acetone furnished 0.82 g. of the $\Delta^{1,3,5(10)}$-triene as fine colorless needles, m.p. 245–247°, $[\alpha]_D$ −19°, λ_{max} 280 mμ (log ϵ 3.40), $\nu_{max}^{CHCl_3}$ free hydroxyl band only.

Anal. Calcd. for $C_{26}H_{36}O_2$: C, 78.74; H, 9.15. Found: C, 78.91; H, 9.46.

A similar hydrogenation was carried out with the above mentioned oily mother liquors (66.4 g.) from the aromatization of 136 g. of II, dissolved in 1 l. of ethyl acetate, over 10 g. of the 5% palladium-on-charcoal catalyst, for 12 hours at room temperature and 50 lb. pressure. The semi-solid product was chromatographed on 1.2 kg. of ethyl acetate washed alumina and the fractions eluted with benzene–ether on crystallization from acetone yielded 11.2 g. of the phenol IVa, m.p. 235–240°, $[\alpha]_D$ −22°, λ_{max} 280 mμ (log ϵ 3.42). The total yield of useful aromatic products from the $\Delta^{1,4,6}$-trien-3-one II was thus raised to 21%.

19-Nor-$\Delta^{1,3,5(10)}$-22a-spirostatrien-3-ol Methyl Ether (IVb).—A boiling solution of 2.5 g. of the phenol IVa in 250 cc. of methanol was treated twice alternately with 20 cc. of a 50% potassium hydroxide solution and 20 cc. of dimethyl sulfate. After being refluxed for 1 hour, the mixture was cooled, and 25 cc. of concentrated ammonia solution was added. The precipitated methyl ether was collected and washed well with water; it weighed 1.02 g., and showed m.p. 146–152°. The filtrate on dilution with aqueous acetic acid furnished 1.46 g. of recovered starting material, m.p. 230–238°. The analytical sample of the methyl ether was obtained by crystallization from hexane, and exhibited m.p. 153–155°, $[\alpha]_D$ −28°.

Anal. Calcd. for $C_{27}H_{38}O_3$: C, 78.98; H, 9.33. Found: C, 78.98; H, 9.70.

3-Methoxy-17-acetyl-$\Delta^{1,3,5(10),16}$-estratetraene (Vb).—A mixture of 1.35 g. of the above methyl ether and 20 cc. of acetic anhydride was heated in a bomb tube at 195–200° for 8 hours, poured into water, extracted with ether, washed well with sodium carbonate solution, dried and evaporated. The resulting oily "furosten" (1.3 g.) was oxidized with chromium trioxide and the oily "diosone" subjected to bicarbonate saponification exactly as described for the degradation of Δ^7-22a,5α-spirosten-3β-ol acetate.[19] Crystallization of the product from ethyl acetate furnished 0.36 g. of the unsaturated ketone, m.p. 186–189°. The analytical sample showed m.p. 193–194°, $[\alpha]_D$ +115°, λ_{max} 230 mμ (log ϵ 4.19) and 278 mμ (log ϵ 3.45), ν_{max}^{mull} 1660 cm.$^{-1}$, no free hydroxyl band.

Anal. Calcd. for $C_{21}H_{26}O_2$: C, 81.25; H, 8.44. Found: C, 81.55; H, 8.55.

3-Methoxy-17β-acetyl-$\Delta^{1,3,5(10)}$-estratriene (VIb).—A solution of 0.20 g. of the unsaturated ketone Vb in 50 cc. of ethyl acetate was shaken in an atmosphere of hydrogen with 0.10 g. of a pre-reduced 5% palladium-on-barium sulfate catalyst until uptake of gas ceased (*ca.* 1 hour). Filtration, concentration and crystallization of the residue from ace-

(15) *Cf.* the change diosgenin acetate ($[\alpha]^{20}_D$ −118°; $[M]_D$ −538) to "pseudodiosgenin" diacetate ($[\alpha]^{20}_D$ −31°, $[M]_D$ −154) (S. Kaufmann and G. Rosenkranz, THIS JOURNAL, **70**, 3502 (1948)).

(16) Rotations were determined at 20° in chloroform solution unless specified otherwise.

(17) Melting points are uncorrected. Ultraviolet absorption spectra were determined in 95% ethanol solution. Infrared spectra were obtained with a Perkin–Elmer model 12C single beam spectrophotometer with sodium chloride prism. We are indebted to Miss P. Revaque (Mrs. P. Lopez) for these measurements and to Miss A. Barba for the microanalyses. Thanks are due to Miss Olga Harris and Miss Carmen Fernandez for valuable technical assistance.

(18) We are indebted to Mr. Humberto Flores for carrying out this pyrolysis.

(19) C. Djerassi, J. Romo and G. Rosenkranz, *J. Org. Chem.*, **16**, 754 (1951).

TABLE I

MOLECULAR ROTATION DATA OF RING A AROMATIC STEROIDS[16]

Series	$[M]^{Sat.}_D$ (3β-Acetoxy-5α)	$[M]^{IIIa}_D$ (19-Nor-$\Delta^{1,3,5,8}$-tetraen-3-ol)	$[M]^{IVa}_D$ (19-Nor-$\Delta^{1,3,5}$-trien-3-ol)	$[M]^{IX}_D$ (19-Nor-1-methyl-3-acetoxy-$\Delta^{1,3,5,8}$-tetraene)	$[M]^{X}_D$ (19-Nor-1-methyl-3-acetoxy-$\Delta^{1,3,5}$-triene)	$[M]^{IIIa}_D - [M]^{sat.}_D$	$[M]^{IVa}_D - [M]^{sat.}_D$	$[M]^{IX}_D - [M]^{sat.}_D$	$[M]^{X}_D - [M]^{sat.}_D$
Androstan-17-one (dioxane)	+232[a]	−340[9a]	+437[9a]	−305[13a]	+714[13a]	−572	+205	−537	+482
Androstan-17β-ol acetate	− 9[a]	−633[9b]	+148[9b]	−548[13a]	+411[13a]	−624	+157	−539	+420
Methyl etianate	+135[b]	−215[c]	+339[c]	−294[c]	+721[c]	−350	+204	−429	+586
Δ^{16}-Pregnen-20-one	+150[d]	....	+349[6]	−350[6]	.....	...	+199	−500	...
Cholestane	+ 60[e]	−216[10]	+276[10]	−422[13c]	.....	−276	+216	−482	...
22a-Spirostane	−316[a]	−796[f]	− 75[f]	−810[f]	+212[f]	−480	+241	−498	+528

[a] Determined in these laboratories. [b] L. Ruzicka, E. Hardegger and C. Kauter, *Helv. Chim. Acta*, **27**, 1164 (1944). [c] A. Sandoval, G. Rosenkranz, C. Djerassi and F. Sondheimer, THIS JOURNAL, in press. [d] P. A. Plattner, L. Ruzicka, H. Heusser and E. Anliker, *Helv. Chim. Acta*, **30**, 385 (1947). [e] D. H. R. Barton, *J. Chem. Soc.*, 813 (1945). [f] This paper.

tone–hexane afforded 0.16 g. of the methoxy ketone VIb, m.p. 134–137°, λ_{max} 278 mμ (log ε 3.42), $\nu^{CHCl_3}_{max}$ 1700 cm.$^{-1}$. Identity with an authentic specimen[6] (m.p. 134–136°) was established through mixture m.p. determination and infrared comparison.

1-Methyl-19-nor-$\Delta^{1,3,5(10),8}$-22a-spirostatetraen-3-ol Acetate (IX).—A mixture of 3.0 g. of finely powdered $\Delta^{1,4,6}$-22a-spirostatrien-3-one (II)[3] suspended in 75 cc. of acetic anhydride containing 1.0 g. of *p*-toluenesulfonic acid was stirred at room temperature for 20 hours. As the reaction proceeded a homogeneous solution resulted, but after the 20-hour period a new precipitate had separated. This solid, which proved to be the desired rearrangement product, was collected and washed well with water; it weighed 0.69 g. and showed m.p. 164–169°. The filtrate was poured into water, the precipitated solid was taken up in ethyl acetate, and the solution was washed well with sodium bicarbonate and water, dried and evaporated. Trituration of the residue with methanol furnished another 0.22 g. (total yield 0.91 g., 28%) of the phenol acetate, m.p. 162–168°. The analytical sample was obtained through crystallization from chloroform–methanol and formed glistening plates, m.p. 170–172°, $[\alpha]_D$ −180°, λ_{max} 224 mμ (log ε 4.44) and 266 mμ (log ε 3.97), $\nu^{CHCl_3}_{max}$ 1744 cm.$^{-1}$, no free hydroxyl band.

Anal. Calcd. for $C_{29}H_{38}O_4$: C, 77.30; H, 8.50. Found: C, 77.62; H, 8.72.

When the above dienone phenol rearrangement was performed at steam-bath temperature, the same product could be isolated, but in considerably lower yield.

1-Methyl-19-nor-$\Delta^{1,3,5(10)}$-22a-spirostatrien-3-ol Acetate (X).—The tetraene acetate IX (0.50 g.) dissolved in 50 cc. of ethyl acetate was hydrogenated with 0.20 g. of a 5% palladium-on-charcoal catalyst overnight at atmospheric pressure and room temperature. Crystallization of the product from ethyl acetate–hexane furnished 0.39 g. of the triene acetate with m.p. 210–215°. The analytical specimen formed felted needles, m.p. 218–219°, $[\alpha]_D$ +47°, λ_{max} 270 mμ (log ε 2.57), $\nu^{CHCl_3}_{max}$ 1744 cm.$^{-1}$, no free hydroxyl band.

Anal. Calcd. for $C_{29}H_{40}O_4$: C, 76.95; H, 8.91. Found: C, 77.32; H, 9.08.

MEXICO CITY 17, D. F.

[CONTRIBUTION FROM THE CHEMICAL RESEARCH SECTION, PICATINNY ARSENAL]

Contribution to the Chemistry of Benzfuroxan and Benzfurazan Derivatives

BY R. J. GAUGHRAN, J. P. PICARD AND J. V. R. KAUFMAN

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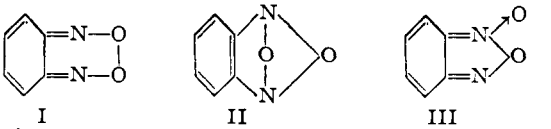
Chemical and physical data are offered in support of the unsymmetrical quinonoid structure for benzfuroxan and its derivatives. The metallic salts obtained from 4,6-dinitrobenzfuroxan are discussed in view of structures previously postulated. Sufficient infrared data were obtained to establish the general absorption difference between benzfuroxan and benzfurazan. In addition, five new compounds were prepared: 5-methoxybenzfuroxan, 1,3-dinitro-4,6-diazidobenzene, 5-azido-6-nitrobenzfuroxan, nitrobenzdifuroxan and 5-methoxybenzfurazan.

Introduction

The wide variety of applications suggested for benzfuroxan and its derivatives as dyes,[1] fungicides, parasiticides[2] and explosives[3] is mostly responsible for the numerous attempts found in the literature to elucidate its structure.

In 1907, Forster and Fierz[4] stated that benzfuroxan and its derivatives could not be considered true dinitroso compounds but should be regarded as dioxime peroxides, I. Green and his group[1] suggested the epoxide ring structure II and this structure subsequently received support from Forster, *et al.*,[5] who observed that no isomer due to the orientation of extra annular oxygen in structure III could be isolated. Hammick[6] (1931) studying the action of bromine upon benzfuroxan and benzfurazan derivatives obtained results which were interpreted as indicating that these compounds had quinonoid properties.



I II III

Of the three previously suggested structures, the peroxide and epoxide derivatives should be capable of forming symmetrical difuroxan compounds IV while such symmetrical derivatives would not be realized if the structure were *o*-quinonoid in nature.

(1) A. G. Green and F. M. Rowe, *J. Chem. Soc.*, **101**, 2457 (1912).

(2) Ter Horst, U. S. Patent 2,424,199(1947); *C. A.*, **41**, 7642 (1947).

(3) H. Rathsburg, British Patent 190,844 (1921); *C. A.*, **17**, 2960 (1923).

(4) M. O. Forster and H. E. Fierz, *J. Chem. Soc.*, **91**, 1943 (1907).

(5) M. O. Forster and M. F. Barker, *ibid.*, **103**, 1918 (1913).

(6) D. L. Hammick, W. A. M. Edwardes and E. R. Steiner, *ibid.* 3308 (1931).