Claisen flask in a bath at 130°. The fraction, b.p. 89° (3.5 mm.), was collected (23.1 g., 92%). For analysis the product was recrystallized from *n*-hexane to yield pale yellow crystals, m.p. 62.5–63°. Absorption spectra were obtained on this and related azomethines at concentrations of approximately 10^{-4} *M* in absolute alcohol. $\lambda_{\max.}$ 225, 287, 325 mμ; log ε 4.11, 4.27, 4.30; $\lambda_{\min.}$ 250, 303 mμ; log ε 3.59, 4.26.

Anal. Calcd. for $C_{11}H_8NOBr$: C, 52.82; H, 3.22; N, 5.60. Found: C, 52.97; H, 3.22; N, 5.68.

1-N-*p*-phenylazophenylimino-5-phenylamino-2-hydroxypenta-2,4-diene Hydrochloride.[11]—N-*p*-Phenylazophenylfurfurylideneimine (2.75 g.[12]; $\lambda_{\max.}$ 225, 240, 367 mμ; log ε 4.16, 4.15, 4.24; $\lambda_{\min.}$ 233, 267 mμ; log ε 4.15, 3.85) was dissolved in a minimum amount of anhydrous ethanol, and 1.29 g. of aniline hydrochloride was added. The solution turned purple and deposited 3.29 g. (81%) of purple crystals, m.p. 157° dec. The product was washed with an excess of ether–alcohol (2–1) and then dried under diminished pressure. The melting point and color were unaltered. Fresh solutions[8] of the dianils were examined in absolute alcohol: form A, $\lambda_{\max.}$ 245, 310, 395, 555, 590 mμ; log ε 4.24, 3.96, 4.65, 3.60, 3.58; $\lambda_{\min.}$ 230, 290, 515, 580 mμ; log ε 4.22, 3.92, 3.51, 3.45.

Anal. Calcd. for $C_{23}H_{21}N_4OCl$: C, 68.2; H, 5.2; N, 13.84; Cl, 8.75. Found (cor. for ash): C, 67.6; H, 5.1; N, 13.85; Cl, 8.6.

Conversion of Form A to Form B.—The lower-melting form was dissolved in methanol at room temperature. The solution was chilled, and the purple crystals were washed with methanol–ether; m.p. 174° dec. Further recrystallization and drying under diminished pressure did not alter the melting point; $\lambda_{\max.}$ 245, 295, 392, 540 mμ; log ε 4.24, 3.93, 4.54, 3.73; $\lambda_{\min.}$ 230, 290, 320, 500, 610 mμ; log ε 4.19, 3.92, 3.91, 3.63, 3.61.

Anal. Found (cor. for ash): C, 67.8; H, 4.9; N, 13.8; Cl, 8.7.

1-N-*p*-Bromophenylimino-5-phenylamino-2-hydroxypenta-2,4-diene Hydrochloride.—N-*p*-Bromophenylfurfurylideneimine (0.83 g.) was dissolved in a minimum amount of anhydrous ethanol. A solution of aniline hydrochloride (1.3 g.) in anhydrous ethanol was added, and the mixture was allowed to stand. The purple crystals (0.5 g., 40%), m.p. 151° dec., were collected and washed with anhydrous ethanol. The melting point and color were unchanged upon repeated recrystallization and drying under diminished pressure at 76°. The compound was extremely hygroscopic and retains one molecule of water of crystallization upon exposure to moist air.

Anal. Calcd. for $C_{17}H_{16}N_2ClOBr \cdot H_2O$: C, 51.3; H, 4.56; N, 7.05; Br, 20.10; Cl, 8.92; H_2O, 4.53. Found: C, 51.6; H, 4.4; N, 6.99; Br, 20.01; Cl, 8.88; H_2O (by loss of weight at 100° under diminished pressure), 4.51.

1-N-*p*-Hydroxyphenylimino-5-phenylamino-2-hydroxypenta-2,4-diene Hydrochloride.—To 7.0 g. of N-*p*-hydroxyphenylfurfurylideneimine[13] in 50 ml. of ethanol, a solution of 4.9 g. of aniline hydrochloride in 20 ml. of ethanol was added. On standing, the solution deposited 8.3 g. (70%) of purple crystals, m.p. 163–166° dec. For analysis the compound was recrystallized from ethanol and dried under diminished pressure. The purple product melted at 171–172° dec.; $\lambda_{\max.}$ 250, 292, 520 mμ; log ε 3.93, 3.83, 4.18; $\lambda_{\min.}$ 230, 272, 400 mμ; log ε 3.87, 3.78, 3.61.

Anal. Calcd. for $C_{17}H_{17}N_2O_2Cl$: C, 64.46; H, 5.41; N, 8.85. Found: C, 64.76; H, 5.71; N, 8.81.

1-*p*-Bromophenylimino-5-*p*-bromophenylamino-2-hydroxypenta-2,4-diene Hydrochloride.—To a solution of 1.72 g. of *p*-bromoaniline in 20 ml. of absolute alcohol was added 0.96 g. of furfural. The mixture was heated to 60° and then allowed to cool to room temperature. A solution of 2.09 g. of *p*-bromoaniline hydrochloride in 25 ml. of absolute alcohol was added with stirring. On standing, the solution deposited 1.4 g. of purple dianil hydrochloride, m.p. 159–160° dec. The crystals were collected and washed with alcohol–ether (1–1). For analysis the compound was dried under diminished pressure. Recrystallization from absolute alcohol did not affect the melting point of the crystals. An additional amount of product was obtained from the mother liquors to give a total yield of 3.92 g. (86%).

Anal. Calcd. for $C_{17}H_{15}N_2OClBr_2$: C, 44.5; H, 3.3. Found: C, 44.6; H, 3.3.

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[11] For simplicity of nomenclature it is assumed throughout this paper that no interchange has caused inversion of substituents between the 1- and 5-positions.

[12] M. Betti, *Gazz. chim. ital.*, **281**, 243 (1898).

[13] H. Schiff, *Ann.*, **201**, 355 (1880), prepared this compound, m.p. 180–182°. Our imine obtained by recrystallization from warm ethanol melted at 185–186°. *Anal.* Calcd. for $C_{11}H_9NO_2$: C, 70.6; H, 4.85; N, 7.48. Found: C, 70.8; H, 4.87; N, 7.56; $\lambda_{\max.}$ 223, 286, 342 mμ; log ε 4.02, 4.19, 4.30. $\lambda_{\min.}$ 226, 253, 306 mμ; log ε 3.87, 3.77, 4.03. Rombaut and Smets reported m.p. 187–188°, and $\lambda_{\max.}$ 285, 341 mμ; log ε 4.21, 4.33.

Isomerization of Isospirostans to Furostenols with Pyridine Hydrochloride as the Catalyst

BY WILLIAM G. DAUBEN AND GERHARD J. FONKEN

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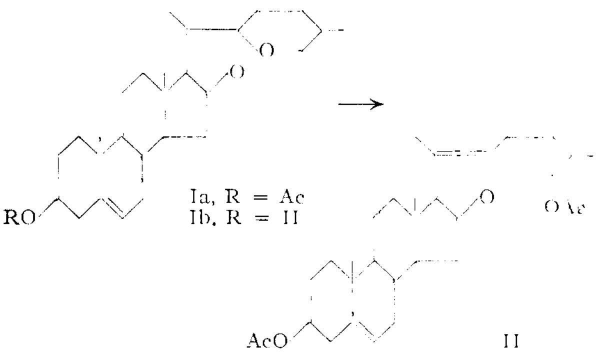
The isomerization of an isospirostan to a furostenol was studied by Gould, Staeudle and Hershberg[1] and they found that the conversion could be achieved at the boiling point of acetic anhydride in the presence of a Lewis acid such as aluminum chloride or acetyl chloride. Similar conditions, using acetyl chloride, also have been employed to convert $\Delta^{4,6}$-22-isospirostadiene-3-one to the corresponding 3-acetoxy-3,5,7-triene.[2] Although this latter reaction was complicated by the tendency of the starting ketone to form 3,26-diacetoxy-3,5,7,-20(22)-furostatetraene, the major product always contained the side-chain intact. In contrast, however, when the enol acetylation was conducted in the presence of one equivalent of pyridine (per mole of steroid), the enol acetate of furostatetraene was obtained in a yield of 40%. In view of the increased reactivity of the reaction system toward isospirostan ring isomerization when the pyridine was present, the role of this base in such a conversion has been evaluated.



Ia, R = Ac
Ib, R = H

II

It was found that when 22-iso-5-spirosten-3β-ol acetate (diosgenin acetate, Ia) was allowed to

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[1] D. H. Gould, H. Staeudle and E. B. Hershberg, THIS JOURNAL, **74**, 3685 (1952).

[2] W. G. Dauben, J. F. Eastham, R. A. Micheli, K. H. Takemura, L. Mandell and J. M. Chemerda, *ibid.*, **75**, 3255 (1953).

react with acetyl chloride and acetic anhydride in the presence of one mole equivalent of pyridine (per mole of steroid) for three hours at reflux temperature, the majority of the starting material was recovered. When the reaction time was increased to 15 hours, the furostadiene diacetate II was obtained in 55% yield and if the heating period was further extended to 24 hours, II was isolated in a yield of 85%. The Schering workers[1] have reported that in the absence of pyridine the reaction proceeds in a period of 4 hours, but no yield of the reaction product is given. Nevertheless, the present results are in marked contrast to the ease of ring opening in the enol acetylation studies and suggest that the base itself is not the effective catalyst. Since in the latter reaction pyridine hydrochloride would be present in the mixture, the isomerization was attempted on 22-iso-5-spirosten-3β-ol (Ib) itself, and it was found that after 5 hours the furostadiene diacetate II could be obtained in 80% yield. That such an increased reactivity was due to the pyridine hydrochloride was demonstrated by allowing the acetate Ia to react with acetic anhydride and the salt for 5 hours, whereupon the diacetate II was isolated in a yield of 84%. Furthermore, the salt must be of a strong acid since the monoacetate Ia was obtained from the free alcohol Ib when only acetic anhydride and pyridine were employed.

It was found, however, that when the isospirostan was allowed to react with pyridine hydrochloride in a non-acetylating solvent such as methanol, only the starting material was recovered. Such a result emphasizes the fact that the formation of the 26-acetate is a necessary step in the isomerization reaction. This latter might be expected in view of the reported[1] reconversion of II to I under acidic hydrolysis conditions.

Experimental

Reaction of 22-Iso-5-spirosten-3β-ol Acetate (Ia) in Presence of Pyridine.—A mixture of 1.00 g. (2.1 mmoles) of the acetate (m.p. 188–190°), 5 ml. of acetic anhydride, 1 ml. of acetyl chloride (purified) and 0.168 g. (2.1 mmoles) of pyridine was heated under reflux for 3 hours, cooled to 50° and the solvents removed under reduced pressure. The dark red solid residue was dissolved in hot methanol, treated with Norit and the solution deposited 0.87 g. of white crystals, m.p. 170–177°. Recrystallization yielded 0.68 g., m.p. 187–189°. Concentration of the mother liquors yielded only a small amount of crystalline material which upon further recrystallization melts from 140–145°.

When the reaction was allowed to reflux for 15 hours and processed as above, the solid from the first methanol recrystallization amounted to 0.56 g., m.p. 87–91°, and the mother liquor upon standing deposited a further quantity of similar material. The total solid was recrystallized from ethanol (Norit); yield 0.59 g. (55%), m.p. 95–98°, $[\alpha]^{25}\mathrm{D}$ −48.8° ($CHCl_3$). Gould, Staeudle and Hershberg[1] report m.p. 93–98° for their crude material from the aluminum chloride catalyzed isomerization and m.p. 98.5–100.5°, $[\alpha]^{25}\mathrm{D}$ −47.0° ($CHCl_3$), after chromatography.

When 2.0 g. of the acetate Ia was allowed to react with 10 ml. of acetic anhydride, 2 ml. of acetyl chloride and 0.336 g. of pyridine for 24 hours and processed as above, 1.83 g. (85%) of the diacetate was obtained, m.p. 94–97°, $[\alpha]^{25}\mathrm{D}$ −47.2° ($CHCl_3$). The infrared spectrum was identical with that prepared by the aluminum chloride method.

Reaction of 22-Iso-5-spirosten-3β-ol (Ib) in Presence of Pyridine.—A mixture of 2.0 g. (4.7 mmoles) of the alcohol Ib, m.p. 204–206°, 10 ml. of acetic anhydride, 2 ml. of acetyl chloride and 0.37 g. (4.7 mmoles) of pyridine was heated under reflux for 5 hours, the reaction mixture concentrated under reduced pressure and the residue dissolved in 50 ml. of methanol. After concentration to 25 ml. and cooling, 1.2 g., m.p. 92–95°, of solid was obtained and further concentration of the mother liquor yielded an additional 0.9 g. The combined materials were recrystallized from 20 ml. of methanol; yield 1.86 g. (80%), m.p. 95–98°, $[\alpha]^{21}\mathrm{D}$ −47.8° ($CHCl_3$).

Reaction of 22-Iso-5-spirosten-3β-ol Acetate in Presence of Pyridine Hydrochloride.—A mixture of 2.0 g. of the acetate, 10 ml. of acetic anhydride and 0.65 g. of dry pyridine hydrochloride was heated for 5 hours and processed by pouring into ice-water. After filtration and recrystallization, the diacetate II was identical with the above; yield 1.8 g. (84%).

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The Reaction of Diphenyliodonium Ion with Hydroxide Ion[1]

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The decomposition of diaryliodonium salts has been represented both as an ordinary nucleophilic displacement on the aromatic system by the anion,[2] and as a unimolecular decomposition to give an aryl cation and the aryl iodide.[3] Qualitative evidence on the direction of fission of unsymmetrical iodonium salts[4,2a] and on the stabilities of salts with anions of different nucleophilic power[5] both suggested that the unimolecular mechanism was unlikely in that the results of both are predictable on the basis of an analogy to the bimolecular displacement of chlorine from substituted chlorobenzenes.[2b] This evidence does not rigorously exclude the unimolecular mechanism, however, since the systems were in most cases heterogeneous. Because of our interest in aryl cations derived from diazonium salts, we have searched for other sources of these ions, and had investigated the hydrolysis of iodonium salts from this viewpoint, before the appearance of the further evidence of Beringer and co-workers[2a] which made the unimolecular mechanism very improbable.

Not only is the order not definitely established but the products are complicated by the possibility of consecutive reactions. By the bimolecular path the reactions would be 1 and 2

$$(C_6H_5)_2I^+ + OH^- \longrightarrow C_6H_5I + C_6H_5OH \qquad (1)$$

$$(C_6H_5)_2I^+ + OC_6H_5^- \longrightarrow C_6H_5I + (C_6H_5)_2O \qquad (2)$$

Diphenyl ether has indeed been detected by Beringer,[2a] but since it might also arise from the phenyl cation, the unimolecular reaction cannot be eliminated on this basis.

Kinetic measurements of even a crude sort will tell whether or not the rate of decomposition of diphenyliodonium ion is dependent on the hydrox-

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(1) From the M.A. Thesis of C. A. Stout, **1953**.

(2) (a) F. M. Beringer, A. Brierly, M. Drexler, E. M. Gindler and C. C. Lumpkin, THIS JOURNAL, **75**, 2708 (1953); (b) J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 273 (1951).

(3) H. J. Lucas, E. R. Kennedy and C. A. Wilmot, THIS JOURNAL, **58**, 157 (1936).

(4) R. B. Sandin, M. Kulka and R. McCready, *ibid.*, **59**, 2014 (1937).

(5) R. B. Sandin, F. T. McClure and F. Irwin, *ibid.*, **61**, 2944 (1939).