SO_3H and $C_6H_5 \cdot CH{=}CH \cdot SO_3H$. In our case, the analogous initial product would lose two molecules of water instead of one. It would seem not impossible that the cycloisomerization of allylbenzenes proceeds *via* similar addition products.

Experimental

1,1-Diphenylpropanol has been prepared from propiophenone and phenylmagnesium bromide,[7] m.p. 95° (from ethanol) (lit.[8] m.p. 94–95°). The dehydration was carried out according to Klages[8]; **1-1,diphenylpropylene** boiled at 149° (11 mm.).

2-Methyl-3-phenylbenzothiophene 1,1-Dioxide (I). A.—A mixture of 2 g. of 1,1-diphenylpropylene and 20 ml. of concentrated sulfuric acid was kept at room temperature for 1 week and poured into cold water. The solid was filtered and recrystallized from petroleum ether (b.p. 90–100°), yield 0.5 g., m.p. 114°. In all experiments, the balance of material consisted of water-soluble, sulfonated products which were not further investigated.

B.—A mixture of 10 g. of 1,1-diphenylpropanol and 50 ml. of concentrated sulfuric acid was kept at room temperature for 7 days and the brownish green solution was poured into water. The precipitate (7 g.) was recrystallized from petroleum ether (b.p. 70–90°) and formed needles, m.p. 114°.

Anal. Calcd. for $C_{15}H_{12}O_2S$: C, 70.3; H, 4.7; S, 12.5; mol. wt., 256. Found: C, 70.4; H, 5.0; S, 12.4; mol. wt., 248 (Rast method).

2-Methyl-3-phenyl-2,3-dihydrobenzothiophene 1,1-Dioxide.—The foregoing substance (4 g.) in 120 ml. of boiling propanol was treated for 4 hr. with hydrogen in the presence of palladium on barium sulfate (2 g.). On cooling, the filtered solution deposited the dihydro derivative of I, which was recrystallized from propyl alcohol and melted at 169–170°. The yield was almost quantitative.

Anal. Calcd. for $C_{15}H_{14}O_2S$: C, 69.7; H, 5.4. Found: C, 69.8; H, 5.4.

5-Chloro-3-(*p*-chlorophenyl)-2-methylbenzothiophene 1,1-Dioxide.—The reaction of *p*-chlorophenylmagnesium bromide (3 moles) and ethyl propionate (1 mole) gave, after the usual work-up, a product of sharp boiling point (178° at 2 mm.) which, however, according to the analysis consisted of a mixture of 1,1-di(*p*-chlorophenyl)propylene and 1,1-di(*p*-chlorophenyl)propanol; it was used directly for the next step.

Anal. Calcd. for $C_{15}H_{12}Cl_2$: C, 68.4; H, 4.6. Calcd. for $C_{15}H_{14}Cl_2O$: C, 64.0; H, 5.0. Found: C, 65.6; H, 4.5.

A mixture of 1 g. of the product and 10 ml. of concentrated sulfuric acid was kept at room temperature for 4 days and poured into ice–water. The solid product was filtered and recrystallized from ethanol. Thus, 440 mg. (yield 40%) of a colorless product, m.p. 236°, was obtained.

Anal. Calcd. for $C_{15}H_{10}Cl_2O_2S$: C, 55.4; H, 3.1; Cl, 21.8; S, 9.9. Found: C, 55.6; H, 3.1; Cl, 21.8; S, 10.2.

The n.m.r. spectra were measured in deuteriobenzene at 60 Mc., using tetramethylsilane as internal standard.

(7) C. Hell and H. Bauer, *Ber.*, **37**, 230 (1904).

(8) A. Klages, *ibid.*, **35**, 2646 (1902); A. Klages and S. Heilmann, *ibid.*, **37**, 1447 (1904).

16-Keto 19-Norsteroids.[1] Long-Range Conformational Effects

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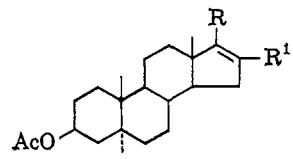
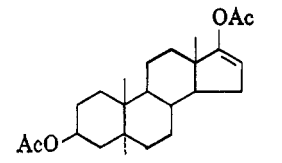
The presence of long-range conformational effects in steroids has been a well-recognized phenomenon.[2] These effects are reflected in rate differences of reactions at specific sites due to structural changes in distant parts of the molecule. This Note reports on an even more drastic effect on reactions in ring D due to structure alterations in ring A. An attempt is also made to define the cause for this effect.

Both 17-oxo-5α-androstan-3β-ol and 17-oxo-estra-1,3,5(10)-trien-3-ol give the respective enol diacetates Ia and II in essentially quantitative yield under mild conditions.[3] However, the corresponding 16-keto compounds give widely divergent results. 16-Oxo-5α-androstan-3β-ol yields the enol diacetate Ib although in consistently poorer yield than the corresponding 17-keto compound[4]; in contrast, the 16-keto estrogen derivative IV failed to yield any enol acetate under various conditions.[5,5a] Clearly, this change in the ease of enolization of the 16-ketone must be occasioned by the changes in ring A structure, *i.e.*, aromatic unsaturation and lack of the C-19 methyl group. In an effort to isolate the cause, the effect of only one of these changes on the enolization of the 16-ketone was of interest. The 16-keto-19-norandrostane structure provides a suitable substrate since it lacks

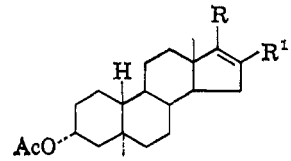


Ia, R = CH_3COO; R^1 = H

b, R = H; R^1 = CH_3COO

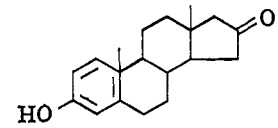


II

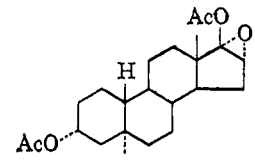


IIIa, R = CH_3COO; R^1 = H

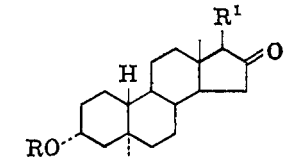
b, R = H; R^1 = CH_3COO



IV



V



VIa, R = H; R^1 = OH

b, R = CH_3CO; R^1 = CH_3COO

c, R = CH_3CO; R^1 = H

d, R = R^1 = H

(1) This research was supported by a grant from the American Cancer Society and Grant CA 03704 from the National Cancer Institute.

(2) D. H. R. Barton, F. McCapra, P. J. May, and F. Thudium, *J. Chem. Soc.*, 1297 (1960).

(3) N. S. Leeds, D. K. Fukushima, and T. F. Gallagher, *J. Am. Chem. Soc.*, **76**, 2943 (1954).

(4) J. Fajkos and J. Joska, *Chem. Ind.* (London), 872 (1960); J. Fishman, *ibid.*, 1078 (1961).

(5) J. Fishman, *J. Am. Chem. Soc.*, **82**, 6143 (1960).

(5a) NOTE ADDED IN PROOF.—The preparation of the enol diacetate from 16-oxoestra-1,3,5(10)-trien-3-ol has just been reported: J. R. Rhone and M. N. Huffman, *Tetrahedron Letters.*, **No. 19**, 1395 (1965). The authors have informed us that the reaction is successful only in the presence of *anhydrous* *p*-toluenesulfonic acid as catalyst, and they confirm our findings that the reaction fails when *p*-toluenesulfonic acid monohydrate is used. Since the estrone IV and androstane 16-keto VIa derivatives yield enol diacetates in the presence of the monohydrate a significant difference in the enol stability must exist and the views offered in this Note require no amendment.

(6) D. K. Fukushima and S. Dobriner, *J. Org. Chem.*, **26**, 3022 (1961).

the C-19 methyl group but has no unsaturation in ring A. The desired compound was prepared using 17-oxo-5α-estran-3α-ol[6] as the starting material. The enol diacetate IIIa was prepared without difficulty and was treated with perbenzoic acid, to yield the epoxy compound V, which was not isolated, but was directly hydrolyzed and rearranged with methanolic sodium hydroxide to the 16-keto-17β,3α-diol VIa.[3,5] The diacetate VIb prepared from VIa was then deacetoxylated with zinc in acetic acid[7] to yield the desired 16-oxo-5α-estran-3α-ol acetate VIc which was hydrolyzed to the free 3-hydroxy compound, VId.

The new 19-nor 16-ketone upon exposure to the usual conditions of exchange with isopropenyl acetate yielded the enol diacetate IIIb in a yield comparable to the corresponding androstan-16-one compound. The structure of the new enol diacetate was assigned by analogy to the enol diacetate obtained from the corresponding C-19 derivative,[4] with enolization occurring towards C-17, although it is possible that a small percentage of the isomeric Δ^{15}-enol acetate was also present. The results obtained confirm what might have been predicted, that the aromatic nature of ring A accounts for the difference observed in ring D and that "buttressing"[2] effects of the C-19 methyl group are immaterial as far as this aspect of ring D chemistry is concerned.

There appears to be no obvious reason for the failure of the C-16 ketone with an aromatic ring A to enolize and yield an enol acetate, in contrast to the corresponding ring A saturated compounds. It is possible that an extension of the conformational argument used to explain the lesser enolization of C-16 ketone *vs.* C-17 ketone in the androstane series[5] can be applied. By this rationale, the stability difference between the C-16 and C-17 ketones is magnified in the presence of an aromatic ring A due to long-range conformational effects. The resultant greater energy difference between the C-16 ketone and its enol in the ring A aromatic compound will then account for the lack of formation of the enol acetate. Admittedly, the angular distortions due to these long-range conformational effects are not apparent from models, but they may be of a more subtle nature and also the models are not adequately representational of ring D conformation.

Experimental[8]

5α-Estr-16-ene-3α,17-diol Diacetate (IIIa).—To a solution of 2.8 g. of 3α-hydroxy-5α-estran-17-one in 30 ml. of isopropenyl acetate was added 5 ml. of isopropenyl acetate containing 0.1 ml. of H_2SO_4. The solution was allowed to distil slowly, so that after 1.5 hr. 10 ml. of distillate was collected. Another 15 ml. of isopropenyl acetate containing 0.02 ml. of H_2SO_4 was then added, and the solution was concentrated to half volume by slow distillation during 1.5 hr. The reaction mixture was cooled and diluted with 200 ml. of ethyl ether and was then washed with cold sodium bicarbonate solution and water. After drying, the solvent was removed and the residue was taken up in hot petroleum ether (b.p. 30–60°) and filtered through a short (5 g.) acid-washed alumina column. Concentration of the petroleum ether gave 2.6 g. of IIIa, m.p. 158–162°, $[\alpha]^{24}D$ −145°.

Anal. Calcd. for $C_{22}H_{32}O_4$: C, 73.30; H, 8.95. Found: C, 73.42; H, 9.21.

16-Oxo-5α-estrane-3α,17β-diol (VIa).—A solution of 2.0 g. of enol diacetate IIIa in 25 ml. of chloroform was allowed to stand with a 10% excess of perbenzoic acid at 5° for 20 hr. The solution was then washed with 0.1 *N* NaOH solution and water, dried, and evaporated. The colorless oily residue containing the epoxide V was dissolved in 250 ml. of methanol, and 120 ml. of 1 *N* NaOH solution was added. After standing at room temperature for 72 hr., the reaction mixture was concentrated to one-third volume *in vacuo* and extracted well with ether, which was washed with water, dried, and evaporated. The residue was chromatographed on silica. Elution with chloroform and crystallization from dilute methanol gave the VIa, m.p. 160–164°.

Anal. Calcd. for $C_{18}H_{28}O_3$: C, 73.93; H, 9.65. Found: C, 74.10; H, 9.43.

The diacetate VIb prepared in the usual manner resisted crystallization.

16-Oxo-5α-estran-3α-ol (VId).—A solution of 750 mg. of oily diacetate VIb in 90 ml. of acetic acid and 4 ml. of acetic anhydride was refluxed with 40 g. of zinc dust for 24 hr. The metal was filtered off and washed well with hot ethanol. The filtrate was concentrated under vacuum, diluted with water, and extracted with ether. The ether was washed with 5% sodium bicarbonate solution and then water, dried, and evaporated. The residue was chromatographed on acid-washed alumina. Elution with 4:1 petroleum ether–benzene and crystallization from petroleum ether–acetone gave 140 mg. of 16-oxo-5α-estran-3α-ol acetate (VIc), m.p. 90–92°, $[\alpha]^{24}D$ −138°.

Anal. Calcd. for $C_{20}H_{30}O_3$: C, 75.43; H, 9.50. Found: C, 75.24; H, 9.28.

The acetate VIc was hydrolyzed in the usual manner in refluxing methanolic potassium hydroxide to give, after work-up and crystallization from acetone–petroleum ether, VId, m.p. 153–155°, $[\alpha]^{24}D$ −140°.

Anal. Calcd. for $C_{18}H_{28}O_2$: C, 78.21; H, 10.21. Found: C, 77.92; H, 9.82.

5α-Estr-16-ene-3α,16-diol Diacetate (IIIb).—A 50-mg. sample of VIc was dissolved in 6 ml. of isopropenyl acetate and 0.2 ml. of a solution prepared from 0.1 ml. of H_2SO_4, and 5 ml. of isopropenyl acetate was added. The reaction solution was slowly distilled so that one-third of the volume distilled in 1.5 hr. An additional 3 ml. of isopropenyl acetate and 0.1 ml. of the catalyst solution was added, and the slow distillation was continued for another 1.5 hr. The work-up and chromatography were carried out as described above to give 24 mg. of crystalline enol diacetate IIIb, m.p. 139–142°. Recrystallization from petroleum ether gave the analytical sample, m.p. 142–145°.

Anal. Calcd. for $C_{22}H_{30}O_4$: C, 73.71; H, 8.44. Found: C, 73.46; H, 8.53.

(7) R. S. Rosenfeld and T. F. Gallagher, *J. Am. Chem. Soc.*, **77**, 4367 (1955).

(8) Melting points were determined on a Fisher-Johns block and are uncorrected. Analyses were by Spang Laboratory, Ann Arbor, Mich.

7-Phenyldibenz[*a*,*h*]anthracene and Benzo[*e*]naphtho[1,2-*b*]pyrene[1,2]

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There have been three general methods applied to the preparation of dibenz[*a*,*h*]anthracene derivatives. The first which was developed by Clar,[4] is based on the Elbs reaction in which an appropriate ketone is converted to the dibenz[*a*,*h*]anthracene by pyrolysis. This method affords by far the most rapid and economical method known for the synthesis of the parent hydrocarbon but is not entirely satisfactory for the preparation of its derivatives since cleavage often occurs during pyrolysis. No substituents can be put in the

(1) The nomenclature used in this paper is that presented in the "Definitive Rules for Nomenclature of Organic Chemistry," *J. Am. Chem. Soc.*, **82**, 5545 (1960).

(2) Presented before the Division of Organic Chemistry at the Southeastern Regional Meeting of the American Chemical Society, Charlotte, N. C., Nov. 1963.

(3) Abstracted in part from the M.S. Thesis of P. D. H. presented to the Virginia Polytechnic Institute, 1962. National Defense Education Act Fellow, 1960–1963; Eastman Kodak Fellow, 1963–1964.

(4) E. Clar, *Ber.*, **62**, 350 (1929).