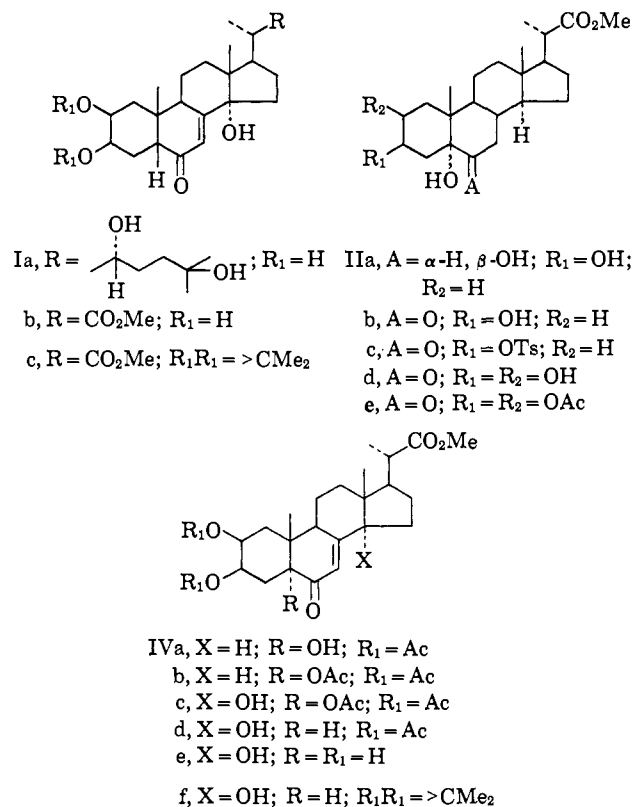


acetamide then gave $2\beta,3\beta$ -diacetoxy- 5α -hydroxy-6-keto-23,24-bisnorchol-7-en-22-oic acid methyl ester (IVa; mp 241–245°, $[\alpha]_D +32^\circ$, $\lambda_{\max} 247 \text{ m}\mu$ ($\epsilon 11,800$)). Acid-catalyzed acetylation of the latter led to the triacetate IVb (mp 184.5–185.5°, $[\alpha]_D +58^\circ$)⁹ into which the 14α -hydroxyl function was introduced directly by reaction with selenium dioxide in dioxane.¹⁰ The tertiary acetoxy group was removed from the derived 14α -hydroxy-6-keto- $2\beta,3\beta,5\alpha$ -triacetoxy-23,24-bisnorchol-7-en-22-oic acid methyl ester (IVc; mp 230–232°, $[\alpha]_D +75^\circ$, ν_{18-H} shifted downfield 2 cps by 14α -OH) by reaction with chromous chloride with stereospecific α -face entry of hydrogen to yield solely the thermodynamically less stable epimer, namely, the *trans* A/B fused product IVd (mp 250–254°, $[\alpha]_D +24^\circ$, nmr 40.5 cps (18-H)). Hydrolysis to the noncrystalline $2\beta,3\beta,14\alpha$ -triol IVe and inversion at C-5¹¹ under equilibrating conditions by treatment of IVe with 0.33% K_2CO_3 in aqueous MeOH furnished a 3:2 mixture of 6-keto- $2\beta,3\beta,14\alpha$ -trihydroxy-23,24-bisnor- 5β -chol-7-en-22-oic acid methyl ester (Ib; mp 232–235°, $[\alpha]_D +62^\circ$) and recovered IVe. The observed 19-proton resonance



of Ib (60.5 cps, pyridine solution) compares favorably with the frequency reported for ecdysone² (64 cps) while being well removed from the observed figure for the 5α epimer IVe (ν_{19-H} 77.5 cps).

An even more favorable ratio of $5\beta:5\alpha$ epimers was obtained by equilibration of the $2\beta,3\beta$ -acetonide IVf (mp 248–253° dec, $[\alpha]_D +116^\circ$) derived from the $2\beta,3\beta$ -diol IVe with *p*-toluenesulfonic acid and acetone, which afforded a 3:1 mixture of 6-keto- $2\beta,3\beta,14\alpha$ -

(9) The triester IVb was also obtained from the triol IID by successive acid-catalyzed acetylation, bromination, and dehydrobromination, but with an over-all lower yield.

(10) Cf. A. Zürcher, H. Heusser, O. Jeger, and P. Geistlich, *Helv. Chim. Acta*, **37**, 1562 (1954).

(11) The synthesis was designed specifically to obtain inversion at C-5 in a 6-keto steroid by relief of a severe 1,3-diaxial nonbonded interaction between the 2β -hydroxyl and 10β -methyl groups.

trihydroxy-23,24-bisnor- 5β -chol-7-en-22-oic acid methyl ester 2,3-acetonide (Ic; mp 226–232° dec, $[\alpha]_D +65^\circ$) and recovered starting material.

Arrival at structures Ib and Ic completed the synthesis of the tetracyclic skeleton of ecdysone with correct substitution pattern and stereochemistry.¹²

(12) Satisfactory analyses were obtained for all crystalline compounds.

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 A. D. Cross, J. A. Edwards, J. H. Fried

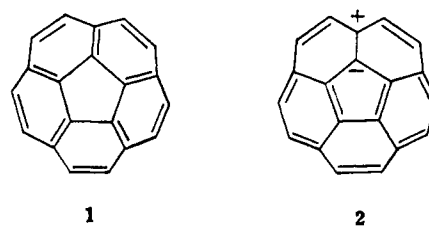
Institute of Steroid Chemistry, Syntex Research
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Received December 13, 1965

Dibenzo[ghi,mno]fluoranthene

Sir:

The polycyclic aromatic hydrocarbon, dibenzo[ghi,mno]fluoranthene (1), provides an interesting molecular structure for chemical studies. Within its structural framework is an unusual strain resulting from the geo-



metrical requirement that the bond angles deviate appreciably from the normal values found for benzenoid compounds. Undoubtedly this strain is distributed evenly across the five symmetry axes; however, *a priori*, it is difficult to predict whether a planar or bowl-shaped structure would result. It is also of interest to consider the possible contribution of polar resonance forms such as 2 to the actual electronic distribution of this system. This polar resonance form is unique in that it contains two charged concentric conjugated systems, the inner cyclopentadienyl anion and the outer cyclopentadecaheptenyl cation, each of which satisfies the requirements of Hückel's $4n + 2$ rule.^{1,2} The consideration of these structural and electronic factors led us to the synthesis of dibenzo[ghi,mno]fluoranthene to which we have assigned the trivial name "corannulene."³

Bromination of methyl 4,5-methylenephenanthrene-3-carboxylate⁴ (3) with *N*-bromosuccinimide afforded a 90% yield of the bromo ester 4 [mp 149–150°; $\lambda_{\max}^{\text{CHCl}_3}$ (μ) 5.80; τ_{CDCl_3} 1.75–2.2 (7 H, multiplet), 3.30 (1 H, singlet), and 5.92 (3 H, singlet) ppm. *Anal.* Found: C, 62.47; H, 3.26; Br, 24.35] which was used to alkylate triethyl 1,1,2-ethanetricarboxylate in the presence of potassium *t*-butoxide-*t*-butyl alcohol.⁵ The resulting

(1) See the discussion of peripheral conjugated systems by W. Barker and J. F. W. McCome in "Nonbenzenoid Aromatic Hydrocarbons," D. Ginsburg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, p 485.

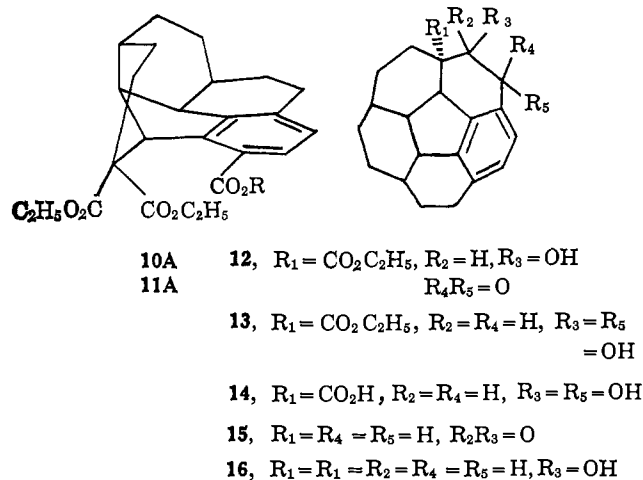
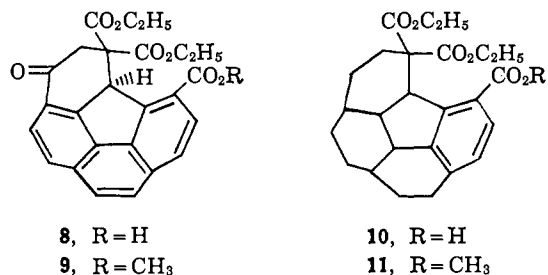
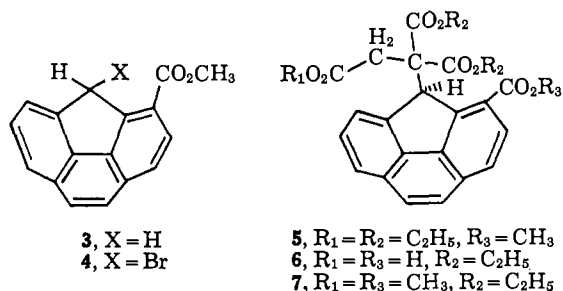
(2) A molecular orbital calculation by Gleicher has indicated that this polar form would probably contribute to the molecule and that the structure has considerable resonance energy. We wish to thank Dr. G. J. Gleicher for this information.

(3) The name is derived from the latin: *cor* meaning heart or within, and *annula* meaning ring. The name was also chosen so as to connote its relationship to coronene, its parent. We wish to thank the Classical Studies Department of the University of Michigan for discussion regarding the name.

(4) A. Sieglitz and W. Schidlo, *Chem. Ber.*, **96**, 1098 (1963).

(5) See, for example: W. Bachmann and J. Sheehan, *J. Am. Chem. Soc.*, **62**, 2687 (1940).

tetraester **5** was not isolated, but hydrolyzed by aqueous potassium hydroxide to the diacid diester **6** [97% overall yield from **4**; mp 202–207°; $\lambda_{\text{max}}^{\text{CHCl}_3-\text{Et}_3\text{N}}$ (μ) 5.80 and 6.12; τ_{pyridine} overlapping triplets at 8.65 and 8.7 (6 H), 7.38 (2 H, doublet), and 5.48 (4 H, quartet) ppm⁶] which was characterized as the dimethyl diethyl ester **7** [mp 141–142.5°; $\lambda_{\text{max}}^{\text{CHCl}_3}$ (μ) 5.89; $\lambda_{\text{max}}^{\text{EtOH}}$ ($m\mu$): 233 ($\epsilon 2.6 \times 10^4$), 258 ($\epsilon 3 \times 10^4$), and 315 ($\epsilon 1.15 \times 10^4$); τ_{CDCl_3} 8.75 (3 H, triplet) overlapping 8.62 (3 H, triplet), 8.12 (1 H, doublet), 6.6 (3 H, singlet), 6.03 (3 H, singlet), 5.74 (2 H, quartet) overlapping 5.55 (2 H, quartet), 3.92 (1 H, singlet), and 1.75–2.55 (7 H, multiplet). *Anal.* Found: C, 67.84; H, 5.57].



Cyclization of the diacid diester **6** was effected by treatment with polyphosphoric acid at 80°, producing a 70% yield of the keto acid diester **8** [mp 235–236°; $\lambda_{\text{max}}^{\text{CHCl}_3}$ (μ) 5.82, 5.99, and 6.20; $\lambda_{\text{max}}^{\text{EtOH}}$ ($m\mu$) 262 ($\epsilon 8 \times 10^4$), 298 ($\epsilon 2.7 \times 10^4$), and 330 ($\epsilon 3.2 \times 10^4$); τ_{CDCl_3} 9.75 (3 H, triplet), 8.71 (3 H, triplet), 6.59 (2 H, quartet), 6.40 (2 H, doublet), 5.58 (2 H, multiplet), and 4.60 (1 H, singlet) ppm. *Anal.* Found: C, 69.89; H, 4.70; methyl ester **9**, mp 158.5–160°]. Hydrogenolysis of the keto acid diester **8** in order to remove the keto group

(6) The very interesting features of the nmr spectra will be discussed in the full paper. Spectra were obtained on a Varian A-60.

was unexpectedly effective. Prolonged treatment of **8** at room temperature with hydrogen in an acetic acid slurry of 5% palladium on carbon at 50 psi afforded a single compound, **10**, in which not only the keto group had been removed but, in addition, two of the three aromatic rings had been hydrogenated! The dodecahydrobenzofluoranthrene diester acid (**10**) [mp 214–216°; $\lambda_{\text{max}}^{\text{CHCl}_3-\text{Et}_3\text{N}}$ 5.80 and 6.20 (broad); $\lambda_{\text{max}}^{\text{EtOH}}$ 245 ($\epsilon 6 \times 10^3$) and 290 ($\epsilon 1.79 \times 10^3$); τ_{CDCl_3} 8.70 (3 H, triplet) overlapping 8.78 (3 H, triplet), complex saturated CH, 5.75 (4 H, quartet), 3.1 (1 H, doublet), and 2.5 (1 H, doublet) ppm. *Anal.* Found: C, 70.21; H, 6.92] must have a stereochemistry derived by the addition of hydrogen to **8** exclusively on the side opposite the geminal carboethoxy groups. This structure was perfectly suited to our eventual needs, since the reduced rings allow the ester group on the concave side of the molecule at position 5 and the group on the aromatic ring to come quite close to one another (**10A**).

Treatment of the diester acid **10** with diazomethane produced the triester **11** [mp 115.5–117°; $\lambda_{\text{max}}^{\text{CHCl}_3}$ (μ) 5.82 and 6.21; $\lambda_{\text{max}}^{\text{EtOH}}$ ($m\mu$) 250 ($\epsilon 8 \times 10^3$) and 290 ($\epsilon 2.6 \times 10^3$); τ_{CDCl_3} 8.73 (3 H, triplet) overlapping 8.74 (3 H, triplet), complex saturated C–H, 6.20 (3 H, singlet), 5.77 (4 H, quartet), 2.67 (1 H, doublet), and 3.11 (1 H, doublet) ppm. *Anal.* Found: C, 70.83; H, 7.30] which upon treatment with 4 equiv of sodium in liquid ammonia–ether afforded the acyloin ester **12** [mp 138–140°; $\lambda_{\text{max}}^{\text{CHCl}_3}$ (μ) 5.82, 5.98, and 6.21; $\lambda_{\text{max}}^{\text{EtOH}}$ ($m\mu$) 222 ($\epsilon 1.1 \times 10^5$), 270 ($\epsilon 9 \times 10^4$), and 310 ($\epsilon 4 \times 10^4$); τ_{CDCl_3} 8.64 (3 H, triplet), 6.03 (1 H, doublet), 5.68 (2 H, quartet), 5.1 (1 H, singlet), 2.96 (1 H, doublet), and 2.36 (1 H, doublet) ppm. *Anal.* Found: C, 75.44; H, 7.15]. Reduction of the acyloin with sodium borohydride gave the diol ester **13** which, without isolation, was hydrolyzed with potassium hydroxide–aqueous propanol to the diol acid **14** [mp 216 dec]. The unpurified diol acid upon heating to 225° was transformed to the ketone **15** [$\lambda_{\text{max}}^{\text{CHCl}_3}$ (μ) 5.88; τ_{CDCl_3} 3.1 (2 H, singlet); dinitrophenylhydrazone mp 225–227°], a versatile intermediate for the preparation of corannulene and substituted derivatives. Borohydride reduction of **15** afforded 4-hydroxytetradecahydrocorannulene (**16**) which upon dehydrogenation over 5% palladium on carbon produced corannulene (**1**) as pale yellow prisms, mp 268–269° (sealed capillary under nitrogen).

The structure was indicated by the single sharp peak in the nmr at τ 2.19 as well as its molecular weight of 250 as determined by mass spectrometry⁷ and its analysis [Found: C, 95.77; H, 4.23]. Corannulene has a simple infrared spectrum with absorptions at 5.87 (weak), 7.00, 7.65, 8.85, 11.1, and 11.9 (strong) μ . The maxima in the ultraviolet occur at 246, 249, 253, and 288 $m\mu$ ($\epsilon 6 \times 10^4$, 5.4×10^4 , 9.1×10^4 , and 3.3×10^4 , respectively). The compound appears to be thermally stable in the absence of oxygen and can be sublimed at 170° (0.04 mm).

We are actively investigating the chemical and physical properties of corannulene and its derivatives.

(7) We wish to thank Dr. Don DeJongh of Wayne State University for this determination.

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