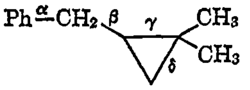
conveniently in high yield by irradiating stilbene oxide (0.3 *M*)[8] in neat 2-methyl-2-butene for 50 hr. Both IVa and IVb had been prepared previously from 2-methyl-2-butene, benzal bromide, and methyllithium.[9] However, the generation of arylcarbenes by photofragmentation of epoxides in the presence of alkenes currently appears to be the method of choice for the synthesis of aryl-substituted cyclopropanes.[10] It should be noted that, in spite of the photoinstability of IVa and IVb in benzene, they may be prepared in very high yield photochemically from IV without formation of substantial amounts of II if the conditions described above are employed.

It is assumed that the conversion of I to IV occurs in a concerted fashion with methyl migration accompanying cyclization. A mechanism involving formation of a common transitory intermediate (perhaps related to VI; *vide infra*) which collapses to II directly or alternatively to IVa and IVb cannot be excluded, however, even though a pathway exists for facile conversion of IV to II.

If II is indeed the primary photolysis product of IVa and IVb it is inviting to propose that a hydrogen atom is transferred in a cyclic five-membered transition state (VI) accompanying cleavage of the cyclopropane ring. Such intramolecular hydrogen migrations have been[11] proposed in related n,π^* and π,π^* excited states and would account for the seemingly unfavorable 1,4 transfer of a *primary* hydrogen atom in this case as well as in four other related alkyl-substituted phenylcyclopropyl systems.[12]

The formation of II could be rationalized by homolysis of the γ bond of the cyclopropane VII (formally derived from I by an unprecedented 1,4-hydrogen shift), subsequent hydrogen transfer, and cyclization. This alternate mechanism for the conversion of I to II without methyl migration has been considered and rejected for the following reasons. Photolysis of cyclopropylphenylmethane in the vapor phase, studied by Leermakers and co-workers,[13] gave a complicated spectrum of products together with extensive formation of polymer. No rearrangement to isomeric hydrocarbons was observed. Photochemical transformation of cyclopropylphenylmethane or its alkyl derivatives in solution is unknown and unlikely. Furthermore, the δ bond, in closer proximity to the chromophore, would certainly, in case of homolysis, cleave in preference to the γ bond.



VII

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[8] A. C. Cope, P. A. Trumbull, and E. R. Trumbull, *J. Am. Chem. Soc.*, **80**, 2844 (1958).

[9] G. L. Closs and R. A. Moss, *ibid.*, **86**, 4042 (1964).

[10] H. Kristinsson and G. W. Griffin, *Angew. Chem.*, **77**, 859 (1965).

[11] M. J. Jorgenson and N. C. Yang, *J. Am. Chem. Soc.*, **85**, 1698 (1963); J. Zirner and S. Winstein, *Proc. Chem. Soc.*, 235 (1964), and references cited therein.

[12] H. Kristinsson and G. W. Griffin, unpublished results.

[13] P. A. Leermakers and G. F. Vesley, *J. Org. Chem.*, **30**, 539 (1965).

Synthetic Studies on Insect Hormones. I. Synthesis of the Tetracyclic Nucleus of Ecdysone[1]

Sir:

The insect hormone ecdysone[2] has been shown recently by X-ray study to have the structure and stereochemistry represented by Ia.[3] The first synthesis of the complete tetracyclic skeleton of this vital compound from readily available starting materials is the subject of this communication.

3β-Acetoxy-23,24-bisnorchol-5-en-22-oic acid methyl ester[4] was prepared in quantity from 3β-hydroxy-23,24-bisnorchol-5-en-22-oic acid by successive acetylation, then methylation with diazomethane. *trans* hydroxylation of the double bond according to the Fieser procedure[5] followed by mild methanolic sodium hydroxide hydrolysis of the 3β-acetate function led to 3β,5α,6β-trihydroxy-23,24-bisnorcholan-22-oic acid methyl ester (IIa; mp 232–234°, $[\alpha]_D$ −17°). The 6-ketone IIb (mp 227–229°, $[\alpha]_D$ −49°) was obtained from the triol IIa by selective oxidation with N-bromosuccinimide in aqueous dioxane.[5] The derived tosylate IIc (mp 153–155°, $[\alpha]_D$ −62°) underwent elimination on treatment with lithium carbonate–dimethylacetamide to furnish the desired 6-keto-5α-hydroxy-23,24-bisnorchol-2-en-22-oic acid methyl ester (III; mp 149–151°, $[\alpha]_D$ −27°) in 50% over-all yield by the seven-step sequence from the starting acid.[6]

cis hydroxylation of the olefin III with silver acetate and iodine in moist acetic acid[7] led to an amorphous triol IId which was converted by conventional methods (acetic anhydride–pyridine) to the corresponding diacetate IIe (mp 251–253°, $[\alpha]_D$ −52°). The 19-proton resonance frequency of the latter ($\nu_{19\text{-H}}$ 61 cps) confirmed β-face hydroxylation.[8] Bromination of the 6-ketone IIe under acid catalysis (Br_2–HBr–AcOH) afforded a monobromo analog (IIe, 7α-bromo; mp 195–196.5°, $[\alpha]_D$ +4°, λ_{max} 332 mμ (ϵ 120)). Dehydrobromination with lithium carbonate–dimethyl-

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[1] Steroids. CCXCI. For Steroids CCXC, see J. P. Turnbull and J. H. Fried, *Tetrahedron Letters*, in press.

[2] For a review of published researches at the biological and chemical level up to 1963, see P. Karlson, *Angew. Chem.*, **75**, 257 (1963). Later work is covered in a series of four articles by Karlson, Hoffmeister, and their collaborators, *Chem. Ber.*, **98**, 2361 (1965).

[3] R. Huber and W. Hoppe, *ibid.*, **98**, 2403 (1965).

[4] E. Fernholz, *Ann.*, **507**, 128 (1933).

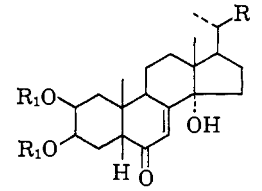
[5] L. F. Fieser and S. Rajagopalan, *J. Am. Chem. Soc.*, **71**, 3938 (1949).

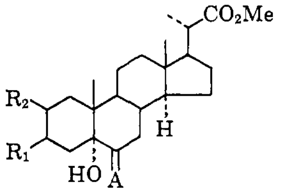
[6] Several other routes to 5,6-dioxygenated Δ^2-steroids were explored. A discussion of these experiments and of much related chemistry will be the subject of later detailed reports.

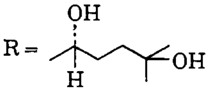
[7] L. B. Barkley, M. W. Farrar, W. S. Knowles, H. Raffelson, and Q. E. Thompson, *J. Am. Chem. Soc.*, **76**, 5014 (1954).

[8] Nmr spectra were recorded on a Varian A-60 spectrometer using deuteriochloroform as solvent when possible. Comparisons of calculated *vs.* observed frequencies for angular methyl proton resonances were used throughout to check structure and stereochemistry. Nmr spectra for all reported compounds are consistent with the assigned structures, as are other physical and analytical data.

acetamide then gave 2β,3β-diacetoxy-5α-hydroxy-6-keto-23,24-bisnorchol-7-en-22-oic acid methyl ester (IVa; mp 241–245°, [α]D +32°, λ_{max} 247 mμ (ε 11,800)). Acid-catalyzed acetylation of the latter led to the triacetate IVb (mp 184.5–185.5°, [α]D +58°)[9] into which the 14α-hydroxyl function was introduced directly by reaction with selenium dioxide in dioxane.[10] The tertiary acetoxyl group was removed from the derived 14α-hydroxy-6-keto-2β,3β,5α-triacetoxy-23,24-bisnorchol-7-en-22-oic acid methyl ester (IVc; mp 230–232°, [α]D +75°, $\nu_{18\text{-H}}$ 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°, [α]D +24°, nmr 40.5 cps (18-H)). Hydrolysis to the noncrystalline 2β,3β,14α-triol IVe and inversion at C-5[11] under equilibrating conditions by treatment of IVe with 0.33% K_2CO_3 in aqueous MeOH furnished a 3:2 mixture of 6-keto-2β,3β,14α-trihydroxy-23,24-bisnor-5β-chol-7-en-22-oic acid methyl ester (Ib; mp 232–235°, [α]D +62°) and recovered IVe. The observed 19-proton resonance of Ib (60.5 cps, pyridine solution) compares favorably with the frequency reported for ecdysone[2] (64 cps) while being well removed from the observed figure for the 5α epimer IVe ($\nu_{19\text{-H}}$ 77.5 cps).





Ia, R =


; R_1 = H

b, R = CO_2Me; R_1 = H

c, R = CO_2Me; R_1R_1 = >CMe_2

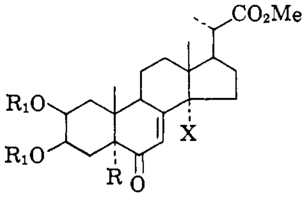
IIa, A = α-H, β-OH; R_1 = OH; R_2 = H

b, A = O; R_1 = OH; R_2 = H

c, A = O; R_1 = OTs; R_2 = H

d, A = O; R_1 = R_2 = OH

e, A = O; R_1 = R_2 = OAc



IVa, X = H; R = OH; R_1 = Ac

b, X = H; R = OAc; R_1 = Ac

c, X = OH; R = OAc; R_1 = Ac

d, X = OH; R = H; R_1 = Ac

e, X = OH; R = R_1 = H

f, X = OH; R = H; R_1R_1 = >CMe_2

An even more favorable ratio of 5β:5α epimers was obtained by equilibration of the 2β,3β-acetonide IVf (mp 248–253° dec, [α]D +116°) derived from the 2β,3β-diol IVe with *p*-toluenesulfonic acid and acetone, which afforded a 3:1 mixture of 6-keto-2β,3β,14α-trihydroxy-23,24-bisnor-5β-chol-7-en-22-oic acid methyl ester 2,3-acetonide (Ic; mp 226–232° dec, [α]D +65°) 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]

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[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.

[12] Satisfactory analyses were obtained for all crystalline compounds.

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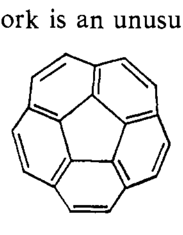
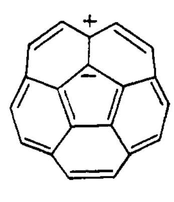
Dibenzo[*ghi,mno*]fluoranthene

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 geometrical 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 4*n* + 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]



1



2

Bromination of methyl 4,5-methylenephenanthrene-3-carboxylate[4] (**3**) with N-bromosuccinimide afforded a 90% yield of the bromo ester **4** [mp 149–150°; $\lambda_{max}^{CHCl_3}$ (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

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[1] See the discussion of perpheral 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).