The Synthesis of Corannulene

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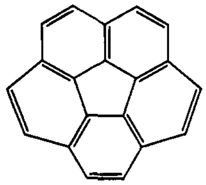
Contribution from the Chemistry Department, University of Michigan, Ann Arbor, Michigan. *Received September 24, 1970*

Abstract: Studies leading to the synthesis of the polycyclic aromatic hydrocarbon, dibenzo[*ghi*,*mno*]fluoroanthene (**1**), are described. This compound, which has been assigned the trivial name "corannulene," is of interest because of its strained structure and its unique electronic distribution. The structure is bowl shaped as a result of strain distortions. The highly symmetrical, nonalternant arrangement of sp^2 carbon atoms provides a framework which might support concentrically charged, conjugated systems: an inner cyclopentadienyl anion, and an outer cyclopentadecaheptaenyl cation. Bromination of 3-carbomethoxy-4*H*-cyclopenta[*def*]phenanthrene with *N*-bromosuccinimide afforded the 4-bromo ester, which was used to alkylate triethyl 1,1,2-ethanetricarboxylate in the presence of potassium *tert*-butoxide and *tert*-butyl alcohol. The resulting tetraester was hydrolyzed with aqueous potassium hydroxide to 4-(1,1-dicarbethoxy-2-carboxyl-1)-4*H*-cyclopenta[*def*]phenanthrene-3-carboxylate. Cyclization of the diacid diester with polyphosphoric acid at 80° produced 5,5-dicarbethoxy-6-carboxy-3-oxo-3,4,5,5a-tetrahydrobenzo[*ghi*]fluoranthene, which upon hydrogenolysis over 5% palladium on carbon gave 5,5-dicarbethoxy-1,2,2a,2b,3,4,5,5a,9,10,10a,10b-dodecahydrobenzo[*ghi*]fluoranthene-6-carboxylate. Esterification of the dodecahydro diester acid with diazomethane followed by treatment with sodium in liquid ammonia–ether solution produced the acyloin ester, 2a-carbethoxy-2-hydroxy-1-oxo-1,2,2a,2b,3,4,4a,4b,5,6,6a,6b,7,8-tetradecahydrocorannulene. Sodium borohydride reduction of the acyloin ester followed by hydrolysis with potassium hydroxide in *n*-propyl alcohol produced the diol acid, which was converted to 2-oxo-1,2,2a,2b,3,4,4a,4b,5,6,6a,6b,7,8-tetradecahydrocorannulene upon acid dehydration followed by thermal decarboxylation. Sodium borohydride reduction of the ketone and subsequent aromatization at 270° over 5% palladium on carbon led to corannulene, mp 268–269°. The structure was indicated by a single peak at τ 2.19 in its proton magnetic resonance spectrum, a molecular weight of 250 by mass spectrometry, and a suitable microanalysis and X-ray structure determination. The synthesis and reactions of various related compounds having the 4*H*-cyclopenta[*def*]phenanthrene, benzo[*ghi*]fluoranthene, or corannulene carbon skeletons are also described.

A continuing challenge for synthetic organic chemistry resides in the design and construction of molecules in which a compromise is forced between the factors of strain and aromaticity. Among the many candidates which embody this characteristic, one particular highly symmetrical, highly strained nonalternate structure captured our imagination—dibenzo[*ghi*,*mno*]fluoranthene (**1**). The nonalternate designation, which is extremely rare for a hydrocarbon consisting of benzene rings joined by fusion only, indicates the molecular orbital prediction that its ground state electronic charge be permanently displaced from one π electron per carbon.[2] A search for the most satisfying manner to accommodate this electronic displacement leads to the attractive hypothesis that dibenzo[*ghi*,*mno*]fluoranthene might approach that of **2**, a form which contains two concentric conjugated systems. Since each of these systems—the inner, familiar cyclopentadienyl anion and the peripheral, as yet unknown, cyclopentadecaheptaenyl cation—alone satisfies the requirements of Huckel's $4n + 2$ rule, even qualitative valence bond–molecular orbital arguments predict that this form would contribute to the resonance hybrid. A sophisticated SCF–MO calculation to evaluate more thoroughly these points has been performed by Gleicher.[3] His results suggest that the polar form would indeed contribute significantly to the π electron distribution of the system.



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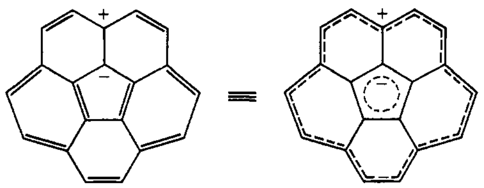

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Superimposed upon the unusual electronic features of the dibenzo[*ghi*,*mno*]fluroanthene framework is a considerable structural strain resulting from the geometrical requirement that the bond angles deviate appreciably from the optimum value of 120°. Although this strain is undoubtedly symmetrically disposed, thus minimizing the total strain energy, it is difficult to predict *a priori* how it would be distributed among the various in-plane and out-of-plane distortions available and whether an essentially planar or bowl-shaped structure should result. A dependable prediction as to the shape of the molecule requires a knowledge of various combined stretching and bending force constants and bond lengths with relation to π overlap and aromaticity so as to find the potential minimum for the system. The problem of choosing suitable energy parameters for this calculation is formidable. Also, the question regarding the importance of such often neglected or unknown fac-

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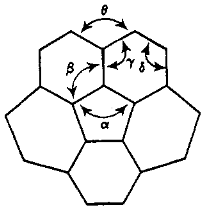
(1) Taken in part from the Ph.D. Thesis of W. E. Barth, University of Michigan, 1966. Summer Fellowships from American Cyanamid Co., Union Carbide Corp., and E. I. duPont de Nemours and Co. are gratefully acknowledged.

(2) (a) D. P. Craig in "Nonbenzenoid Aromatic Hydrocarbons," D. Ginsburg, Ed., Interscience, New York, N. Y., 1959, p 15; (b) see W. Baker and J. F. W. McOmie, ref 2a, pp 485–489; (c) G. Ferguson and J. M. Robertson, *Advan. Phys. Org. Chem.*, **1**, 203 (1963).

(3) G. J. Gleicher, *Tetrahedron*, **23**, 4257 (1967).

tors as, for example, σ–π system interactions remains unanswered with respect to this molecule. Nevertheless, some success at predicting the shape of the molecule has been achieved.[3]

If one assumes a planar molecule (**3**) with all the bond lengths equivalent (1.4 Å), then the geometrically required 108° bond angle (α) of the central five-membered ring demands a 126° angle for the inside angles of the benzene rings (β). These distortions from 120° force the remaining angles of the molecule to assume rather implausible values, $\gamma = 108°$, $\delta = 126°$, and $\theta = 144°$. The obvious angle strain created by this situation can be moderated by the development of a bowl- or dish-shaped structure (**4**), but only at the expense of some of the aromaticity of the system, since each benzene ring would then be bent out of coplanarity with the adjacent rings. This latter factor aside, if the out-of-plane bending were more facile than in-plane bond angle distortions so as to produce the extreme bowl shape, then the angle of the aromatic rings to the plane of the central five-membered ring would come to about 38°. The planar and very steep bowl configurations are, we now know,[4] extremes on the potential energy surface for the molecule, but they allow one to visualize the unique confrontation between the factors of strain and aromaticity that exist in this structure. Intrigued by the novel aspects of this unusual molecule, we were led to attempt its synthesis[5] and, with the characteristic optimism of organic chemists, carried out the traditional tagging of the structure with a convenient trivial name, corannulene. The name was derived from the Latin (*cor*, heart; *annula*, ring) and chosen to connote the relationship to the parent, coronene, as well as to imply the concentric nature of the proposed major resonance contributor.



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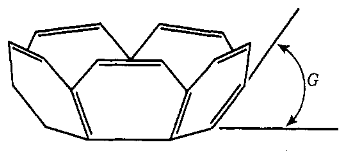

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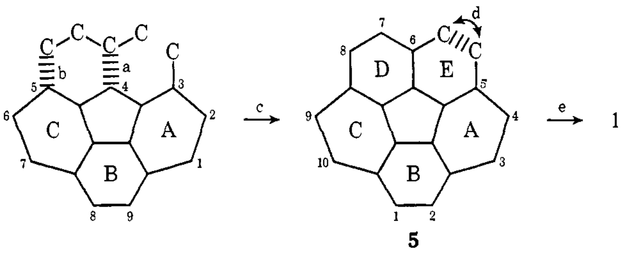
Synthetic Plan

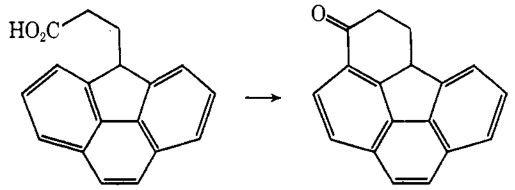
The synthetic operations leading to corannulene were conditioned by the obvious strain that would be encountered and it appeared that the route of most probable success would involve the obtention of a 5,6-disubstituted benzofluoranthene[6] skeleton so that ring closure could be caused to occur between these substituted positions (**5**). The question as to the reduction state of the framework was recognized as important, since this could potentially reduce the distance between the two substitution points, but it was uncertain at the outset how the introduced stereochemical features and the reduced aromatic rings could be manipulated.

The anticipated general plan of operations included (a) suitable alkylation of a 3-substituted methylene phenanthrene at the methylene position with a 4-carbon unit, (b) intramolecular cyclization to form the "D" ring, (c) necessary transformations to establish the geometry required for the final closure, (d) intramolecular cyclization to form the "E" ring, and (e) removal of the excess functionality (Scheme I).

Scheme I



3-Carbomethoxy-4*H*-cyclopenta[*def*]phenanthrene (**6**)[7] was chosen as the starting material for the synthesis of corannulene (**1**) because it offered a sizable portion of the corannulene structure and possessed conveniently placed functionality which would facilitate completion of the structure. The delocalizing effects of the aromatic system and the carbomethoxy group were expected to combine to stabilize either a negative charge or free radical generated on the methylene carbon, thus allowing alkylation at that position. Suitable methylene alkylation, in turn, would allow completion of an additional six-membered ring by electrophilic intramolecular cyclization to the unsubstituted ring, as demonstrated in a closely analogous case by Campbell and Reid,[8] who obtained ketone **8** upon treating a benzene solution of carboxylic acid **7** with phosphorus pentachloride, followed by stannic chloride. The utilization of a four-carbon fragment in the alkylation and the presence of the 3-carbomethoxy group in the starting material were expected to help in the final and perhaps most difficult ring closure by allowing the use of a variety of intramolecular cyclization methods. This route thus circumvented the problems associated with forming strained rings by electrophilic substitution on an aromatic nucleus as would be required if an unsubstituted 4*H*-cyclopenta[*def*]phenanthrene were used instead. Rapoport and coworkers[9, 10] have discussed the advantages of this approach for the synthesis of strained compounds and have demonstrated it by synthesizing ketones **10** and **13** from precursors **9** and **12**, respectively



7 **8**

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(4) J. C. Hanson and C. E. Nordman, Abstracts of American Crystallographic Association Summer Meeting, Aug 1967, University of Minnesota, Minneapolis, Minn., p 69 (N8), and personal communication.

(5) W. W. Barth and R. G. Lawton, *J. Amer. Chem. Soc.*, **88**, 380 (1966). Interestingly, dibenzo[*ghi,mno*]fluoranthene does not appear to have been suggested in the literature prior to our synthesis. In addition, to the time of our first report, it appears this structure had neither adorned the jacket or end cover of any book nor served as a symbol of an international symposium. J. T. Craig and M. D. W. Robins [*Aust. J. Chem.*, **21**, 2237 (1968)] have recently reported an unsuccessful attempt to synthesize **1**.

(6) Numbering of the aromatic systems follows L. M. Patterson, L. T. Capell, and D. F. Walker, "The Ring Index," American Chemical Society, Washington, D. C., 1960. Examples of numbering for cyclopenta[*def*]phenanthrene and benzo[*ghi*]fluoranthene are given in Scheme I.

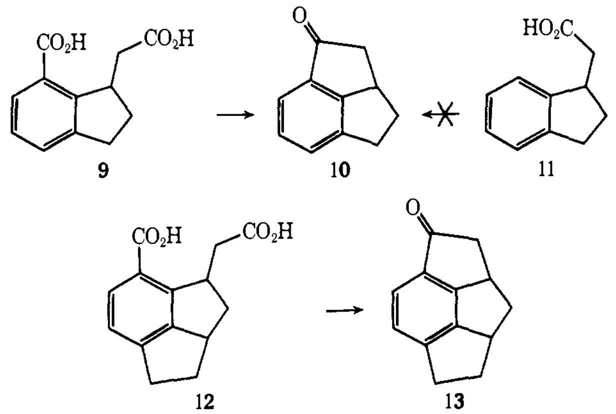
(7) A. Sieglitz and W. Schidlo, *Chem. Ber.*, **96**, 1098 (1963).

(8) N. Campbell and D. H. Reid, *J. Chem. Soc.*, 3281 (1952).

(9) H. Rapoport and G. Smolinsky, *J. Amer. Chem. Soc.*, **79**, 5831 (1957).

(10) H. Rapoport and J. Z. Pasky, *ibid.*, **78**, 3788 (1956).

Scheme II

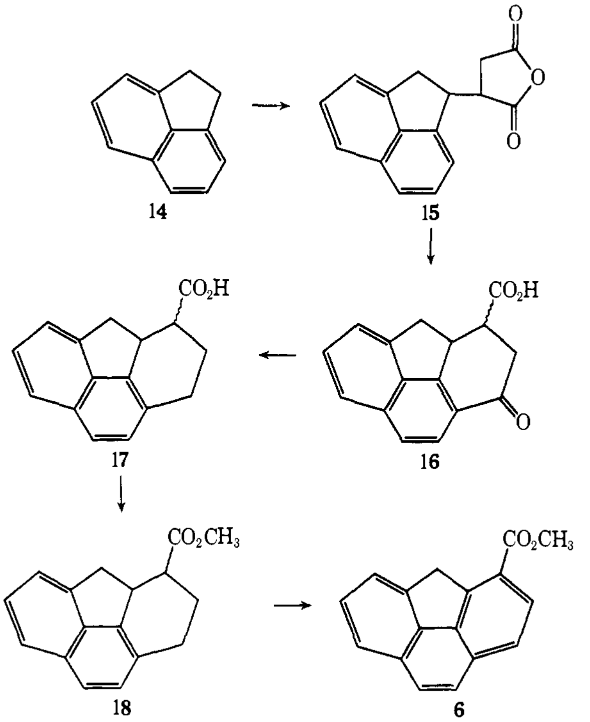


(Scheme II). Other workers[11] had previously failed to synthesize even the less strained of these, ketone **10**, using Friedel–Crafts-type reactions on carboxylic acid **11** or derivatives having the same carbon skeleton.

Synthesis

The 3-carbomethoxy-4*H*-cyclopenta[*def*]phenanthrene (**6**) used in our work was prepared by the method of Sieglitz and Schidlo[7] (Scheme III). Their method involves heating acenaphthene (**14**) with maleic anhydride at 210–240° to form anhydride **15**, which upon treatment with a eutectic melt of aluminum chloride–sodium chloride yields keto acid **16**. A Wolff–Kishner reduction of the keto acid **16** followed by methyl esterification and aromatization over palladium on carbon catalyst in refluxing *p*-cymene completes the sequence, affording the desired methyl ester (**6**).

Scheme III



Several attempts were made to alkylate suitably the methylene position of the starting material (**6**) by generating either the methylene anion or free radical in the presence of β-substituted α,β-unsaturated carbonyl compounds. These efforts met with little success, the most favorable result being a 4% yield of triester **19**, isolated after esterification (methanol, sulfuric acid) of the crude product obtained upon heating a mixture of ester **6** and maleic anhydride at 200° for 4 days. Most of the products from this series of experiments appeared to be polymeric, suggesting that both anionically initiated and free radical initiated polymerization occur more readily than the desired alkylation. The sluggishness of the desired reactions seemed at least partly attributable to an electronic interference caused by the carbomethoxy group adjacent to the reactive site.[12]

In an effort to decrease the supposed electronic interference to alkylation due to the carbomethoxy group, it was reduced to a methyl group, forming compound **20**. Several problems arose during the course of this reduction which can be attributed mainly to the strain of the 4*H*-cyclopenta[*def*]phenanthrene system and because the results are pertinent to the success of the total synthesis they are included here. Reduction of methyl ester **6** with lithium aluminum hydride afforded the hydroxymethyl derivative (**21**). This alcohol, found to be only slightly soluble in many organic solvents, was converted to its highly soluble acetate (**22**) to facilitate hydrogenolysis to the hydrocarbon (**20**). During preparations for hydrogenolysis, a sample of the acetate was dissolved in acetic acid and a catalytic amount of 70% perchloric acid added; almost immediately, precipitation began and continued until nearly all of the starting acetate was removed from solution. The solid precipitate was found to be rather insoluble in ether, ethanol, and acetone, while soluble in chloroform and benzene. Its proton magnetic resonance (pmr) spectrum, which consisted mainly of broad, low-intensity, unresolved peaks, indicated that polymerization had occurred, and revealed that two-thirds of the acetate groups originally present in the starting material had been lost. This situation, apparently involving solvolysis from a benzylic-like position of a strained aromatic system, is in fact one in which some degree of polymerization might have been anticipated. Enhanced solvolysis rates as well as enhanced electrophilic substitution rates have been previously attributed to strained aromatic systems.[13] As the strain increases in these systems one would expect that both the electrophilicity and the nucleophilicity would increase, thus enhancing intermolecular reaction, making polymerization likely. Further studies on the solvolysis of this as well as other systems are being carried out.

By adding a trace amount of hydrochloric acid to an acetic acid solution of the acetate (**22**) in the presence of hydrogen and palladium on carbon catalyst, it was possible to hydrogenolyze the acetate group while avoiding polymerization. The crude mixture isolated after 1 equiv of hydrogen had been consumed contained three compounds, **20**, **23**, and **24**, in addition to starting material. Later experiments showed that the relative amounts of these three products depended upon the specific conditions used. Hydrogenolysis of the acetate group appeared to be catalyzed by added mineral acid, whereas hydrogenation of the 8,9-double bond did not.

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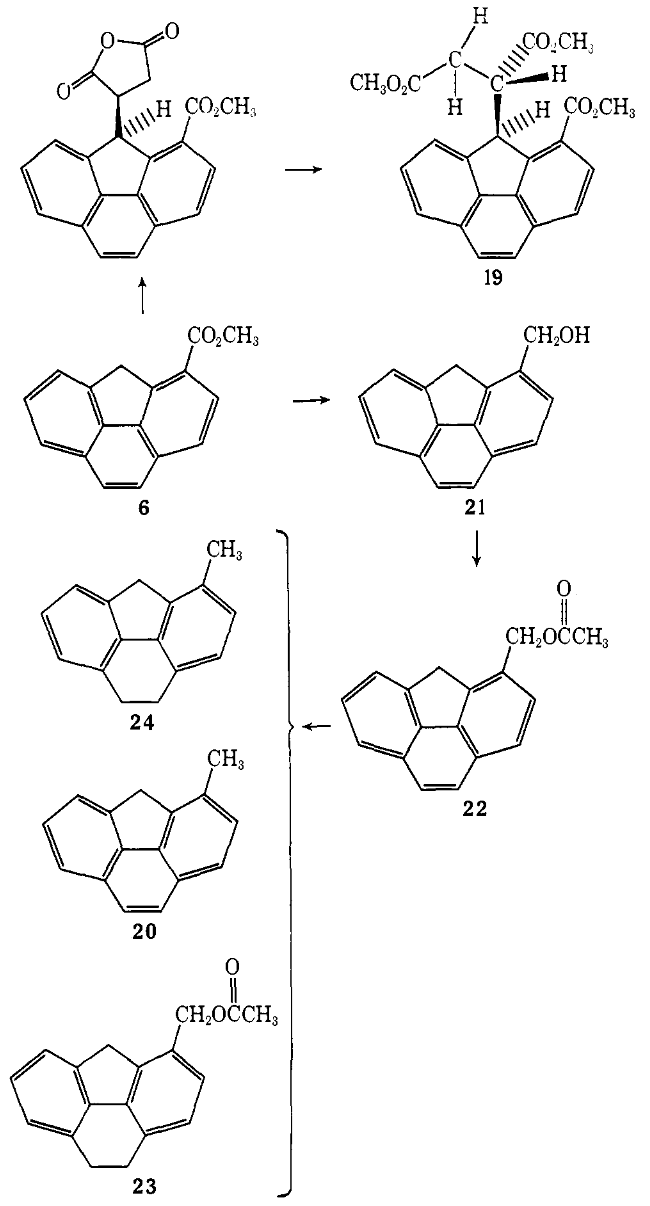
(11) J. V. Braun and K. Weisbach, *Ber.*, **64**, 1785 (1931); G. M. Badger, J. E. Campbell, and J. W. Cook, *J. Chem. Soc.*, 1084 (1949); J. V. Braun, E. Danziger, and Z. Köhler, *Ber.*, 50, 56 (1917).

(12) We now know this is not a factor. In contrast to fluorene, 4*H*-cyclopenta[*def*]phenanthrene does not add to maleic anhydride.

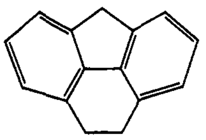
(13) E. Berliner, D. M. Falicione, and J. L. Riemenschneider, *J. Org. Chem.*, **30**, 1812 (1965).

Thus, the rate constants were such that either hydrocarbon **24** or acetate **23** could presumably be obtained in good yield upon hydrogenation of acetate **22** depending upon whether or not a strong acid was added, but no combination of conditions seemed likely to favor the formation of hydrocarbon **20** (Scheme IV).

Scheme IV



The unexpected ease with which the 8,9-double bond of the acetate (**22**) was hydrogenated may be attributed to the strain of the system, and hydrogenation experiments conducted with 4*H*-cyclopenta[*def*]phenanthrenes revealed that hydrogenation at the 8,9-double bond is generally facile although the rate is greatly influenced by substituents. 4*H*-Cyclopenta[*def*]phenanthrene itself was found to hydrogenate quite easily under the conditions mentioned above to yield 8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene (**25**), a compound previously obtained by Fieser[14] upon high-pressure hydrogenation of 4*H*-cyclopenta[*def*]phenanthrene at 160° over a copper chromite catalyst. In contrast 3-carbomethoxy-4*H*-cyclopenta[*def*]phenanthrene (**6**) hydrogenated very slowly under the same conditions to yield its 8,9-dihydro derivative (**26**). Interestingly, this same dihydro derivative was found (pmr) to be a major byproduct in the formation of the 3-carbomethoxy-4*H*-cyclopenta[*def*]phenanthrene (**16**) starting material. Thus, some of the hydrogen removed from ester **17** during aromatization of ring A re-added to the 8,9-double bond of the product.



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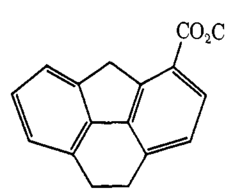

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In returning to the attempts to add the four-carbon units to the methylene group, a superior two-step method for achieving the methylene substitution of methyl ester **6** was found. Bromination of 3-carbomethoxy-4*H*-cyclopenta[*def*]phenanthrene (**6**) with *N*-bromosuccinimide afforded a 92% yield of the methylene-substituted bromo ester (**27**), which then treated with an excess of triethyl 1,1,2-ethanetricarboxylate in the presence of potassium *tert*-butoxide gave a nearly quantitative yield of tetraester **28**. The tetraester was not isolated, but hydrolyzed either partially or completely to carboxylic acids. This alkylation approach had been previously shown effective in a closely analogous situation by McDowell, Smolinsky, and Rapoport.[15]

Direct treatment of crude tetraester **28** with aqueous sodium hydroxide at reflux followed by acidification, also at reflux, caused complete hydrolysis and subsequent decarboxylation of the malonic acid moiety of **29** to give triacid **31**. Methanol–sulfuric acid esterification of the triacid afforded its trimethyl ester (**19**), which proved to be identical with the triester earlier isolated after esterification of the products from the thermal reaction of 3-carbomethoxy-4*H*-cyclopenta[*def*]phenanthrene (**6**) with maleic anhydride. Although the triester possesses two asymmetric centers, its pmr spectrum indicated the presence of a single stereoisomer (racemic). The stereochemistry of this isomer, while not rigorously proven, was thought to be that shown for structure **19** after a comparison was made of its chemical shifts and coupling constants with values estimated for favorable conformers of the possible diastereomers.

Since there is a dramatic shielding of one of the methylene protons relative to the other (quartet, centered at τ 7.9 and 8.9, C_2 of the ethyl side chain) it is suggested that the OCH_3 group which is most shielded (τ 6.6) is on the carbomethoxy group attached to this methylene carbon and that this portion of the side chain lies over the aromatic surface. The carbomethoxy group attached at carbon one on the side chain (τ 5.7) is placed in an environment similar to the aromatic carbomethoxy group (τ 6.00) only when it projects away from the aromatic portion of the molecule. These facts combined with the assumption that the most stable diastereomer is that having the least steric interaction of groups indicate structure **19**.

The next problem was to achieve closure of the fourth six-membered ("D") ring, while leaving adequate substitution to allow closure of the final ("E") ring. Ini-

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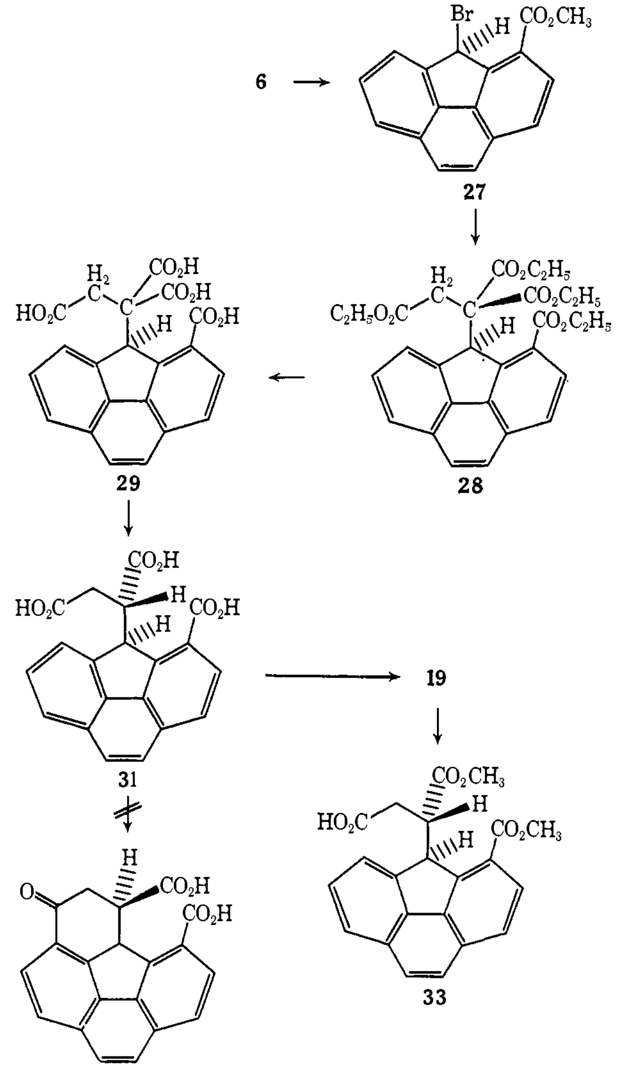
(14) L. F. Fieser and J. Cason, *J. Amer. Chem. Soc.*, **62**, 1293 (1940).

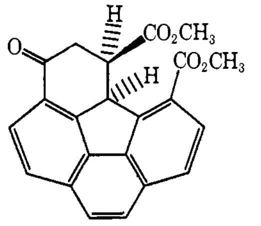
(15) B. L. McDowell, G. Smolinsky, and H. Rapoport, *ibid.*, **84**, 3531 (1962).

tially, the triacid (**31**) was subjected to mild Friedel–Crafts conditions in hopes that intramolecular acylation would occur. Treatment with liquid, anhydrous hydrogen fluoride as well as with a combination of phosphorus pentachloride and stannic chloride and other more vigorous methods proved to be insufficient; unchanged starting material was recovered upon aqueous work-up. As the multifunctionality of the triacid appeared unsuitable for cyclization, attempts were made to prepare acid diester **33** (Scheme V). Partial hydrolysis of the triester **19** with 1 equiv of dilute methanolic potassium hydroxide afforded a complex mixture of hydrolysis products and since attempts to separate this mixture of crystallization proved unsuccessful, the whole crude mixture was dissolved in benzene and treated with phosphorus pentachloride followed by stannic chloride. Upon work-up, a very small amount of crystalline keto diester **34** was isolated as the neutral component of the product, demonstrating that this approach for formation of the "D" ring was feasible but lacking practicality.

Scheme V



The pmr spectrum of the keto diester indicated the stereochemistry shown. The sharp singlet at τ 5.94 (3 H) was attributed to one of the carbomethoxy groups, located in a normal magnetic environment. The singlet at τ 7.03 (3 H) was attributed to the other carbomethoxy group; its upfield position revealed considerable shielding, indicating that the carbomethoxy group lies above the plane of the aromatic system. In the alternative structure (**35**), both carbomethoxy groups would lie roughly in the plane of the aromatic system and exhibit normal pmr peak positions. If the stereochemical assignments for both the triester (**32**) and the keto diester (**34**) are correct, epimerization must have occurred at some intermediate point.



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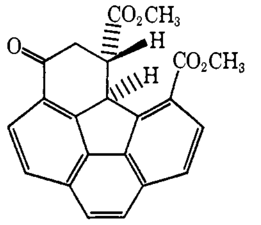

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A more promising pathway for the conversion of tetraester **28** to keto diester **34** became evident when it was observed that careful hydrolysis of the crude tetraester (**28**) with potassium hydroxide in aqueous methanol led to a nearly quantitative yield of diacid diester **36**. The excellent conversion to a single partially hydrolyzed product may be attributed, in this case, to the considerable difference in reactivity among the three different types of ester groups: hydrolysis of the primary carbethoxy group being relatively fast, hydrolysis of the aromatic carbomethoxy group being almost as fast, especially as a result of the steric interference to coplanarity with the aromatic system, and hydrolysis of the two sterically hindered, geminal carbethoxy groups being extremely slow. There was no evidence of assisted hydrolysis due to intramolecular participation of the adjacent carboxylate anion in the diacid diester as might be expected from the work of Bruice and Pandit.[16]

Esterification of the diacid diester (**36**) afforded the dimethyl diethyl ester (**37**) without any noticeable ester interchange, further evidence of the unreactivity of the geminal carboethoxy groups. In contrast to the triacid (**31**), the diacid diester (**36**) was found to undergo facile intramolecular acylation and upon treatment with polyphosphoric acid gave keto acid diester **38** in 73% yield. Esterification of the keto acid diester with either diazomethane or methanol–sulfuric acid led to keto triester **39** (Scheme VI).

Several interesting features of the keto triester (**39**) are revealed by its pmr spectrum (Figure 1). One of the carbethoxy groups is seen to be quite shielded while the other is not, supporting the conclusions reached earlier regarding keto diester **34**. The peaks attributable to the methylene of the in-plane ester group (centered at τ 5.6) are seen to be abnormally split into an ABC_3 pattern, indicating that the rotation of this group is sufficiently hindered that the two methylene protons appear magnetically nonequivalent.[17]

In retrospect, the difficulty experienced in causing cyclization of the triacid may have been due to the steric interaction of the two carboxyl groups (aromatic and at C_1 on side chain) in the transition state during the ring closure, since monoacid **7** closes easily.[8] As noted previously, the small amount of closed product **34** was apparently a result of epimerization of **31** to a small

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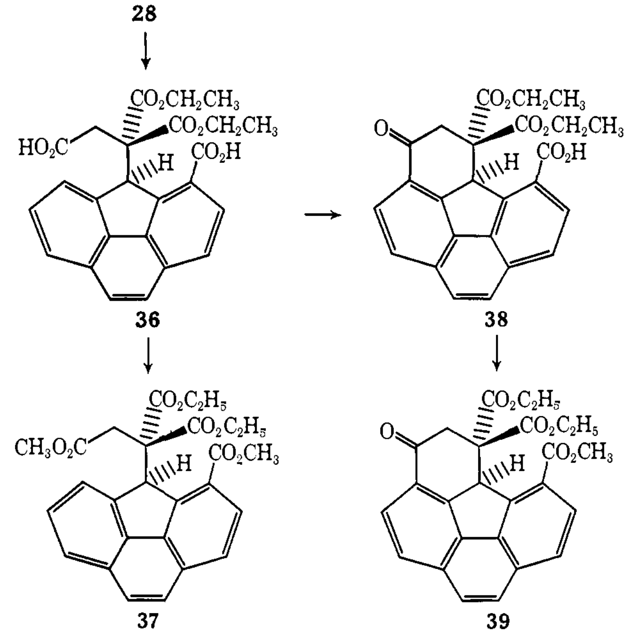
(16) T. Bruice and V. Pandit, *J. Amer. Chem. Soc.*, **82**, 5858 (1960).

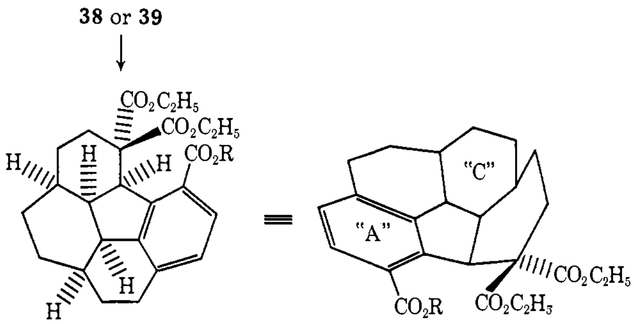
(17) W. L. Meyer, D. L. Davis, L. Foster, A. S. Levinson, V. L. Sawin, D. C. Shaw, and R. F. Weddleton, *ibid.*, **87**, 1573 (1965).

Scheme VI



amount of its unstable diastereomeric partner, followed by closure, a sequence in which the proposed steric interaction does not occur. The effect of geminal substituents on ring closing reactions is well documented, but exactly how it operates in the instance of diacid diester is still obscure.

The keto acid diester (**38**) was found to be resistant to hydrolysis with methanolic potassium hydroxide, a result not particularly surprising in view of the highly hindered ester groups. Before trying stronger hydrolytic conditions, however, it seemed wise to remove the α-keto group, thus reducing the likelihood of reopening the "D" ring or polymerizing the starting material *via* aldol reactions. As was discovered much later the precaution was unwarranted, the interrelation of **38** with **35** being accomplished with refluxing KOH in ethylene glycol followed by esterification. Fortunately, hydrogenolysis was chosen for the purpose of removing the keto group. Prolonged treatment at room temperature with hydrogen (50 psi) in an acetic acid slurry of 5% palladium on carbon catalyst, containing also a small amount of perchloric acid, was overly effective, however, and gave acid diester **40**, in which not only had the keto group been removed, but in addition, two of the three aromatic rings had been hydrogenated. Hydrogenation of the 8,9-double bond of the "B" ring had been anticipated on the basis of the earlier hydrogenation studies with the 4*H*-cyclopenta[*def*]phenanthrenes. Hydrogenation of the "C" ring was unexpected and demonstrated the increased strain developed within the system upon closure of the "D" ring. Mechanistically, hydrogenation of the "C" ring must have occurred by the addition of hydrogen exclusively on the side opposite the geminal carbethoxy groups, thus stereoselectively introducing four new asymmetric centers to form a somewhat cup-shaped structure. The hydrogenated compound (**40**) seemed ideally suited for further studies directed toward closing the final ring because it possessed a relatively strain free, somewhat flexible structure, and most importantly, one in which the "inside" carbethoxy group and the carboxylate group were allowed to come quite close to each other. Evidence for the nearness of these groups was found again in the nonequivalence of the methylene protons of the ester ethoxyl group in the pmr spectrum. This effect, as previously discussed, is attributable to severe steric hindrance. That no appreciable esterification occurred upon extended treatment of the diester acid with methanol and sulfuric acid served as a further indication that the carboxylate group was quite hindered.



40, R = H
41, R = CH_3

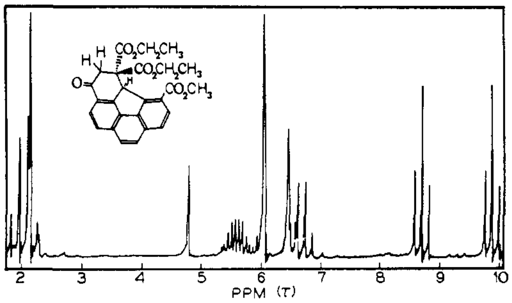


Figure 1. Nmr spectra of keto triester **39**.

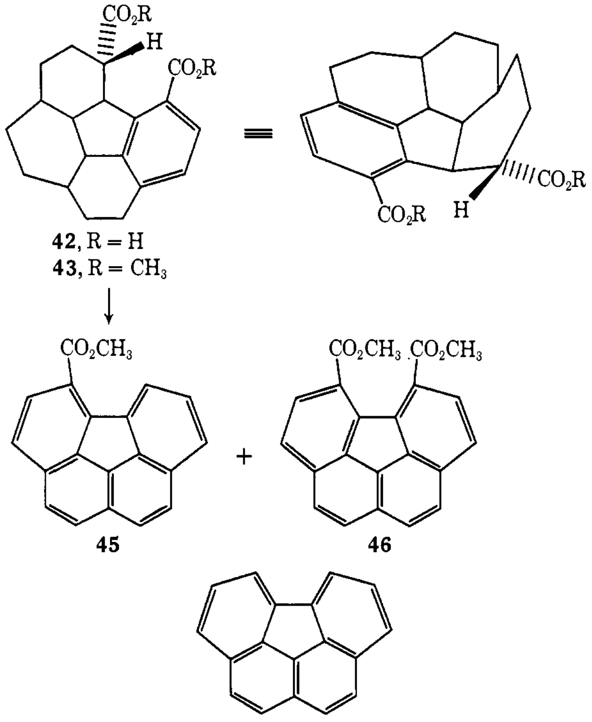
At this point several pathways to our eventual goal were available. The sequence of steps—removal of the extra carboxyl group, interconnection of the two remaining groups with closure of the last ring, and aromatization—could be easily interchanged, but the above route was selected primarily because it provided compounds which were of simplified structure and which could be utilized to test the rearomatization of the framework. In actuality, alternate routes were intermittently explored.

Acid–diester **40** was hydrolyzed and decarboxylated to form diacid **42** upon treatment with potassium hydroxide in refluxing ethylene glycol. Esterification of the diacid with methanol and sulfuric acid afforded a single diester, **43**, believed to have the exo configuration shown, in which the aliphatic ester group is positioned away from the carbomethoxy group on the benzene ring. This stereochemistry seems reasonable since the equilibrating conditions used to form the diester would favor the more stable isomer, and that would logically be the least sterically hindered one in this case. Nevertheless, it was possible that protonation of the enolate might occur from the less hindered side to give the desired stereochemistry. Several experimental observations, however, gave further support to the assigned stereochemistry. Upon treatment with sodium in liquid ammonia, reduction of the benzene ring occurred instead of an intramolecular acyloin closure as would have been likely had the carbomethoxy groups been close to each other. Also, lithium aluminum hydride reduction proceeded smoothly to the corresponding diol and all subsequent attempts to form a cyclic ether failed. Again this result would not have been likely had the compound had the endo configuration.

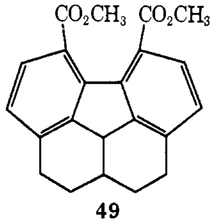
Several attempts were made to modify the structure of the diester (**43**) in such a way that the two carbomethoxy groups would become suitably positioned for intramolecular closure. The first of these involved an attempt to aromatize completely the diester to 5,6-dicarbomethoxybenzo[*ghi*]fluoranthene (**46**), thus removing the asymmetry while forcing the two carbomethoxy groups to lie essentially in the same plane, and the second approach was an attempt to prepare the endo epimer of diester **43**.

After heating an intimate 1:1 mixture of the diester **43** and 5% palladium on carbon catalyst at 260° for 14 hr under nitrogen, three products were isolated: benzo[*ghi*]fluoranthene (**44**), 5-carbomethoxybenzo[*ghi*]fluoranthene (**45**), and 5,6-dicarbomethoxybenzo[*ghi*]fluoranthene (**46**) (Scheme VII). The relative composition of the product mixture was found to be strongly dependent upon the conditions used; final temperature and rate of heating were especially critical factors. Milder conditions than those mentioned favored retention of the carbomethoxy groups and resulted in mixtures containing as high as 80% diester **46**. Under yet milder conditions two other compounds, presumably intermediates in the aromatization, could be obtained in yields up to 90%; after heating a 1:1 mixture of catalyst and diester **43** for 4.5 hr, during which time the temperature was increased slowly from 100 to 240°, nearly the whole product was found to be comprised of the epimeric diesters **47** and **48**. These experimental results, while providing the desired diester (**46**) and indicating the structure of **40**, more importantly revealed that the relatively large aliphatic network could be smoothly dehydrogenated in a stepwise manner to a strained aromatic hydrocarbon, although decarboxylation could occur under vigorous conditions. The question as to whether closure can be effected across the two carbons of the 5,6-disubstituted, fully aromatic benzofluoranthene, a distance of about 3 Å,[18] remains to be investigated.

Scheme VII



In an experiment related to the aromatization studies just discussed, a mixture of benzo[*ghi*]fluoranthene (**44**) and the two carbomethoxy derivatives, **45** and **46**, was subjected to hydrogenation at room temperature in acetic acid over palladium on carbon at 1 atm hydrogen pressure (no mineral acid added). The pmr spectrum of the crude product, isolated after 17 hr, revealed that the diester (**46**) remained unaffected while the benzo[*ghi*]fluoranthene (**44**) and the monocarbomethoxy derivative (**45**) had been at least partially hydrogenated. A repeat experiment, in which a small amount of perchloric acid was also added, resulted in partial hydrogenation of the diester, principally to its hexahydro derivative, **49**. In a separate experiment, a pure sample of benzo[*ghi*]fluoranthene was hydrogenated under the conditions mentioned above including the perchloric acid. The principal product appeared to be hydrocarbon **50** on the basis of the pmr spectrum of the crude product.



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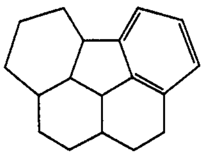

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With this knowledge of the chemistry of this system gained from the above experiment an attempt was made to prepare the endo epimer (C-5) of diester **43** by first preparing diester **47**, predicted to be more stable than its epimer (**48**) on the basis of the known stability of the keto diester **34**, and then catalytically hydrogenating it under neutral conditions on the chance that hydrogenation of rings "B" and "C" would again occur stereoselectively from the less hindered face as before (Scheme VIII). Both **47** and **48** had been obtained earlier in the aromatization studies, but remained unidentified until they were prepared by the following study. Treatment of keto acid diester **38** with a refluxing solution of potassium hydroxide in ethylene glycol afforded keto diacid **51**, which upon methyl esterification (methanol, sulfuric acid) gave the same keto diester, **34**, previously obtained in low yield by cyclization of the mixture of diester acids containing **33**. Reduction of the keto diacid (**51**) in a modified Wolff–Kishner procedure led, upon esterification of the product, to a mixture of epimers **47** and **48** in the ratio of about 5:1. After being isolated chromatographically, diester **47** was treated with hydrogen (1 atm) at room temperature in an ethanol slurry of 5% palladium on carbon containing no mineral acid. Only diester **52** was formed under these conditions; hydrogen added to the "B" ring, but not to the "C" ring. Hydrogenation of the "C" ring as previously observed in the case of the keto acid diester (**38**) might have been accomplished with acid catalysis but these routes were not pursued as the monobenzenoid diester acid (**41**) was a more available intermediate and a pathway utilizing it

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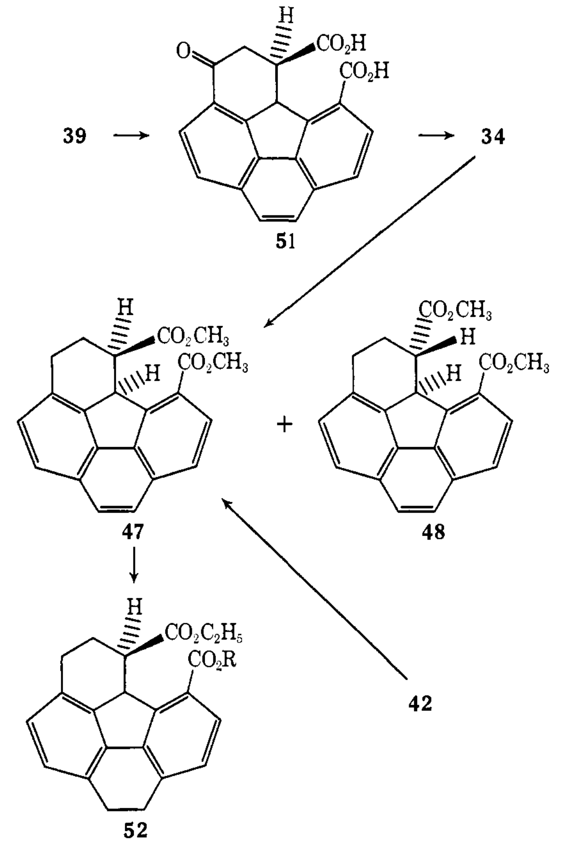
(18) H. W. W. Ehrlich and C. A. Beevers, *Acta Crystallogr.*, **9**, 602 (1956).

Scheme VIII

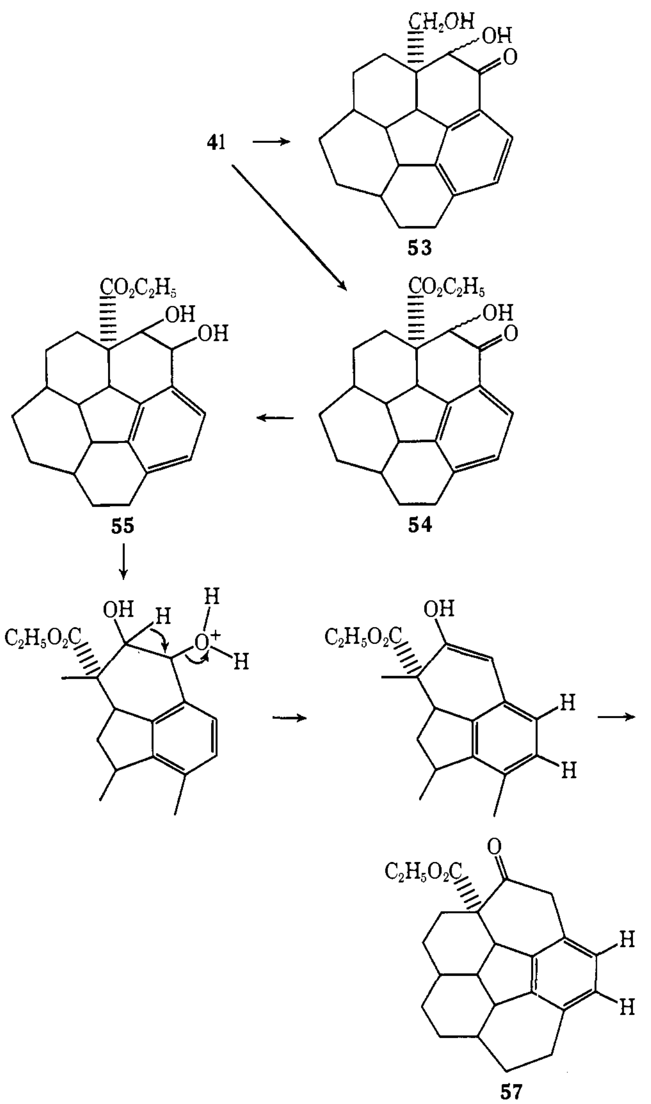


in the closure of ring "E" prior to removal of the extra carboxyl group had become available.

Triester **41**, obtained by esterifying acid diester **40** with diazomethane, was treated with excess sodium in a solution of liquid ammonia and ether.[19] Under these conditions the triester, having both exo and endo carbethoxy groups, was expected to undergo an acyloin closure with formation of the "E" ring if the endo carbethoxy group were sufficiently close to the carbomethoxy group. The major product of this reaction, obtained as a crystalline solid after work-up and crystallization from methanol, exhibited a carbonyl adsorption at 5.98 in the infrared. The pmr spectrum revealed that all of the ester groups had been lost, and showed new peaks at 5.36 (1 H, singlet) and 6.28 (2 H, singlet) while the aromatic AB quartet of the product resembled that of the starting triester. This evidence, enhanced by a suitable elemental analysis, pointed to acyloin alcohol **53** as the product (Scheme IX). In a refinement of the procedure, only 4 equiv of sodium was used and the temperature of the reaction mixture was kept near that of a Dry Ice and acetone bath (*ca.* −65°). Under these conditions the major product was found to be the acyloin ester, **54**, on the basis of its pmr spectrum, infrared spectrum, and elemental analysis.

This acyloin ester (**54**) was an attractive key intermediate for the corannulene synthesis; it possessed an intact corannulene carbon skeleton with only one extraneous carbon atom directly attached and that, being present as part of a carbethoxy group, promised to be removable upon hydrolysis and decarboxylation. Treatment of the acyloin ester (**54**), first with sodium borohydride, and then with refluxing acetic acid containing a

Scheme IX



few drops of sulfuric acid, afforded the keto ester, **57**, *via* the ester diol, **55**. Not unexpectedly, attempts to hydrolyze the angular carbethoxy group by subjecting the strained keto ester (**57**) to acidic hydrolysis conditions resulted in polymer formation. To circumvent the problems associated with the keto ester, the more stable ester diol, **55**, was used as the starting material and subjected to *basic* hydrolysis conditions. Treatment for 3 hr with a refluxing solution of potassium hydroxide in methanol proved ineffective; the ester diol was recovered unchanged. Treatment under the more vigorous basic conditions provided by potassium hydroxide in refluxing n-propyl alcohol was effective, however, and gave the desired acid diol, **56**.

The acid diol (**56**) was observed to decompose slightly above its 216° melting point, with gas evolution. Since the gas was logically water vapor, carbon dioxide, or both, the sample in the melting point capillary was heated for an additional few minutes until gas evolution ceased. Chromatography of the melting point sample on alumina tlc revealed that, whereas the diol acid (**56**) remained at, or near, the origin, the major product from the capillary tube moved near the front, with an R_f value of about 0.8, suggesting that both dehydration and decarboxylation had occurred, by way of the β-keto acid (**58**), to yield ketone **59** (Scheme X). In order to deter-

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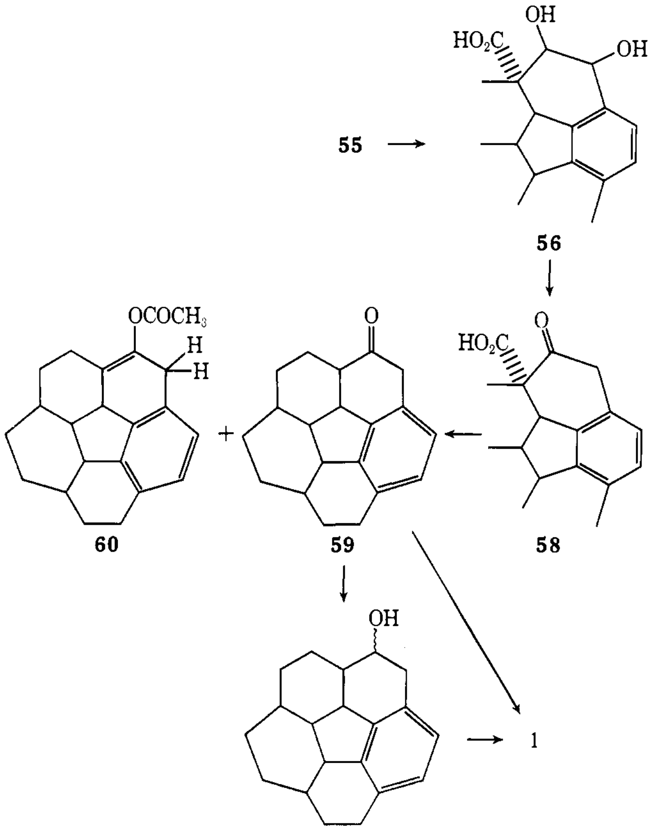
[19] J. C. Sheehan and W. F. Erman, *J. Amer. Chem. Soc.*, **79**, 6050 (1957).

Scheme X



mine the validity of this conjecture, a larger sample was heated in a test tube for 45 min at 220° under nitrogen. During the heating period, a clear condensate was seen to form on the tube sides just above the level of the oil bath used as a heat source. The pmr spectrum of the condensate showed it to be nearly pure ketone (**59**), while the bulk of the product, remaining as a molten residue on the tube bottom, was found to consist of a mixture of products including the ketone and polymeric-like materials. Evidence for assigning the ketone structure to the condensate was derived from its infrared spectrum, having a carbonyl absorption at 5.88, and from its pmr spectrum, which resembled that of keto ester **57** in that it showed a 2 hydrogen singlet at 3.12, indicating that the aromatic protons are in very similar magnetic environments, and a 2 hydrogen singlet at 6.50, attributable to the 2 protons α to both the carbonyl and the benzene ring. In the cases previously encountered, if the α position bore an oxygen function, the aromatic protons appeared as an AB quartet. The unusually high carbonyl frequency of **59** is attributed to the unusual flattening of the cyclohexane ring accompanied by distortion of the C–C(O)–C bond angle to values above 120° forced by the geometry of the molecule.

Then, in a rather optimistic experiment, a small sample of the ketone (**59**) was mixed with an equal amount of 5% palladium on carbon catalyst and the mixture heated gradually, under nitrogen, to 240° over a 2-hr period. After cooling, the product was eluted from the carbon cake with chloroform. Its pmr spectrum showed only one peak, a sharp singlet at 2.19, an indication that all of the protons of the product were aromatic and equivalent and that we had obtained corannulene!

With the validity of the approach tentatively established, the final steps of the synthesis were investigated further in an effort to improve the yields. Since generation of the ketone (**59**) by thermal treatment of the acid diol (**56**) presumably involved the intermediacy of the β-keto acid (**58**), it seemed worthwhile to prepare this β-keto acid in a separate acid-catalyzed step, hoping to then decarboxylate it under milder conditions, and improve the yield of ketone **59**. Upon treatment for 5 min with a refluxing acetic acid solution containing a small amount of hydrochloric acid, the diol acid (**56**) was completely rearranged and partially decarboxylated to afford a mixture composed primarily of keto acid (*ca.* 60%), but also containing ketone (**59**) (*ca.* 30%) and an acetate (*ca.* 10%) on the basis of its pmr spectrum. This crude mixture was heated in a steam bath under reduced pressure for 10 hr. Under these conditions the β-keto acid was found to decarboxylate completely, resulting in nearly pure ketone (**59**), the only obvious impurity in its pmr spectrum being the 10% acetate present. The acetate was isolated by column chromatography, and assigned structure **60** after inspection of its pmr spectrum, which showed a 2 hydrogen singlet at 3.10, a 2 hydrogen AB quartet at 5.64, and no peaks in the vinyl region.

Prior reduction of the ketone (**59**) to the corresponding alcohol, probably a mixture of epimers, was found to facilitate the final aromatization. The enol acetate present as an impurity in the ketone was also reduced, apparently to the same alcohol, upon sodium borohydride treatment. Even when starting with the alcohol, however, the aromatization was found to be capricious, proceeding smoothly sometimes and extremely slowly at other times. In the most favorable experiment, a 51% yield of crude corannulene was extracted from the palladium–carbon catalyst after being heated from 200 to 275° over a 1.5-hr period, and only about 35% of this crude product was recovered as crystalline corannulene, mp 268–269°, after sublimation at 170° (0.04 mm). Corannulene can be crystallized from ethanol to afford almost colorless prisms. Assignment of the structure followed from the single sharp peak at 2.19 in its pmr spectrum, the *m/e* parent peak at 250 in its mass spectrum, the suitable elemental analysis for $C_{20}H_{10}$, and the infrared and ultraviolet (Figure 2) spectra which appeared to be consistent with structure **1**. That portion of the crude product which did not crystallize consisted largely of partially aromatized material on the basis of its pmr spectrum and this material could be aromatized further.

While the spectral results clearly supported the assigned structure, they alone did not provide clear-cut answers to the questions originally posed concerning either the electronic nature or the three-dimensional geometry of the corannulene molecule as it was nearly impossible to interpret meaningfully the data in the absence of suitable model compounds. The X-ray structure of corannulene has been determined by Hanson and Nordman[4] of these laboratories. Their work has been reported[4] but it is worthwhile to consider some of their general results here. The compound crystallizes in space group $P2_1/c$ with eight molecules to the unit cell with the packing shown in Figure 3. The bowl-shaped structure is clearly confirmed, and two views which show the distortion from planarity of a single molecule are de-

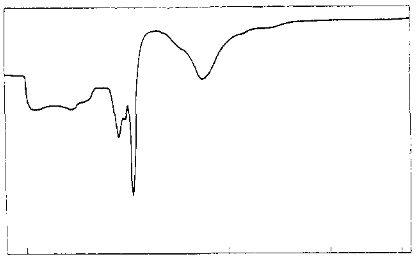


Figure 2. Uv spectra of corannulene.

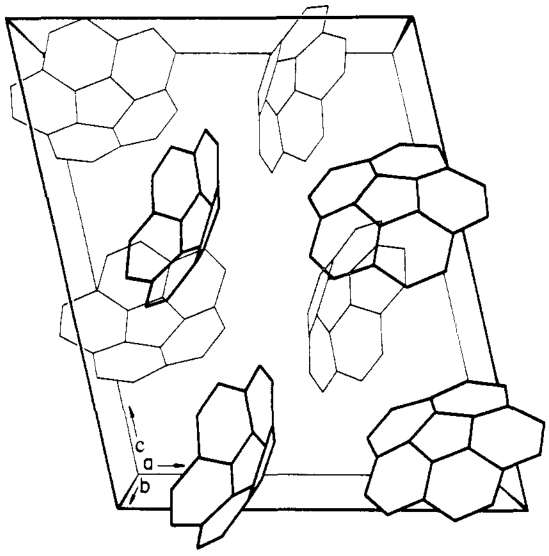


Figure 3. X-Ray unit cell (Hanson and Nordman).

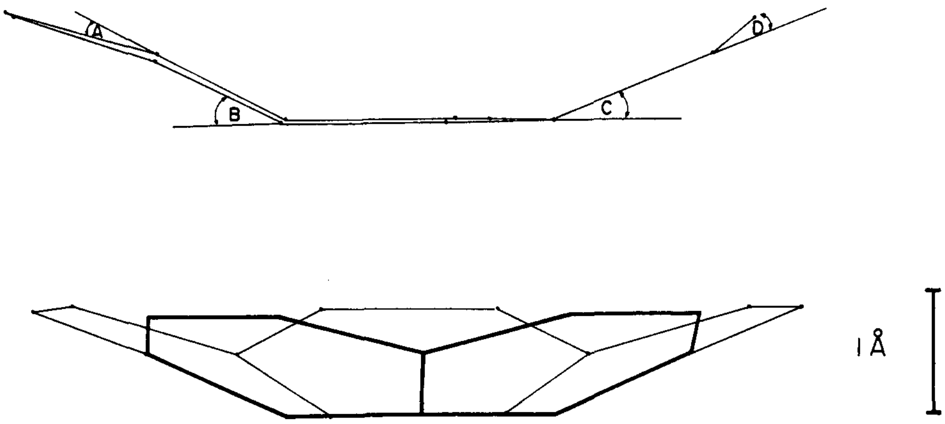


Figure 4. Distortion from planarity of corannulene.

picted in Figure 4. The average angle values of interest are $A = 10.4°$, $B = 26.8°$, $C = 20.4°$, and $D = 12°$. The plane formed by the carbons at the terminus of the radial bonds and the plane formed by the peripheral carbons are, respectively, 0.87 and 1.21 Å above the plane of the five-membered ring. As can be seen from the figure the six-membered rings are bent. The average dihedral angle between five- and the inner portion of the six-membered rings is 26.8°, more than half the 38° calculated for the extreme bowl form. Another view (Figure 5) indicates the bond length and bond angle distortions. The central angle α is the required 108° while β is 123°, 3° less than would be required for a planar molecule. The angle $\gamma = 114.3°$ and $\delta = 122°$ with the largest deviation from the normal benzene angles being $\theta = 130.9°$. This last value again indicates the balance taken between the two extremes of the structure, the extreme bowl shape ($\theta = 120°$) and the planar molecule ($\theta = 144°$). The bond lengths are interesting also, bond $a = 1.413$, $b = 1.391$, $c = 1.44$, and $d = 1.402$ Å. The shortest bonds are the radial bonds joining the two concentric systems, a somewhat surprising result because of their expected single bond character due to the polar resonance contributor **2**. This effect is certainly a reflection of the strain imposed by the σ system. Thus, because of the shorter, radial bonds, the bond angles on the periphery approach the more normal values for aromatics. An unexpected feature of the structure is the bending of the peripheral carbons outward from the concave side of the framework.

Some further observations on the physical data obtained on corannulene are worthy of comment. The τ 2.2 singlet for the chemical shift of the corannulene protons seems anomalous when compared with coronene (τ 1.1). The value is little changed from that of benzene (τ 2.27) and further the ^{13}C–H coupling constant of 158 Hz and the H–H coupling value of 8.7 Hz of corannulene are virtually identical with benzene (^{13}C–H, 159 Hz; H–H, 8.6).[20] These later data are compatible with the outside bond angles as determined by Nordman and Hanson, but the chemical shift observed for corannulene protons was expected to be lower because of the contribution of the polar form **2**. The position of the pmr peak may reflect opposing effects which cancel each other's influence. Qualitatively, an electron-deficient periphery would be expected to cause a down-

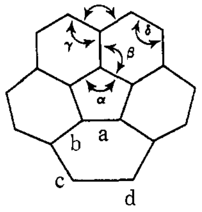


Figure 5. Angle and bond lengths of corannulene.

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(20) H. M. Hutton, W. F. Reynolds, and T. Schaefer, *Can. J. Chem.*, **40** 1758 (1962). We thank Dr. Raymond Ettinger of Varian for the C-13 and H–H coupling constants of corannulene.

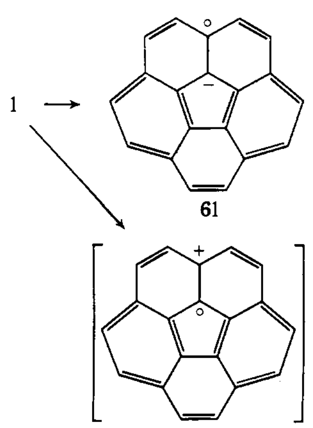
field shift while nonplanarity would be expected to cause an upfield shift as the π-orbital overlap became decreased and the hydrogens develop more olefin character. The upfield shift might also be a reflection of a shielding of the protons by that portion of the aromatic system on the opposite side of the bowl.

The ultraviolet spectrum is remarkable for its simplicity as well as the very sharp absorption at 254 nm. The maximum at 285 nm shows little fine structure, a characteristic of a number of strained aromatic species.[21] Studies on the fluorescence and phosphorescence spectra[22] as well as esr evidence for the photolytically derived triplet state of corannulene have recently been obtained by members of this department.[23]

The mass spectrum of corannulene showed a parent peak at m/e of 250, an $m/2$ peak at 125 (second largest peak, 23% of parent), and an $m/3$ peak at 83 (1.5%).[24]

Corannulene forms a light yellow picrate and a similar trinitrobenzene complex. The colors of these complexes are unusually light and may be an indication of the bowl shape and a reflection of a decrease in the interaction between the donor and acceptor molecules.

The electrochemistry of corannulene has been studied and the blue green radical anion (**61**) has been observed by esr and visible spectroscopy.[25] As might be expected by extrapolation from the neutral molecule, the esr experiments indicate that a minimum of 70% of the spin density resides on the peripheral carbon atoms in the radical anion. Attempts to observe the radical cation (**62**) have so far been unsuccessful.[25]



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Further studies on the chemistry of corannulene promise to indicate more on the nature of the confrontation between the strain and aromaticity of the molecule and the contribution of the polar form to the structure. Some of the features to be considered are substitution, differences between the concave and convex sides of the molecule, the resolution of mono-substituted derivatives, and the obtention of metal complexes.

Experimental Section

Melting points were determined using open capillary tubes in a Thomas Hoover capillary melting point apparatus and are uncorrected. Ultraviolet spectra were determined on samples dissolved in 95% ethanol with a Perkin-Elmer Model 202 spectrophotometer. Infrared spectra were determined for chloroform solutions with a Perkin-Elmer Model 237 spectrophotometer and for solid samples in KBr disks with a Perkin-Elmer Model 21 spectrophotometer. Proton magnetic resonance spectra were determined for deuteriochloroform solutions with a Varian A-60 spectrometer; chemical shifts are expressed in parts per million relative to an internal tetramethylsilane standard (τ scale). Microanalyses were performed by the Spand Microanalytical Laboratory, Ann Arbor, Mich.

Nearly all reactions were run in a nitrogen atmosphere. Unless otherwise indicated, solvent evaporations were carried out at reduced pressure over a steam bath. All preparative chromatographic separations except one, designated accordingly, were achieved on short columns (2–3 × 0.25 in.) of silica gel G (Brinkmann Instruments Co., Inc.) packed as slurries in reagent grade chloroform and eluted with the same solvent.

3-Carbomethoxy-4*H*-cyclopenta[*def*]phenanthrene (6) was prepared by the method of Sieglitz and Schidlo.[7] Yields obtained at the various intermediate stages generally agreed with those reported. The final product, mp 113–115° (lit. mp 114–115°), showed intense infrared bands in KBr at 1712 and 1264 cm^{-1} (aryl ester); its pmr spectrum exhibited a complex multiplet at τ 1.80–2.50 (7 H, aromatic), a singlet at 5.72 (2 H, methylene), and a singlet at 6.03 (3 H, methoxyl).

3-Carbomethoxy-4-(1,2-dicarbomethoxyethyl)-4*H*-cyclopenta[*def*]phenanthrene (19). Thermal Route. After heating 3-carbomethoxy-4*H*-cyclopenta[*def*]phenanthrene (23.8 g, 0.096 mol) with maleic anhydride (7.4 g, 0.076 mol) at 200° for 4 days, the mixture was allowed to cool, and was then esterified by refluxing for 12 hr in methanol (500 ml) and sulfuric acid (0.5 ml). Upon allowing the methanol solution to cool slowly to room temperature a crystalline precipitate (*ca.* 15 g) formed. It was removed by filtration, and found to be primarily starting ester. Refrigeration of the filtrate at about 5° caused further crystal formation. Filtration after a week gave 0.74 g (2.5%) of a material, mp 150–152° (154.5–156°, after methanol recrystallization), which exhibited a rather broad absorption in the infrared, centered at 1735 cm^{-1} (ester carbonyl); its pmr spectrum showed a complex multiplet at τ 1.73–2.75 (7 H, aromatic), a doublet at 4.58 (1 H), a multiplet at 5.39 (1 H), identical singlets at 5.91, 6.00, and 6.68 (3 H each, methoxyl), and an eight-peak multiplet at 7.75–9.08 corresponding to the AB portion of an ABC pattern.

Anal. Calcd for $C_{23}H_{20}O_6$: C, 70.40; H, 5.14. Found: C, 70.47; H, 5.18.

Column chromatography of the total product, excluding the triester which crystallized out, on Merck reagent grade aluminum oxide, prepared in benzene and eluted with benzene–ether, afforded an additional 0.5 g of triester (4.2% total) and 14.3 g of starting ester. The remainder of the product appeared to be polymeric.

3-Acetoxymethyl-4*H*-cyclopenta[*def*]phenanthrene (22). A solution of 3-carbomethoxy-4*H*-cyclopenta[*def*]phenanthrene (**6**) (10.0 g, 0.040 mol) in anhydrous ether–benzene (500 ml, 10:1) was added slowly to a slurry of lithium aluminum hydride (1.00 g, 0.026 mol) in anhydrous ether (50 ml). The resulting suspension was refluxed for 30 min. After cooling, the excess metal hydride was decomposed by the cautious addition of water. The metal alkoxides were decomposed by shaking with 100 ml of cold 10% sulfuric acid. During the latter operation almost all of the product separated as a solid phase between the solvent layers. Most of the ether layer was decanted off and after being washed with water, bicarbonate solution, and water, was evaporated to give 1.0 g (11%) of solid. This product, mp 177–178.5° after crystallization from ethanol, showed infrared absorptions in KBr at 3350 (b), 1020 (s), and 1040 (s) cm^{-1} (alcohol); its pmr spectrum in *o*-dichlorobenzene showed singlets at τ 5.10 and 5.95 (2 H each). The remaining ether solution, the solid precipitate, and the emulsion present were separated from the acidic solution, and after being washed with saturated bicarbonate solution and water were combined and evaporated to a solid residue. Acetic anhydride (100 ml) was added to the residue, and the resulting mixture refluxed for 6 hr, cooled to room temperature, and filtered to remove the gelatinous precipitate of metal salts. Evaporation of the acetic anhydride and crystallization of the residue from ethanol gave 7.8 g (74%) of product, mp 65–66°.

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(21) B. H. Smith, "Bridged Aromatic Compounds," Academic Press, New York, N. Y., 1964, pp 359–384.

(22) J. F. Verdieck and W. A. Jankowski, reported at the Molecular Luminescence Symposium, Aug 1968. See "Molecular Luminescence," E. C. Lim, Ed., W. A. Benjamin, New York, N. Y., 1969, p 829.

(23) J. Gendell and J. Bramwell, *J. Chem. Phys.*, **52**, 5656 (1970), and private communication.

(24) We thank Dr. Jon DeJongh of Wayne State University for this determination.

(25) J. Janata, J. Gendell, C. Y. Ling, W. E. Barth, L. Baches, H. B. Mark, and R. G. Lawton, *J. Amer. Chem. Soc.*, **89**, 3056 (1967).

Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.33; H, 5.38.

The infrared spectrum in KBr showed characteristic acetate bands at 1730 (s) and 1250 (s) cm^{-1}. The pmr spectrum showed a complex multiplet at τ 2.15–2.60 (7 H, aromatic), a singlet at 4.66 (2 H), a singlet at 5.77 (2 H), and a singlet at 7.93 (3 H).

Acetate Solvolysis and Polymerization. After dissolving 1.0 g of 3-acetoxymethyl-4*H*-cyclopenta[*def*]phenanthrene (**22**) in 10 ml of acetic acid and adding 5 drops of 70% perchloric acid, the solution was allowed to stand overnight. A solid white material (0.8 g) separated from solution during that time. After being removed by filtration, the material was found to be insoluble in ether, alcohol, and acetone, but soluble in chloroform and benzene. Its pmr spectrum exhibited broad peaks and the ratio of acetate methyl to aromatic protons was 1:7.

Hydrogenolysis and Hydrogenation of 3-Acetoxymethyl-4*H*-cyclopenta[*def*]phenanthrene (22). The acetate (0.7 g) was hydrogenated (room temperature, 1 atm of H_2) in acetic acid (10 ml) containing 0.1 g of palladium on carbon catalyst (5%) and a few drops of concentrated hydrochloric acid. After 4 hr the catalyst was removed by filtration; 1.3 mol of hydrogen had been consumed. Ether was added to the solution and it was then washed six times with water and with saturated sodium bicarbonate solution before being dried (anhydrous $MgSO_4$) and evaporated. The white solid residue was crystallized from ether to give, in the first crop, a dihydro acetate (**23**), mp 113–114°, having bands in its pmr spectrum at τ 2.75–3.00 (5 H, complex multiplet), 4.88 (2 H, singlet), 6.15 (2 H, singlet), 6.90 (4 H, singlet), and 7.97 (3 H, singlet). The pmr spectra of the later crops of crystals revealed two compounds in addition to the dihydro acetate and the starting acetate. One of the compounds showed bands at τ 5.94 (2 H, singlet) and 7.50 (3 H, singlet). It was assigned structure **20**. The other compound, which could also be obtained in yields up to 90% upon extended hydrogenation (3 atm) of the crude mixture in acetic acid–ethyl acetate in the presence of palladium on carbon (5%) and a trace of perchloric acid, gave a pmr spectrum having a complex multiplet at τ 2.68–3.17 (*ca.* 5 H) and a singlet at 7.72 (3 H). It was assigned structure **24**.

8,9-Dihydro-4*H*-cyclopenta[*def*]phenanthrene (25). 4*H*-Cyclopenta[*def*]phenanthrene (1 g, Aldrich Chemical) was hydrogenated for several hours under 1 atm of hydrogen at room temperature in acetic acid–benzene containing also 0.1 g of acid. Upon work-up and crystallization from ethanol, a white crystalline product was obtained as platelets having a melting point of 140–141° (lit.[14] 140.5–141.2°).

The pmr spectrum of the product in carbon tetrachloride exhibited a multiplet at τ 2.72–3.13 (6 H, aromatic), a singlet at 6.28 (2 H), and a singlet at 6.97 (4 H), whereas the pmr spectrum of the starting material showed a complex multiplet at τ 2.25–2.65 (8 H) and a singlet (2 H) at 5.94.

Hydrogenation of 3-Carbomethoxy-4*H*-cyclopenta[*def*]phenanthrene (6). 3-Carbomethoxy-4*H*-cyclopenta[*def*]phenanthrene (10.0 g) in 80 ml of acetic acid containing also 40 ml of benzene and 2.55 g of palladium on carbon (10%) was shaken for over 15 hr under 3 atm of hydrogen. The pmr spectrum of the product revealed that *ca.* 90% of the starting material remained unchanged. The products were then again subjected to hydrogenation conditions, this time in acetic acid–ethyl acetate–benzene with 3.4 g of catalyst and 1 ml of 70% perchloric acid. After 3 days the product was found to consist of half starting ester and half dihydro derivative **26**, having pmr bands at τ 6.01 (2 H, singlet), 6.10 (3 H, singlet), and 7.05 (4 H, singlet).

4-Bromo-3-carbomethoxy-4*H*-cyclopenta[*def*]phenanthrene (27). 4*H*-Cyclopenta[*def*]phenanthrene (27.4 g, 0.11 mol) was dissolved in 685 ml of carbon tetrachloride containing a suspension of *N*-bromosuccinimide (21.6 g, 0.12 mol), and the resulting mixture was heated at reflux for 12 hr. After cooling to room temperature and filtration to remove the succinimide formed, the filtrate was evaporated to dryness. Methanol (685 ml) was added. The resulting mixture was refluxed for 15 min, and then cooled. After 3 hr at 5° the precipitate was filtered and dried to give 33.3 g (92%) of white crystalline product, mp 145–147°. The analytical sample, mp 147–148°, was obtained after a second crystallization from methanol.

The infrared spectrum in KBr showed sharp bands at 1730 and 1280 cm^{-1} (aryl ester). The pmr spectrum showed a complex multiplet at τ 1.75–2.30 (7 H, aromatic), singlet at 3.30 (1 H), and a singlet at 5.92 (3 H, methoxyl).

Anal. Calcd for $C_{17}H_{11}O_2Br$: C, 62.41; H, 3.39; Br, 24.42. Found: C, 62.47; H, 3.26; Br, 24.35.

Alkylation of the Bromo Ester 27 with Triethyl 1,1,2-Ethanetricarboxylate. 3-Carbomethoxy-4-(1,1,2-tricarbethoxyethyl-1)-4*H*-cyclopenta[*def*]phenanthrene (28). A warm (*ca.* 50°) solution of bromo ester (10.0 g, 0.031 mol) in benzene (100 ml) was added at room temperature to a rapidly stirred solution of triethyl 1,1,2-ethanetricarboxylate (15 ml, *ca.* 0.06 mol) in *tert*-butyl alcohol (125 ml) containing potassium *tert*-butoxide (4.8 g, 0.043 mol). After heating the resulting mixture at 45–55° for 1 hr, 2 ml of water was added, and the solvents were evaporated, leaving a viscous oil which was further utilized in several hydrolysis procedures.

4-(1,2-Dicarboxyethyl)-4*H*-cyclopenta[*def*]phenanthrene-3-carboxylic Acid (31) and Its Trimethyl Ester (19). Methanol (100 ml) and 10% sodium hydroxide solution (150 ml) were added to the viscous crude tetraester **38**, previously mentioned. The resulting solution was distilled at atmospheric pressure until the temperature of the vapor reached 100°. During the distillation, additional methanol was added when needed to keep the solution homogeneous, and additional water was added when needed to keep the total volume above 150 ml. The aqueous solution was then refluxed for 8 hr, acidified to pH 1 with 10% hydrochloric acid, refluxed for 1 additional hr, cooled, and extracted with ethyl acetate. After drying over anhydrous sodium sulfate, the ethyl acetate solution was concentrated and then cooled. Filtration gave 6.6 g (62%) of solid product, mp 220° dec, having characteristic carboxylic acid bands in the infrared (KBr) at 3040 (b), 1705 (s,b), 1420 (m), and 1280 (b) cm^{-1}.

In an esterification procedure patterned after Clinton and Laskowski,[26] the triacid **31** was refluxed for 16 hr in a solution of methanol, H_2SO_4, and 1,2-dichloroethane (20:4:100, by volume). After cooling, the solution was washed with water, saturated bicarbonate solution, and saturated sodium chloride solution, dried over anhydrous sodium sulfate, and evaporated to produce a crystalline product, mp 148–151°, shown by its pmr spectrum to be identical with the 3-carbomethoxy-4-(1,2-dicarbomethoxyethyl)-4*H*-cyclopenta[*def*]phenanthrene (**19**) obtained previously.

Attempts to Cyclize the Triacid 31 Intramolecularly. A. Finely powdered triacid (70 mg) was added with stirring to 50 ml of liquid hydrogen fluoride in an open 4-oz polyethylene bottle in the hood, and the resulting light orange solution stirred until the solvent had evaporated (4 hr). The residue was stirred with sodium bicarbonate solution overnight and then extracted with ethyl acetate. About 5 mg of insoluble residue remained, and an additional 5 mg of dark oil was obtained upon evaporation of the ethyl acetate solution, but neither of these small fractions was investigated further. After neutralization of the bicarbonate solution with hydrochloric acid, it was extracted with ethyl acetate. Upon evaporation of the solvent, about 50 mg of product was obtained, mp 215° dec. Esterification at reflux (21 hr) in a solution of methanol, sulfuric acid, and 1,2-dichloroethane gave a crude product, comprised almost entirely of triester **19** on the basis of its pmr spectrum.

B. In a procedure patterned after Campbell and Reid,[8] phosphorus pentachloride (1.2 g, 0.0058 mol) was added to a benzene (200 ml) slurry of triacid **31** (0.50 g, 0.0014 mol), and the mixture heated to reflux. Solution was complete in 15 min. After refluxing for an additional 15 min, the solution was cooled to room temperature, and 10 ml of benzene containing 5 drops of stannic chloride (*ca.* 0.6 g, 0.0022 mol) was added. The resulting solution was stirred for 10 min and then decomposed by adding 50 ml of concentrated hydrochloric acid with stirring. After separation of the solvent layers, the benzene layer was dried and evaporated. Methyl esterification of the residue by refluxing for 11 hr in a solution of methanol (1 ml), sulfuric acid (5 drops), and 1,2-dichloroethane (12 ml) gave a crude product, the pmr spectrum of which revealed mainly triester **19**, although small amounts of a few unidentified compounds were also seen to be present.

Partial Hydrolysis of the Triester 19. With stirring, 5.4 ml of 1 *N* potassium hydroxide solution (0.0054 mol) was added to a suspension of triester **42** (1.0 g, 0.0026 mol) in 145 ml of methanol, and the mixture heated to reflux. Periodic titration of aliquots revealed that half of the potassium hydroxide had been used up after 5 hr. The mixture was allowed to cool and evaporated under reduced pressure to *ca.* 50 ml, and then water (30 ml) and chloroform (50 ml) were added with stirring. After separation of the solvent layers, the chloroform layer was washed with saturated sodium bicarbonate solution, dried over anhydrous sodium sulfate,

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(26) R. O. Clinton and S. C. Laskowski, *J. Amer. Chem. Soc.*, 70, 3135 (1948).

and evaporated to give 80 mg of starting triester, mp 152–154°. The aqueous layer and the bicarbonate wash were combined, acidified with hydrochloric acid, and extracted with chloroform. Anhydrous benzene (100 ml) was added to the chloroform solution (*ca.* 100 ml) and the solvents were evaporated. The residue crystallized upon the addition of ethyl ether and was dried at reduced pressure over a steam bath to afford 620 mg of a white acid mixture.

***cis*-5,6-Dicarbomethoxy-3-oxo-3,4,5,5a-tetrahydrobenzo[*ghi*]fluoranthene (34).** The mixture of acid esters (0.50 g, *ca.* 0.0013 mol) obtained upon partial hydrolysis of triester **19** was slurried in warm benzene (10 ml). Phosphorus pentachloride (0.4 g, 0.0019 mol) was added. After stirring for 15 min the solution was refluxed for 5 min and cooled to room temperature, and *ca.* 0.8 ml (0.007 mol) of stannic chloride added. An exothermic reaction ensued, resulting in a brownish solution. After cooling the mixture to room temperature it was allowed to stir for 1 hr before being poured into 40 ml of concentrated hydrochloric acid. Extraction with two 40-ml portions of benzene and chloroform (30 ml), followed by multiple washing of the organic extract with sodium bicarbonate solution, gave a neutral fraction, which after being water washed, dried, and evaporated afforded about 40 mg (8%) of product, mp 165–172°. Recrystallization from methanol raised the melting point to 177–181°.

The infrared spectrum ($CHCl_3$) showed prominent bands at 1735 (ester carbonyl), 1695 (aryl ketone), 1275 (aryl ester), and 855 cm^{-1}. The pmr spectrum showed a complex multiplet at τ 1.65–2.25 (6 H, aromatic), a doublet at 4.91 (1 H, 5a position), a sextet at 5.34 (1 H, 5 position), a doublet at 6.73 (2 H, 4 position), and two identical singlets at 5.94 and 7.03 (3 H each, methoxyls).

Anal. Calcd for $C_{22}H_{16}O_5$: C, 73.33, H, 4.48. Found: C, 73.25; H, 4.50.

4-(1,1-Dicarbethoxy-2-carboxyethyl-1)-4*H*-cyclopenta[*def*]phenanthrene-3-carboxylate (36). A resinous mass of crude tetraester **28** (0.031 mol), prepared as before, was dissolved in 250 ml of methanol and aqueous potassium hydroxide solution (20 g in 125 ml) added. The resulting mixture was refluxed for 6.5 hr, cooled, partially neutralized by the addition of 22 ml of concentrated hydrochloric acid, and concentrated by evaporation under reduced pressure to remove the alcohols. After acidification to pH 1 with dilute hydrochloric acid, the mixture was refluxed for 30 min, during which time the product crystallized. After cooling the mixture, the precipitate was removed by filtration, washed with water, and dried at 100° under reduced pressure to produce 13.4 g (97%) of product, mp 202–207° dec.

The infrared spectrum ($CHCl_3$–Et_3N) showed bands of 1725 (ester carbonyl) and 1605 cm^{-1} (carboxylate salt). The pmr spectrum (pyridine) showed a singlet at τ 3.37 (1 H), a quartet at 5.48 (4 H), a doublet at 7.38 (2 H), and overlapping triplets at 8.65 and 8.70 (6 H). The compound was characterized as the dimethyl ester **37**.

3-Carbomethoxy-4-(1,1-dicarbethoxy-2-carbomethoxyethyl-1)-4*H*-cyclopenta[*def*]phenanthrene (37) was prepared from the diester acid **36** (0.5 g) upon refluxing for 20 hr in a solution of methanol (0.5 ml), sulfuric acid (0.3 ml), and 1,2-dichloroethane (10 ml). Normal work-up and crystallization from methanol afforded material of mp 141–142.5° which was used for the analytical sample.

The ultraviolet spectrum exhibited maxima at 233 (ϵ 2.6 × 10^4), 258 (ϵ 3 × 10^4), and 315 (ϵ 1.2 × 10^4) mμ. The infrared spectrum ($CHCl_3$) exhibited prominent maxima at 1725 and 1270 cm^{-1}. The pmr spectrum showed a complex multiplet at τ 1.75–2.55 (7 H, aromatic), a singlet at 3.92 (1 H), overlapping quartets at 5.55 and 5.74 (4 H) coupled with two overlapping triplets at 8.62 and 8.75 (6 H, ethoxyls), two identical singlets at 6.03 and 6.58 (3 H each, methoxyls), and an AB quartet centered at 8.12 (2 H).

Anal. Calcd for $C_{27}H_{26}O_8$: C, 67.77; H, 5.48. Found: C, 67.84; H, 5.57.

5,5-Dicarbethoxy-3-oxo-3,4,5,5a-tetrahydrobenzo[*ghi*]fluoranthene-6-carboxylic Acid (38). A polyphosphoric acid solution prepared by mixing 150 ml of polyphosphoric acid (Hi Laboratories, Whitmore Lake, Mich.) with 50 ml of 85% phosphoric acid was poured into 4.7 g of pulverized diacid diester **36**, and the resulting suspension heated, with stirring, to 80–85° for 1 hr and then poured into 650 ml of ice–water. After extraction with chloroform and washing with saturated sodium chloride solution, the mixture was concentrated to about 20 ml. Benzene (100 ml) was added, and the mixture heated to reflux. Upon cooling, a white crystalline solid separated. After filtration, washing, and drying, there was obtained 3.3 g (73%) of product, mp 223–228°. Recrystallization from methanol afforded the analytical sample, mp 235–236°.

The infrared spectrum ($CHCl_3$–Et_3N) showed characteristic absorption maxima at 1740 (ester carbonyl), 1690 (aryl ketone), and 1620 cm^{-1} (carboxylate salt). The ultraviolet spectrum showed maxima at 262 (ϵ 8 × 10^4), 298 (ϵ 2.7 × 10^4), and 330 mμ (ϵ 3.2 × 10^4). The pmr spectrum showed a complex multiplet at τ 1.65–2.30 (6 H, aromatic; nearly identical with the aromatic multiplet in the pmr spectrum of keto diester **44**), a singlet at 4.60 (1 H), a multiplet at 5.58 (2 H), a doublet at 6.40 (2 H), a quartet at 6.59 (2 H), and identical triplets at 8.71 and 9.75 (3 H each).

Anal. Calcd for $C_{25}H_{20}O_7$: C, 69.44; H, 4.66. Found: C, 69.79; H, 4.70.

5,5-Dicarbethoxy-6-carbomethoxy-3-oxo-3,4,5,5a-tetrahydrobenzo[*ghi*]fluoranthene (39). A. After heating at reflux 4 g of keto acid diester **38** in a solution of methanol (15 ml), sulfuric acid (2 ml), and 1,2-dichloroethane (50 ml) for 15 hr, the solution was washed with water, saturated sodium bicarbonate solution, and saturated sodium chloride solution, dried over anhydrous sodium sulfate, and evaporated to near dryness. The residue was crystallized from methanol to give about 1 g of material in the first crop, mp 143–150°. Concentration of the methanol mother liquors gave a second crop, mp 183–203°, a thin layer chromatogram of which revealed the presence of a substantial amount of the starting keto acid diester. Chromatography of the first crop on silica gel G allowed the major component to be separated. Crystallization from methanol gave material having mp 158–160°.

The pmr spectrum showed a complex multiplet at τ 1.77–2.30 (6 H, aromatic), a singlet at 4.78 (1 H), a multiplet at 5.60 (2 H), a singlet at 6.04 (3 H), a singlet at 6.45 (2 H), a quartet at 6.67 (2 H), and identical triplets at 8.68 and 9.85 (3 H each).

Anal. Calcd for $C_{26}H_{22}O_7$: C, 69.95; H, 4.97. Found: C, 70.08; H, 5.05.

5,5-Dicarbethoxy-1,2,2a,2b,3,4,5,5a,9,10,10a,10b-dodecahydrobenzo[*ghi*]fluoranthene-6-carboxylic Acid (40). An acetic acid solution of keto acid diester **38** (20.0 g, 0.045 mol in 500 ml), to which 8 ml of 70% perchloric acid and 20 g of palladium on carbon catalyst (5%) had been added, was shaken under hydrogen (3 atm) for 22 hr in a Parr shaker. The catalyst was removed by filtration and washed with 500 ml of chloroform. After combining the chloroform wash and the acetic acid solution, the solvents were evaporated under reduced pressure to a white residue, which was crystallized from ethanol to yield 10.4 g (54%) of product, mp 215–220°, in the first crop. After recrystallization the product melted at 218.5–220°.

The infrared spectrum ($CHCl_3$–Et_3N) showed characteristic maxima at 1720 (ester carbonyl) and 1600 cm^{-1} (carboxylate salt). The ultraviolet spectrum showed maxima at 245 (ϵ 6 × 10^3) and 290 mμ (ϵ 1.8 × 10^3). The pmr spectrum showed a broad singlet at τ −0.72 (1 H, carboxyl), two coupled doublets at 2.47 and 7.08 (1 H each, aromatic), a doublet at 5.33 (2 H), a complex quartet at 5.75 (4 H), two identical overlapping triplets at 8.70 and 8.78 (3 H each), and other complex overlapping multiplets from 4.7 to 1.2 (*ca.* 16 H).

Anal. Calcd for $C_{25}H_{30}O_6$: C, 70.40; H, 7.09. Found: C, 70.21; H, 6.92.

5,5-Dicarbethoxy-6-carbomethoxy-1,2,2a,2b,3,4,5,5a,9,10,10a,10b-dodecahydrobenzo[*ghi*]fluoranthene (41). A. An acetic acid (30 ml) solution containing a crude sample, mp 135–152°, of keto triester **39** (0.20 g), 0.20 g of palladium on carbon catalyst (5%), and 5 drops of 70% perchloric acid was hydrogenated (1 atm, room temperature) for 31 hr. Work-up in the usual manner gave a viscous residue which crystallized from methanol solution upon scratching while cooling the solution in a Dry Ice–acetone bath. The crystalline product (0.11 g, *ca.* 55%), mp 105–125°, was chromatographed through a silica gel G column to allow isolation of the major component, mp 115.5–117°, after crystallization from methanol.

The ultraviolet spectrum showed maxima at 250 (ϵ 8 × 10^3) and 290 mμ (ϵ 2.6 × 10^3). The pmr spectrum showed a doublet at τ 2.67 (1 H) coupled with a doublet at 3.11 (1 H), a quartet at 5.77 (4 H), a singlet at 6.20 (3 H, methoxyl), overlapping identical triplets at 8.72 and 8.74 (3 H each), and other complex overlapping multiplets (*ca.* 17 H).

Anal. Calcd for $C_{26}H_{32}O_6$: C, 70.89; H, 7.32. Found: C, 70.83; H, 7.30.

B. An ether solution of diazomethane was prepared according to the procedure given in ref 27, but on a one-tenth scale. A portion of the 0° diazomethane solution, containing approximately 0.029 mol of diazomethane, was added slowly with stirring to a room temperature solution of acid diester **50** (10.2 g, 0.024 mol) in 1500 ml of USP ether. The pale yellow color of the resulting solution, due to the presence of the diazomethane, faded slowly and was still detectable 3 hr after addition. At this time the ether was evaporated, leaving a solid residue. After crystallization from 30 ml of methanol 9.8 g (93%) of product, mp 110–112°, was obtained having a pmr spectrum identical with that of the triester isolated in procedure A.

C. Two attempts were made to obtain the triester **51** by refluxing samples of acid diester **50** in a solution of methanol, sulfuric acid, and 1,2-dichloroethane. Pmr spectra of the crude products revealed no detectable amount of the desired product; the starting material remained unchanged.

***exo*-5,6-Dicarbomethoxy-1,2,2a,2b,3,4,5,5a,9,10,10a,10b-dodecahydrobenzo[*ghi*]fluoranthene (43).** A solution of potassium hydroxide (5.7 g) in ethylene glycol (50 ml) to which 1.20 g of acid diester **40** had been added was refluxed for 6 hr, cooled to room temperature, and after the addition of 30 ml of water, was shaken with 500 ml of ethyl ether. After standing, the resulting aqueous layer was separated, diluted with 300 ml of water, and slowly acidified with 10% hydrochloric acid. A finely divided precipitate formed and was allowed to settle. After filtration, washing with water, and drying, there was obtained 0.92 g (100%) of product, mp 276–280° dec. The acid product (1.4 g) was esterified by refluxing for 21 hr in a solution of methanol (10 ml), sulfuric acid (2 ml), and 1,2-dichloroethane (50 ml) to give, after normal work-up and crystallization from ether, a white crystalline product (1.3 g, 86%), mp 131–132°.

The pmr spectrum showed a doublet at τ 2.40 coupled with a doublet at 3.06 (1 H each, aromatic), two identical singlets at 6.14 and 6.25 (3 H each, methoxyl), and complex overlapping multiplets in the region from 5.6 to 9.4 (*ca.* 17 H).

Anal. Calcd for $C_{22}H_{26}O_4$: C, 74.55; H, 7.39. Found: C, 74.46; H, 7.39.

***exo*-5,6-Bisacetoxymethyl-1,2,2a,2b,3,4,5,5a,9,10,10a,10b-dodecahydrobenzo[*ghi*]fluoranthene.** A solution containing 0.38 g (0.0011 mol) of diester **43** in 40 ml of ether (AR) was added dropwise to a slurry of lithium aluminum hydride (0.18 g, 0.0047 mol) in ether (15 ml), and the resulting suspension refluxed for 1 hr and cooled. The excess metal hydride and the metal alkoxides were hydrolyzed by stirring for 1 hr after the successive addition of 0.2 ml of water, 6 drops of 20% sodium hydroxide solution, and 0.5 ml of water. Removal of the insoluble precipitate by filtration gave a clear filtrate which was washed with saturated sodium chloride solution, dried over anhydrous sodium sulfate, and evaporated to dryness. Crystallization of the residue from ethanol afforded 0.29 g (90%) of product, mp 166–169°, which was analyzed as its diacetate.

The reduction product (30 mg) was refluxed for 3 hr in a solution of acetic anhydride and acetic acid (1 ml of each), and then cooled. Ether and water were added, and the mixture was shaken and separated. The ether layer was washed several times with water, 10% sodium hydroxide solution, and water, dried over anhydrous sodium sulfate, and evaporated to an oily residue. Crystallization from methanol (0.5 ml) gave a product, mp 98–100°, which was analyzed after an additional crystallization (mp 102.5–103°).

The pmr spectrum showed an AB quartet centered at τ 3.05 (2 H, aromatic), and AB quartet centered at 4.85 (2 H, benzylic bearing oxygen), overlapping quartets at 5.75 and 5.88 (1 H each, AB portions of ABC patterns), a singlet at 7.92 (6 H), and complex overlapping multiplets from 6.3 to 9.3 (*ca.* 18 H).

Anal. Calcd for $C_{24}H_{30}O_4$: C, 75.36; H, 7.91. Found: C, 75.37; H, 7.96.

Attempted Acyloin Reaction on the Dimethyl Ester (43). In a procedure patterned after Sheehan and coworkers,[19] a solution of dimethyl ester **43** (95 mg, 0.0027 mol) in dry ethyl ether (4 ml) was added rapidly with stirring to a precooled (Dry Ice–acetone) solution containing 6 ml of anhydrous liquid ammonia, 4 ml of dry ether, and 20 mg (0.0087 g-atom) of sodium metal. The solution, previously blue, immediately turned a pale yellow, and after being stirred in the Dry Ice–acetone bath for 15 min was acidified by the successive cautious addition of 1 drop of methanol in 2 ml of ether, and 1 ml of 5% hydrochloric acid. Ether and water were added, and the mixture was shaken and separated. The ether solution was washed with a saturated sodium bicarbonate solution and a saturated sodium chloride solution, dried over anhydrous sodium sulfate, and evaporated to a viscous oil. The pmr spectrum of the oil showed the presence of two compounds. One compound, comprising slightly less than half of the product, was obviously starting material with ester groups still intact (τ 6.14, 6.25). The major product also retained its ester groups as evidenced by the presence of two identical sharp singlets at τ 6.30 and 6.33. The new compound showed a singlet at 4.20 (2 H), but no bands in the aromatic region.

Aromatization Studies on *exo*-5,6-Dicarbomethoxy-1,2,2a,2b,-3,4,5,5a,9,10,10a,10b-dodecahydrobenzo[*ghi*]fluoranthene (43). A. 5,6-Dicarbomethoxybenzo[*ghi*]fluoranthene (46), 5-Carbomethoxybenzo[*ghi*]fluoranthene (45), and Benzo[*ghi*]fluoranthene (44). An intimate mixture of 50 mg of dimethyl ester **43** and 50 mg of 5% palladium on carbon catalyst was placed in a tube flushed with nitrogen (ketyl washed) and heated at 260° for 14 hr (oil bath). During the heating period some material sublimed from the catalyst cake and condensed on the tube sides above the level of the oil in the heating bath. The material which condensed farthest from the catalyst was almost white, but became progressively more yellow in the direction of the catalyst. After cooling, the product was divided so that the sublimate and the material left in the catalyst cake could be handled separately. Both fractions were dissolved in chloroform and filtered through a Filter Cel pad. The chloroform was evaporated from the solutions and replaced with deuteriochloroform. Pmr spectra of the samples, as well as thin layer chromatograms (alumina G, benzene), revealed that the sublimate fraction contained three major components in about equal amounts, whereas the "catalyst cake" fraction consisted primarily of one of these components, although the other two were also present. Removal of the chloroform from the carbon cake fraction by evaporation left a residue, which on crystallization from methanol formed yellow prisms of **46**, mp 195–196°.

The pmr spectrum showed a doublet centered at τ 2.07 (8 H, aromatic), and a singlet at 5.99 (6 H, methoxyl).

Anal. Calcd for $C_{22}H_{14}O_4$: C, 77.18; H, 4.12. Found (for a 1.7-mg sample): C, 76.87; H, 4.64 (corrected for ash 3.40).

The sublimate fraction was chromatographed through a column of silica gel G, which was prepared and eluted with benzene. The first component off the column was white and after crystallization from petroleum ether (30–60°) was shown to be benzo[*ghi*]fluoranthene (**44**) by comparison of its pmr spectrum and melting point, 146–147°, with those of an authentic sample (Aldrich Chemical), mp 150–150.5° (mixture melting point 146–148°). The second component off the column was yellow and melted at 102–103.5° after crystallization from methanol. Its pmr spectrum showed a complex multiplet at τ 1.65–2.30 (9 H, aromatic) and a singlet at 5.83 (3 H, methoxyl).

Anal. Calcd for $C_{20}H_{12}O_2$: C, 84.49; H, 4.25. Found: C, 84.31; H, 4.41.

B. In a modification of the above aromatization procedure, a 35-mg sample of diester **43** was mixed with an equal amount of catalyst and heated from 200 to 235° over 1 hr, cooled, and extracted with chloroform. Evaporation of the chloroform gave 26 mg of product which consisted, on the basis of its pmr spectrum, of about 80% 5,6-dicarbomethoxybenzo[*ghi*]fluoranthene (**46**), and the rest partially hydrogenated materials; no benzo[*ghi*]fluoranthene or monomethyl ester was evident.

C. ***cis*- and *trans*-Dicarbomethoxy-3,4,5,5a-tetrahydrobenzo[*ghi*]fluoranthene (47, 48).** In another modification of the aromatization procedure, 1.0 g of diester **43** and catalyst were mixed and heated slowly, 1.5 hr from 100 to 200°, 2 hr from 200 to 220°, and 0.5 hr from 220 to 240°. The pmr spectrum of the product (0.61 g total) showed that it consisted almost entirely (90%) of two partially aromatized compounds, the cis and trans epimers of 5,6-dicarbomethoxy-3,4,5,5a-tetrahydrobenzo[*ghi*]fluoranthene (**47** and **48**) in the ratio of 2:1. Identification was made by comparison with samples isolated after hydrolysis and Wolff–Kishner reduction of keto acid diester **38**. The pmr spectra of these two compounds are discussed with the results of the Wolff–Kishner reduction experiment.

Hydrogenation of 5,6-Dicarbomethoxybenzo[*ghi*]fluoranthene (46). A. A 50-mg sample of diester containing small amounts of benzo[*ghi*]fluoranthene and 5-carbomethoxybenzo[*ghi*]fluoranthene (**45**) was added to a slurry of 20 mg of 5% palladium on carbon in 25 ml of acetic acid and stirred under hydrogen (1 atm) for 17 hr. The pmr spectrum of the product, after normal work-up, showed that the starting diester remained unchanged, although the benzo[*ghi*]fluoranthene and 5-carbomethoxybenzo[*ghi*]fluoranthene had been at least partly hydrogenated.

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(27) J. A. Moore and D. E. Reed, "Organic Synthesis," J. D. Roberts, Ed., Wiley, New York, N. Y., 1961, p 16.

B. The product from above was added to a slurry of 5% palladium on carbon (50 mg) in acetic acid (4 ml) containing also 3 drops of 70% perchloric acid, and the mixture stirred under hydrogen (1 atm) for 19 hr. After normal work-up, the crude product was chromatographed on a silica gel G column to remove the nonpolar impurities. A pmr spectrum of the remainder (*ca.* 70% of the total) showed an AB quartet in the aromatic region (4 H, methoxyl), and overlapping multiplets from 6.3 to 9.0.

Hydrogenation of Benzo[*ghi*]fluoranthene (44). Benzo[*ghi*]fluoranthene (33 mg) was added to a slurry of 5% palladium on carbon (33 mg) in 3 ml of acetic acid containing 1 ml of benzene and 3 drops of 70% perchloric acid. The mixture was stirred under hydrogen (1 atm) for 20 hr. After normal work-up, the pmr spectrum of the crude product was seen to be well defined, and showed a complex multiplet at τ 2.6–3.3 (3 H) and complex overlapping multiplets from 6.5 to 9.5 (19 H).

Hydrolysis and Wolff–Kishner Reduction of the Keto Acid Diester 48. *cis*- and *trans*-5,6-Dicarbomethoxy-3,4,5,5a-tetrahydrobenzo[*ghi*]fluoranthene (47 and 48). A solution of potassium hydroxide (0.20 g, 0.003 mol) in ethylene glycol (3 ml) was added to a slurry of the keto acid diester (0.20 g, 0.0005 mol) in ethylene glycol (3 ml), and the resulting solution heated to 165° for 30 min, and then allowed to cool. Hydrazine hydrate (0.05 ml of 99%, *ca.* 0.001 mol) was added and the solution heated to 200°, kept there for 70 min, and then allowed to cool. After twofold dilution with water and acidification with 10% hydrochloric acid, a precipitate formed. The solids were removed by filtration, washed with water, and dried. Esterification was achieved by 24-hr reflux in a solution of methanol (5 ml), sulfuric acid (1 ml), and 1,2-dichloroethane (25 ml). After normal work-up, the pmr spectrum of the crude product showed one major component (*ca.* 60%) and several others. Column chromatography on silica gel G allowed 40 mg of the major component to be isolated, mp 153.5–155.5°. The analytical sample, mp 156–156.5°, was obtained by recrystallization from methanol.

The pmr spectrum showed a complex multiplet at τ 1.70–2.70 (6 H, aromatic), a doublet at 5.02 (1 H), a multiplet at 5.67 (1 H), identical singlets at 6.00 and 7.01 (3 H each, methoxyl), and multiplets from 6.8 to 7.6 (4 H).

Anal. Calcd for $C_{22}H_{18}O_4$: C, 76.29; H, 5.24. Found: C, 76.08; H, 5.13.

A second component (*ca.* 15%) of the crude product mixture was seen to have identical singlets at τ 6.07 and 6.22 (methoxyls) in the pmr spectrum. This same material was also seen to be present with the *cis*-5,6-dicarbomethoxy-3,4,5,5a-tetrahydrobenzo[*ghi*]fluoranthene (**47**) obtained in the aromatization studies (procedure B) and is thought to be the trans epimer at C-5.

A sample of the intermediate hydrolysis product mentioned previously was isolated in a different run (after 4 hr at 165°). Normal work-up and methyl esterification (methanol, sulfuric acid, 1,2-dichloroethane) produced *cis*-5,6-dicarbomethoxy-3-oxo-3,4,5,5a-tetrahydrobenzo[*ghi*]fluoranthene (**34**), identical with that obtained earlier.

Hydrogenation of *cis*-5,6-Dicarbomethoxy-3,4,5,5a-tetrahydrobenzo[*ghi*]fluoranthene (47). The diester (30 mg) in a slurry of 5% palladium on carbon catalyst (30 mg) in benzene (2 ml) and ethanol (1 ml) was stirred under hydrogen (1 atm, room temperature) for 21 hr. The catalyst was removed by filtration and the solution concentrated to a solid residue. Crystallization from methanol gave a product melting at 174–175.5°. Its pmr spectrum showed an AB pattern consisting of two coupled doublets centered at τ 2.17 and 2.85 (2 H total, aromatic), a singlet at 2.99 (2 H, aromatic), a multiplet at 5.75 (2 H), identical singlets at 6.07 and 6.84 (3 H each, methoxyl), and overlapping multiplets from 6.5 to 7.7.

Anal. Calcd for $C_{22}H_{20}O_4$: C, 75.84; H, 579. Found: C, 75.66; H, 580.

Intramolecular Acyloin Closures on 5,5-Dicarbethoxy-6-carbomethoxy-1,2,2a,2b,3,4,5,5a,9,10,10a,10b-dodecahydrobenzo[*ghi*]fluoranthene (41). A. 2a-Hydroxymethyl-2-hydroxy-1-oxo-1,2,2a,2b,3,4,4a,4b,5,6,6a,6b,7,8-tetradecahydrocorannulene (53). A solution of triester **41** (120 mg, 0.00027 mol) in 6 ml of dry ether was added rapidly with stirring to a cooled (Dry Ice–acetone) solution containing 44 mg (0.0018 g-atom) of sodium in 9 ml of anhydrous liquid ammonia (freshly distilled from sodium) and 6 ml of dry ether. After stirring for 50 min, 0.2 ml of methanol in 3 ml of ether was added; stirring was continued for 10 more min, and then 1 ml of 5% hydrochloric acid was added cautiously. The product was isolated by adding water and extracting with ether. The ether solution was washed with water and saturated sodium chloride solution, dried over anhydrous sodium sulfate, and concentrated by evaporation to an oil, which crystallized upon the addition of methanol. The analytical sample, mp 168–172°, was obtained by recrystallization from methanol.

The infrared spectrum ($CHCl_3$) showed maxima at 3470 (broad, hydrogen bonded –OH), 3010 (w), 2930 (s), 2860 (m), 1680 (s, aryl ketone), 1620 (s), and 1270 cm^{-1} (s). The pmr spectrum showed an AB pattern consisting of two coupled doublets at τ 2.39 and 3.02 (2 H total), a singlet at 5.36 (1 H), a singlet at 6.28 (2 H), and complex overlapping multiplets from 5.7 to 9.3.

Anal. Calcd for $C_{21}H_{24}O_3$: C, 77.75; H, 7.47. Found: C, 77.24; H, 7.48.

B. 2a-Carbethoxy-2-hydroxy-1-oxo-1,2,2a,2b,3,4,4a,4b,5,6,6a,-6b,7,8-tetradecahydrocorannulene (54). In a modification of the above procedure, a solution of triester **41** (3.00 g, 0.0068 mol) in 75 ml of dry ether was added rapidly with stirring, under an atmosphere of nitrogen (ketyl washed[28]), to a cooled (Dry Ice–acetone) solution of sodium (0.75 g, 0.030 g-atom) in 180 ml of anhydrous liquid ammonia (freshly distilled from sodium) and 120 ml of dry ether (blue solution). After stirring the reaction mixture for 5 min, 8 ml of methanol in 10 ml of ether was added (yellow solution); after 10 more min, 3 g of ammonium chloride in 100 ml of water was added (solution red during addition, clear after). The Dry Ice bath was removed and the solution stirred for 1.25 hr to allow much of the ammonia to evaporate. Water (100 ml) and ether (100 ml) were than added, the phases were mixed, and the layers separated. The water layer was back-extracted with more ether. The ether extracts were combined, washed with 100 ml of saturated sodium chloride solution, dried over anhydrous sodium sulfate, and evaporated to a viscous oil. Crystallization from methanol afforded 1.21 g (48%) of white product, mp 134–136°, in the first crop. The analytical sample melted at 138–140°.

The ultraviolet spectrum showed maxima at 222 (ϵ 1.1 $\times$ 10^5), 270 (ϵ 9 $\times$ 10^4), and 310 (ϵ 4 $\times$ 10^4) nm. The infrared spectrum ($CHCl_3$) showed maxima at 3470 (broad, but weak), 2925 (s), 1725 (s, ester carbonyl), 1675 (s, aryl ketone), and 1610 (s) cm^{-1}. The pmr spectrum showed an AB quartet consisting of coupled doublets at τ 2.36 and 2.96 (2 H total, aromatic), a singlet at 5.10 (1 H, position C-2), a quartet at 5.67 (2 H) coupled with a triplet at 8.64 (3 H), a doublet at 6.03 (1 H, position C-2b), and overlapping multiplets from 6.1 to 9.2.

Anal. Calcd for $C_{23}H_{26}O_4$: C, 75.38; H, 7.15. Found: C, 75.44; H, 7.15.

The pmr spectrum of the mother liquor residues from the above crystallization (0.87 g total) revealed that it consisted of at least half acyloin ester **54**; the remainder seemed to be made up of products resulting from further reduction of the acyloin ester.

2a-Carbethoxy-2-oxo-1,2,2a,2b,3,4,4a,4b,5,6,6a,6b,7,8-tetradecahydrocorannulene (57). Sodium borohydride (13 mg, 0.00034 mol) in methanol (1 ml) was added to acyloin ester **54** (60 mg, 0.00017 mol) in methanol (5 ml) and the resulting solution refluxed for 10 hr, cooled, neutralized by the addition of 2 drops of acetic acid, and concentrated by evaporation of a viscous oil. The oil was dissolved in 0.5 ml of glacial acetic acid and heated to 110° in an oil bath, a drop of sulfuric acid added, and heating continued at 110° for 4.5 hr. After cooling, water was added and the product extracted with ether. The ether solution was washed with saturated bicarbonate solution and water, dried over anhydrous sodium sulfate, and evaporated to a viscous oil.

Only one compound appeared to be present in the crude product as determined by its pmr spectrum which showed a singlet at τ 3.10 (2 H, aromatic), a quartet at 5.67 (2 H) coupled with a triplet at 8.76 (3 H), a doublet at 5.81 (1 H), a singlet at 6.36 (2 H), and overlapping multiplets from 6.8 to 8.9.

In an attempt to hydrolyze the product, it was dissolved in 0.6 ml of glacial acetic acid, and 0.4 ml of concentrated sulfuric acid in 0.5 ml of water added. The mixture was stirred at 95° for 10 hr and upon work-up gave an intractable red tar.

2-Oxo-1,2,2a,2b,3,4,4a,4b,5,6,6a,6b,7,8-Tetradecahydrocorannulene (59). A. Acyloin ester **54** (48 mg, 0.00014 mol) was dissolved in 3 ml of *n*-propyl alcohol, 16 mg (0.00042 mol) of sodium borohydride added, and the solution allowed to stir at room temperature for 1 hr (in a rerun of this experiment, the product was isolated at this point. Its pmr spectrum showed an AB quartet centered at 2.90 (2 H), a doublet at 5.00 (1 H), a quartet at 5.70 (2 H) coupled to a triplet at 8.64 (3 H), and overlapping multiplets

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[28] L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath and Co., Boston, Mass., 1957, p 299.

from 5.5 to 9.0.) Then a solution of 90 mg (0.0015 mol) of potassium hydroxide in 0.5 ml of water was added and the solution refluxed for 4.5 hr. After cooling, 2 ml of water was added and the solution acidified to pH 1 by adding 2 ml of 4% hydrochloric acid. The precipitate which formed was extracted with ether. The ether solution was washed with water, dried over anhydrous sodium sulfate, and evaporated to a white residue. Crystallization from chloroform gave a material which decomposed at 216° with gas evolution. The pmr spectrum of this intermediate showed an AB quartet at τ 2.87, but no bands to suggest that the ester ethoxyl remained.

The solid material was placed in a test tube under nitrogen and heated to 220° for 45 min, during which time the compound melted and gave off gas bubbles. A liquid condensate was seen to form on the tube sides just above the oil bath used as a heat source. After cooling the tube, the condensate and the residue in the tube bottom were each dissolved in chloroform and handled separately.

The pmr spectrum of the condensate suggested the presence of only one compound, and showed a singlet at τ 3.12 (2 H), a singlet at 6.50 (2 H), and overlapping multiplets from 6.7 to 9.3. The infrared spectrum ($CHCl_3$) showed bands at 3000 (w), 2920 (s), 2860 (m), 1700 (s) cm^{-1}. The pmr spectrum of the residue suggested a complex mixture.

B. In an alternate procedure, 1.40 g (0.0038 mol) of acyloin ester **72** was dissolved in 70 ml of *n*-propyl alcohol, 0.45 g (0.012 mol) of sodium borohydride added, and the solution stirred for 1.5 hr at room temperature. Potassium hydroxide (3.0 g, 0.045 mol) in 12 ml of water was added and the solution refluxed for 4 hr. After cooling, 50 ml of ether was added and the solution acidified to pH 1 by the addition of 5% hydrochloric acid. The two layers which formed were separated and the water layer was extracted with additional ether. The ether extracts were combined, washed with saturated sodium chloride solution, dried over anhydrous sodium sulfate, and evaporated to dryness under reduced pressure over a steam bath. The residue was dissolved in 30 ml of acetic acid containing 2 ml of concentrated hydrochloric acid, and the resulting solution heated to reflux for 5 min and then allowed to cool. Water (100 ml) was added and the mixture extracted with 80 ml of ether. The aqueous layer was back-extracted with an additional 20 ml of ether. The combined ether layers were then washed with an additional 100 ml of water and, after separation, the aqueous layer was again back-extracted with 20 ml of ether. The ether extracts were combined, washed with saturated sodium chloride solution, dried over anhydrous sodium sulfate, and evaporated to dryness. The pmr spectrum of the residue showed the presence of ketone (30%) and acetate (10%) as well as β-keto acid (**58**), which has a characteristic singlet at τ 6.36 (2 H). Decarboxylation of the crude residue was effected by heating it under reduced pressure (water aspirator) over a steam bath for 10.5 hr. The product (1.09 g, 102%) was seen by its pmr spectrum to be nearly pure ketone; the only obvious impurity present was an acetate (*ca.* 10%).

Column chromatography on silica gel G allowed the acetate to be isolated. Its pmr spectrum showed a singlet at τ 3.10 (2 H, aromatic), an AB quartet at 5.64 (2 H), a singlet at 7.96 (3 H), and overlapping multiplets from 6.4 to 9.3, but no band corresponding to carboxyl.

A sample of ketone **59** isolated during the chromatography was used in the preparation of a 2,4-dinitrophenylhydrazone. The derivative melted at 225–227° after recrystallization from chloroform–ethanol.

Corannulene, Dibenzo[*ghi*,*mno*]fluoranthrene (1). **A.** Ketone **59** (20 mg) was placed in the bottom of a 7-mm glass tube, covered with 1 cm of 5% palladium on carbon catalyst, and heated (under nitrogen) in an oil bath for 1 hr at 25–200° and 1 additional hr at 200–240°. After cooling the tube, the product was extracted with chloroform, filtered through a Filter Cell pad to remove catalyst, and recovered by evaporation of the solvent. The pmr spectrum of the product showed only one distinct peak, a sharp singlet at τ 2.19.

In an attempt to repeat this experiment on a larger scale, 110 mg of ketone **59** was heated, as above, with 500 mg of catalyst. Upon work-up, however, only starting material and partially aromatized materials were detected in the product, no singlet being evident at τ 2.19. The product was resubjected to the same conditions, but after work-up, the pmr spectrum still failed to show a peak at τ 2.19.

B. In a modification of the above procedure, 0.22 g (0.058 mol) of sodium borohydride was added, with stirring, to a solution of 1.09 g of ketone **59** (0.0039 mol, from procedure B) in 20 ml of ethanol and 8 ml of benzene. After stirring at room temperature for 0.5 hr, 5 ml of water was added and the solution heated to reflux, and then cooled. Ether (60 ml) was added and the resulting solution washed with 40 ml of 1% hydrochloric acid, saturated sodium bicarbonate solution, and saturated sodium chloride solution, dried over anhydrous sodium sulfate, and evaporated under reduced pressure to 1.03 g (94%) of viscous oil. The pmr spectrum of the oil showed a singlet at τ 3.17 (2 H), a multiplet centered at 5.7, and overlapping multiplets from 6.2 to 9.3. (Acetate impurities in the starting material were not evident at this stage.)

The oil was dissolved in 3 ml of chloroform, and after being slurried with 1.0 g of 5% palladium on carbon, was placed in a 15-mm glass tube closed at one end. After careful evaporation of the chloroform, an additional 1 g of catalyst was placed on top of the residue in the tube, and the sample heated under nitrogen in an oil bath at 110–195° for 0.5 hr, then at 195–275° for 1.5 hr. After cooling the tube, the catalyst was extracted with 60 ml of chloroform. The chloroform solution was filtered through a Filter Cell pad and evaporated to give 0.46 g (51%) of amorphous residue, mp 180–205°. Upon heating the residue to 170° under reduced pressure (0.02 mm) slightly more than half of it sublimed. The sublimate, a mixture of crystals and oil, after being washed with ethanol, gave 160 mg (16% from the ketone) of pale yellow crystals, mp 268–269° (capillary sealed under nitrogen).

The ultraviolet spectrum (ethanol) showed maxima (mμ) at 246 (6.0×10^4), 249 (ϵ 5.4×10^4), 253 (ϵ 9.1×10^4), 288 (ϵ 3.3×10^4), and a tailing shoulder at 320. The infrared spectrum ($CHCl_3$) showed maxima at 3050, 3010, 1430, 1310, 1135, 905, and 840 (strong) cm^{-1}. The pmr spectrum showed only one band, a singlet at τ 2.19. The mass spectrum showed a parent peak at m/e 250, an $m/2$ peak at 125 (the second largest peak, 23%), and an $m/3$ peak at 83 (1.5%).

Anal. Calcd for $C_{20}H_{10}$: C, 95.97; H, 4.03. Found: C, 95.77; H, 4.23.