The pure 2,4-dinitrophenylhydrazone was converted to the ketone by the procedure of Martin and Demaeker.[36] The crude ketone was evaporatively distilled at 45–55° (0.03 mm.) and obtained in 83% over-all yield as a colorless oil, n^{32}D 1.4974.

Anal. Calcd. for $C_{12}H_{20}O$: C, 79.94; H, 11,18. Found: C, 79.44; H, 11.22.

The semicarbazone of V was obtained as small, colorless needles after recrystallization from ethanol; m.p. 201–202° dec.

Anal. Calcd. for $C_{13}H_{23}N_3O$: C, 65.78; H, 9.77. Found: C, 65.73; H, 10.14.

2-(Decahydro-1-naphthyl)-octahydrospiro[1,3-dioxolane-4,1′(2′*H*)-naphthalene] (X).[37]—A 2.0-g. sample of the glycol IX described above was refluxed for 20 minutes with 20 ml. of 20% sulfuric acid. Several evaporative distillations of the product yielded a very viscous oil, b.p. 130–140° (0.02 mm.), n^{25}D 1.5150.

Anal. Calcd. for $C_{22}H_{36}O_2$: C, 79.46; H, 10.92. Found: C, 78.85; H, 10.75.

Prolonged refluxing of the above material with 2,4-dinitrophenylhydrazine hydrochloride in ethanol yielded the 2,4-dinitrophenylhydrazone of *trans*-*trans*-decahydro-1-naphthylcarboxaldehyde, m.p. 170–171.5°.

Infrared Analysis.—The quantitative infrared analyses were carried out in carbon disulfide solution in 0.1-mm. thick cells. A Perkin–Elmer model 21 double-beam instrument was used without compensation for the solvent, and corrections for solvent absorption were applied to the calculations.

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[36] R. H. Martin and J. Demaeker, *Nature*, **173**, 266 (1954).

[37] We are indebted to Dr. Leonard T. Capell of *Chemical Abstracts* for information concerning the nomenclature of this compound.

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

Polynuclear Aromatic Hydrocarbons. IV.[1] Benzo[*c*]phenanthrenes

BY DONALD D. PHILLIPS AND A. WILLIAM JOHNSON

RECEIVED JUNE 9, 1955

A new method for the preparation of benzo[*c*]phenanthrene derivatives has been developed. Advantage is taken of the polyfunctional nature of the readily available β-methallylsuccinic anhydride (I) which, when treated with benzene in the Friedel–Crafts reaction, gives rise to keto acids II and III, both of which may be converted in good over-all yield to the *gem*-dimethyl derivative XIII, and thence to 5-methylbenzo[*c*]phenanthrene (XVIII), Compounds analogous to XIII are of interest as potential carcinogenic agents and may prove useful in establishing the role of coplanarity in carcinogenesis among polynuclear aromatic hydrocarbons.

One of the most intriguing problems in the study of carcinogenic hydrocarbons has been the correlation between chemical structure and biological activity. Numerous theories have been published[2] on this subject but as yet none has been found satisfactory in all respects.

Although coplanarity has been suggested as a requirement for carcinogenic activity,[3] the importance of this structural feature *per se* has not been fully investigated. Badger[4] has found that partial hydrogenation of several carcinogenic hydrocarbons destroys their activity and has ascribed this to a disruption in the coplanarity of the molecule. The recent important discovery by Miller[5] that 3,4-benzpyrene is rapidly bound to protein in the epidermal fraction of mouse skin indicates that some kind of complex formation takes place and the relative importance of coplanarity in this reaction takes on added significance.

As one approach to this problem we have selected for study the benzo[*c*]phenanthrene (*cf.* XVIII) ring system. Our choice was based on the fact that several of its derivatives are known to be carcinogenic[6] and suitably substituted benzo[*c*]phenanthrenes are non-planar because of steric interference between carbons 1 and 12.[7] These would be particularly interesting to examine for activity because they still possess the important[8] 9,10-phenanthrene double bond which was absent in most of the reduced hydrocarbons previously tested.[4,9]

Several synthetic routes to the benzo[*c*]phenanthrene ring system have been reported in the recent literature[10,16] but none of them seemed practical for preparing both the hindered and partially reduced derivatives that we wished to investigate. Moreover, we hoped to devise a synthesis based on readily available starting materials so that a variety of substituted benzo[*c*]phenanthrenes could be examined. In this respect, β-methallylsuccinic anhydride (I) seemed eminently suited to our purpose because of its polyfunctional nature and ease of preparation from maleic anhydride and isobutylene.[11] When condensed with benzene in the pres-

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[1] Paper III, D. D. Phillips and E. J. McWhorter, THIS JOURNAL, **77**, 3856 (1955).

[2] For an excellent review on the subject of chemical constitution and carcinogenic activity see G. M. Badger in "Advances in Cancer Research," Vol. 2, Academic Press Inc., New York, N. Y., 1954, pp. 73–127.

[3] (a) Reference 2, p. 98. (b) Coplanarity is an important feature in the currently popular "electron density hypothesis" theory as applied to carcinogenic hydrocarbons; see A. Pullman, *Ann. chim.*, **2**, 5 (1947); P. Daudel and R. Daudel, *Biol. méd.*, **39**, No. 4, 1 (1950), and ref. 2, p. 101.

[4] G. M. Badger, *Brit. J. Cancer*, **2**, 309 (1948).

[5] E. C. Miller, *Cancer Research*, **11**, 100 (1951). For proof that the binding is covalent in nature see P. M. Bhargava, H. I. Hudler and C. Heidelberger, THIS JOURNAL, **77**, 2877 (1955).

[6] Reference 2, p. 86.

[7] F. H. Herbstein and G. M. J. Schmidt, *J. Chem. Soc.*, 3302 (1954); M. S. Newman and W. B. Wheatley, THIS JOURNAL, **70**, 1913 (1948).

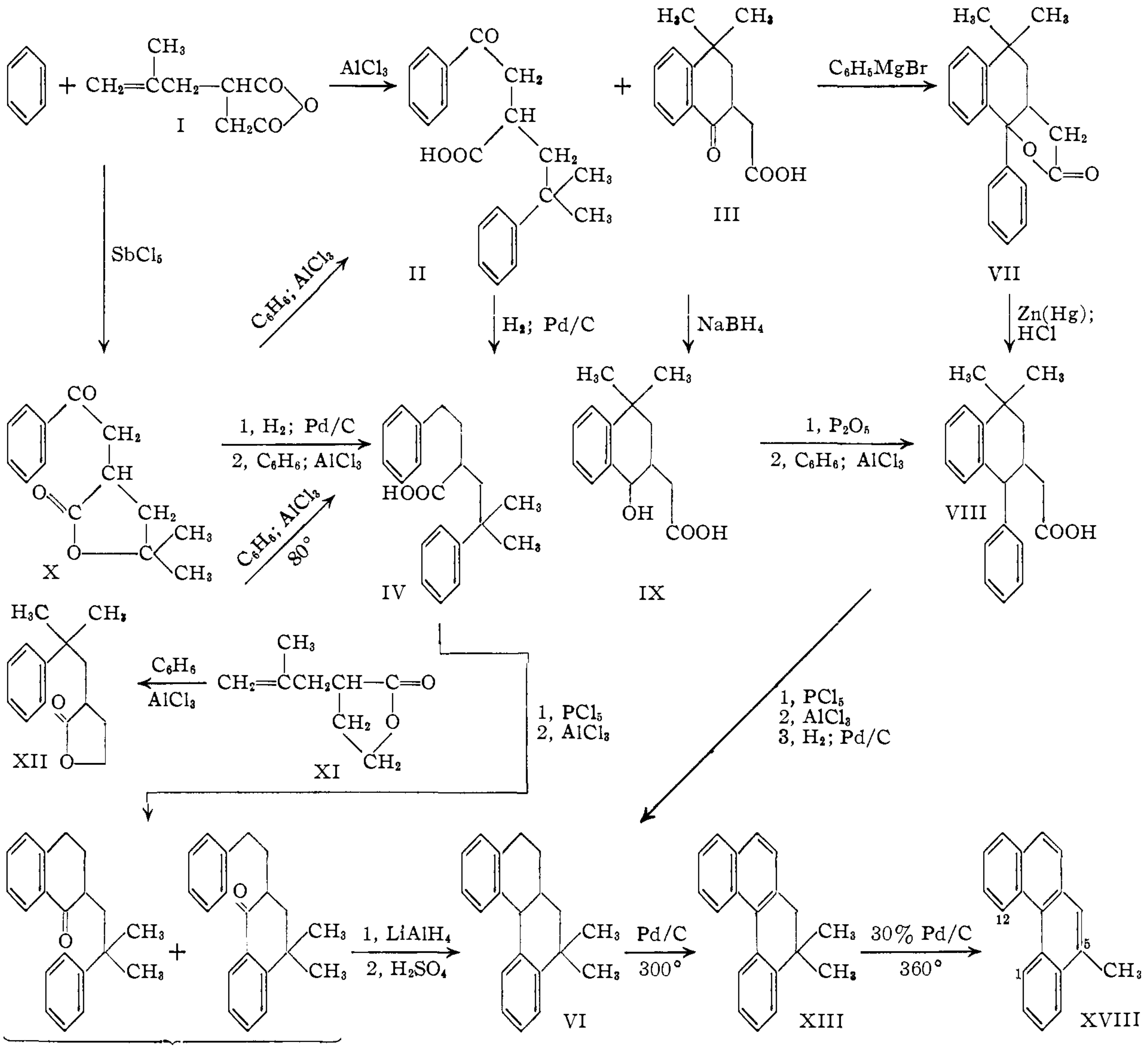
[8] R. Robinson, *Brit. Med. J.*, **I**, 943 (1946); ref. 2, pp. 95–97.

[9] M. J. Shear, *Am. J. Cancer*, **28**, 334 (1936); **33**, 439 (1938); J. L. Hartwell, "Survey of Compounds which Have Been Tested for Carcinogenic Activity," 1st and 2nd Ed., Public Health Service Publication, Washington, D. C., 1940 and 1951.

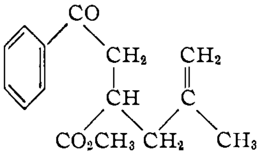
[10] M. S. Newman, H. V. Anderson and K. H. Takemura, THIS JOURNAL, **75**, 347 (1953); J. Szmuszkovicz and E. J. Modest, *ibid.*, **70**, 2542 (1948); **72**, 566 (1950); C. Djerassi and T. T. Grossnickle, *ibid.*, **76**, 1741 (1954); A. L. Wilds and R. G. Werth, *J. Org. Chem.*, **17**, 1154 (1952); S. M. Mukherji, V. S. Gaind and P. N. Rao, *ibid.*, **19**, 328 (1954); G. T. Tatevosyan and V. O. Babayan, *J. Gen. Chem.*, **22**, 1421 (1952).

[11] K. Alder, F. Pascher and A. Schmitz, *Ber.*, **76B**, 47 (1943).

CHART 1



ence of aluminum chloride, the anhydride formed three products, two of which could be carried through to our original objective. The major product of the reaction was the tetraloneacetic acid (III) which resulted from an alkylation followed by intramolecular acylation. In addition to III there was isolated the intermolecularly alkylated derivative II which incorporated in one step, albeit in low (6%) yield, *all* the carbons of the desired ring system. A third acidic compound was isolated from the reaction but its structure still remains obscure. Because the methyl ester of this unknown acid showed strong infrared absorption at 5.77, 5.98, 6.13 and 11.23 μ, we originally suspected that it was the monoacylated product XIV but an unequivocal synthesis of XIV from phenylmagnesium bromide and I established their non-identity.


XIV

In an effort to improve the yield of (II), the Friedel–Crafts reaction was carried out in the presence of antimony pentachloride.[12] With this catalyst none of the ketoacid II was formed, but instead the keto lactone X was isolated in 44% yield. This lactone could be condensed further with benzene and *aluminum chloride* to give the desired ketoacid II in essentially quantitative yield, so that the two-step process represented a far superior synthetic method.

Since the initial condensation between benzene and the substituted anhydride I could give rise to two position isomers, we deemed it advisable to confirm that the "α"-isomer II was indeed the major product.[13] To this end, α-(β-methallyl)-γ-bu-

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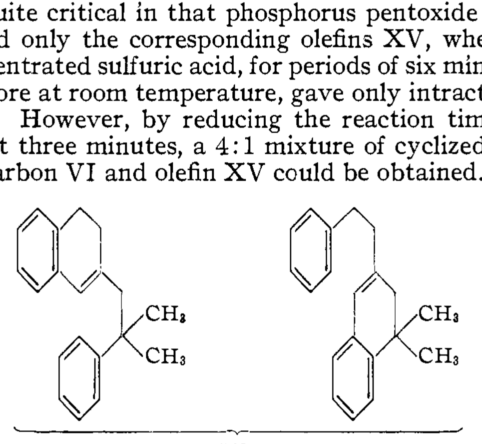
[12] Antimony pentachloride is known to be a catalyst in the Friedel–Crafts ketone synthesis and is next to aluminum chloride in efficiency (O. C. Dermer, D. M. Wilson, F. M. Johnson and V. H. Dermer, THIS JOURNAL, 63, 2881 (1941)).

[13] For a discussion of the Friedel–Crafts reaction with substituted succinic anhydrides see E. Berliner in "Organic Reactions," Vol. 5, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 242.

tyrolactone (XI) was prepared and condensed with benzene in the presence of aluminum chloride to give a lactone XII that was isomeric with the reduction product of X, and, in small yield, the reduced acid IV. Because the methallyl group in the butyrolactone XI is α to the potential carboxyl, it follows that IV (and hence II) must also be an α-substituted acid. Further confirmation was derived from the reaction between benzene and the isomeric lactone XII at higher temperatures, where the reduced acid IV was once again obtained.

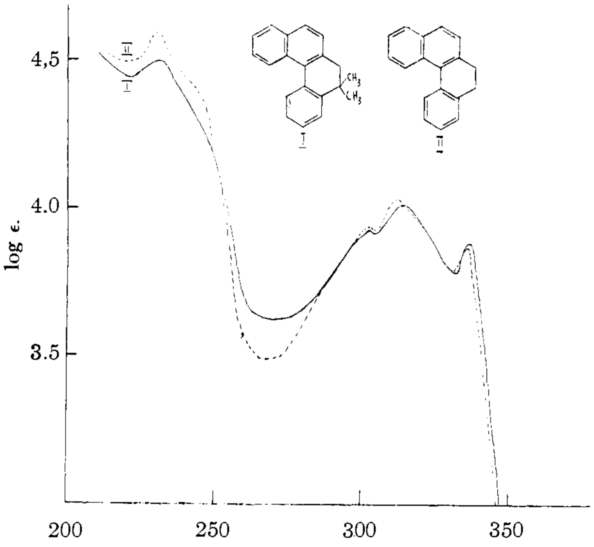
The carbonyl group in II was reduced by Horning and Reisner's catalytic[14] method and the resultant acid IV was cyclized to a mixture of tetralones V by an excellent intramolecular acylation technique developed by Johnson and Glenn.[15] No attempt was made to separate this mixture of ketones or to determine its relative composition since both isomers could be converted to the same hydrocarbon VI. This transformation was accomplished by first reducing the carbonyl group with lithium aluminum hydride and then subjecting the mixture of alcohols to an acid-catalyzed cyclodehydration. The conditions for this dehydration were found to be quite critical in that phosphorus pentoxide produced only the corresponding olefins XV, whereas concentrated sulfuric acid, for periods of six minutes or more at room temperature, gave only intractable tars. However, by reducing the reaction time to about three minutes, a 4:1 mixture of cyclized hydrocarbon VI and olefin XV could be obtained. An earlier experiment had demonstrated that the olefins XV could be cyclodehydrogenated to XIII so that the mixture was not normally separated but was dehydrogenated directly to 5,5-dimethyl-5,6-dihydrobenzo[*c*]phenanthrene (XIII).



XV

The ultraviolet absorption spectrum of XIII was almost superimposable on that of 5,6-dihydrobenzo[*c*]phenanthrene[16] (Fig. 1) which strongly suggests that the correct structure has been assigned to this hydrocarbon. In confirmation of this assumption, XIII was dehydrogenated to 5-methylbenzo[*c*]phenanthrene (XVIII), the picrate of which was identical in all respects with an authentic sample.

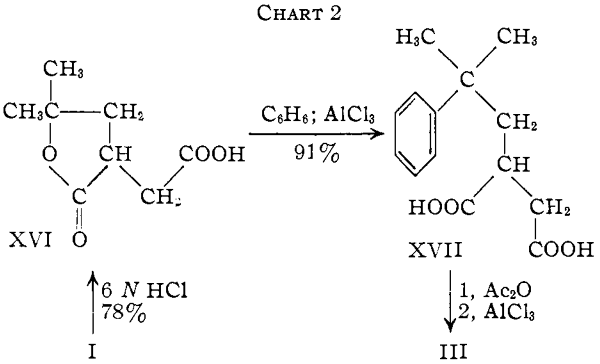
When the initial reaction between benzene and β-methallylsuccinic anhydride I was catalyzed by aluminum chloride, the major product was the tetraloneacetic acid (III). This compound was also a suitable precursor to substituted benzo[*c*]phenanthrenes as illustrated in Chart I. For instance, it could be converted to the intermediate acid VIII by treatment with phenylmagnesium bromide, followed by reduction of the resultant lactone VII. A less satisfactory method in terms of yield involved as a first step the reduction of III to the hydroxy acid IX. Initially, we had planned to lactonize IX and then condense it with benzene and aluminum chloride to obtain acid VIII. All lactonization attempts failed with IX, however, but it could be dehydrated with phosphorus pentoxide and the resultant crude olefin gave VIII when treated with benzene in the usual fashion.[17] Acid VIII was cyclized intramolecularly and the ketone obtained was reduced to VI in good yield,



Fig, 1.

When the above-mentioned reactions had been completed it became obvious that III was a useful adjunct to our original scheme, but a more satisfactory method of preparation was desirable in view of the low (17%) yield of III obtained from the reaction between I and benzene. Consequently, the anhydride I was hydrolyzed in aqueous hydrochloric acid, and the lactone XVI[18] (Chart 2) was obtained in 78% yield. This lactone was condensed with benzene and aluminum chloride to give

CHART 2



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[14] E. C. Horning and D. B. Reisner, THIS JOURNAL, **71**, 1036 (1949).

[15] W. S. Johnson and H. J. Glenn, *ibid.*, **71**, 1092 (1949).

[16] E. D. Bergmann and Z. Pelchowicz, *J. Org. Chem.*, **19**, 1383 (1954).

[17] This reaction is now being used to prepare sterically hindered benzo[*c*]phenanthrenes (by exchanging *p*-xylene, etc., for benzene). The preparation and resolution of such compounds will form the basis for a later communication.

[18] Lactone XVI was also obtained as a by-product in the initial condensation between isobutylene and maleic anhydride.

the dibasic acid XVII which was converted to the anhydride and intramolecularly cyclized to III, the over-all yield for the process being 60%. An unequivocal synthesis of III by the alkylation of 4,4-dimethyltetralone with bromoacetic ester established the identity of the compound.

The reactions in Chart I illustrate the versatility of this method for preparing substituted benzo[*c*]phenanthrenes. It is obvious that slight changes in the aromatic components will allow us to prepare a great variety of hydrocarbons for biological testing and work along these lines is in progress.

Acknowledgment.—The authors are grateful to the Research Corporation for their generous support of this work in the form of a Frederick Gardner Cottrell grant.

Experimental[19]

β-Methallylsuccinic Anhydride (I).—A mixture of 134 g. (2.4 moles) of isobutylene, 100 g. (1.0 mole) of maleic anhydride and 100 cc. of benzene was heated to 180° in a steel bomb and held at this temperature for 4 hr. Excess isobutylene and benzene were removed at atmospheric pressure and the residue was distilled *in vacuo* to give 98.5 g. (64%) of the anhydride, b.p. 137–138° (9 mm.), m.p. 61–62°, and 8–10 g. of lactone XVI, b,p. 140–180° (2 mm.), m.p. 141–142°. The yield of lactone could be increased by heating the high-boiling residues to 90° in 6 *N* hydrochloric acid and allowing the lactone to crystallize from the reaction mixture.

Alder and co-workers[11] report a maximum yield of 33% for this reaction when carried out at 200°.

Friedel–Crafts Reaction between β-Methallylsuccinic Anhydride (I) **and Benzene. A. Aluminum Chloride Catalyst.**—To a rapidly stirred suspension of 171 g. (1.3 moles) of aluminum chloride in 200 ml. of benzene was added over 0.5 hr. at 0–5° a mixture of 60 g. (0.39 mole) of anhydride I in 200 ml. of benzene. The reaction mixture was stirred at room temperature for 48 hr. with a stream of nitrogen passing through the solution to remove hydrogen chloride. The usual workup resulted in 47 g. of acidic material which was esterified (methanol–HCl) and distilled to give three fractions: A, 5.0 g., b.p. 98–104° (1.3 mm.); B, 16.0 g., b.p. 134–135° (0.5 mm.); and C, 7.2 g., b.p. 175–178° (0.3 mm.).

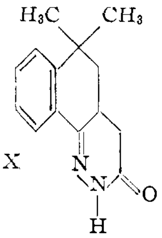
Fraction A has not been identified as yet but the following data on it have been accumulated: *Anal.* C, 67.71, 67.79; H, 7.62, 7.71. These figures fit the empirical formula $C_{11}H_{14-16}O_3$. The compound is a keto ester as evidenced by (a) its infrared spectrum (λ_{max} 5.77 and 5.98 μ), (b) its ultraviolet absorption spectrum (λ_{max} 237 mμ, log ε 4.15 and 282 mμ, log ε 2.19), (c) formation of a red 2,4-di-dinitrophenylhydrazone (m.p, 149.5–150.5° (ethanol–ethyl acetate), λ_{max} 383 mμ, log ε 4.56) and (d) saponification to the acid, m.p. 92–94°, The refractive index and density were $n^{20}D$ 1.4980 and $d^{21}{}_4$ 1.089, respectively. The compound decolorizes bromine water and permanganate but is recovered unchanged when subjected to ozonolysis.

Fraction B, which is the methyl ester of **4,4-dimethyl-1-tetralone-2-acetic acid** (III), crystallized from aqueous ethanol as colorless needles, m.p. 60–61.5°. The ester formed a yellow-orange **2,4-dinitrophenylhydrazone**, m.p. 159–161° (ethanol).

Anal. Calcd. for $C_{21}H_{22}N_4O_6$: C, 59.15; H, 5.20; N, 13.14. Found: C, 59.10; H, 5.36; N, 13.23.

When treated with hydrazine the ester formed the characteristic **dihydropyridazone** (**XIX**) as colorless plates from ethanol, m.p. 172.5–173.5°,

Anal. Calcd. for $C_{14}H_{16}N_2O$: C, 73.65; H, 7.07. Found: C, 73.75; H, 7.04.


XIX

The free acid (III), λ_{max} 248 mμ, log ε 4.06, and 290 mμ, log ε 3.19, crystallized from acetone–hexane as fine, colorless needles, m.p. 120–121°.

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.38; H, 6.94; neut. equiv., 232.3. Found: C, 72.03; H, 6.94; neut. equiv., 231.5.

Fraction C, $n^{20}D$ 1.5475, was identified as the methyl ester of α-(β-**methyl**-β-**phenylpropyl**)-β-**benzoylpropionic acid** (II); λ_{max} 243 mμ, log ε 4.1 and 280 mμ, log ε 3.0. The ester formed the corresponding **dihydropyridazone**, colorless needles from ethanol, when treated with hydrazine.

Anal. Calcd. for $C_{20}H_{22}N_2O$: C, 78.40; H, 7.24; N, 9.15. Found: C, 78.66; H, 7.30; N, 9.17.

The free acid (II) crystallized from acetone–hexane as a colorless, microcrystalline powder, m.p. 106.5–108°.

Anal. Calcd. for $C_{20}H_{22}O_3$: C, 77.34; H, 7.15; neut. equiv., 310.4. Found: C, 77.38; H, 7.27; neut. equiv., 309.8.

B. Antimony Pentachloride Catalyst.—To a rapidly stirred mixture of 67 g. (0.22 mole) of antimony pentachloride and 250 ml. of benzene was added at 0° over two hr. a solution of 20 g. (0.13 mole) of anhydride (I) in 75 ml. of benzene. The reaction mixture was stirred for 18 hr. at room temperature, decomposed in the usual fashion and washed thoroughly with acid to remove all of the antimony pentachloride. Acidic material (1.5 g.) was extracted with carbonate solution and proved to be the lactone-acid XVI. The neutral material consisted of 13.3 g. (44%) of a brown semi-solid which crystallized from dilute alcohol as colorless plates, m.p. 69–70°. Although the carbon analysis was slightly high, the infrared spectrum (λ_{max} 5.66, 5.94, 6.25, 6.32 μ) and the subsequent conversion to acid II (see below) indicated that this was α-**phenacyl**-γ-**methyl**-γ-**valerolactone** (**X**).

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.41; H, 6.94. Found: C, 73.03; H, 7.01.

The 2,4-dinitrophenylhydrazone crystallized as orange microneedles from ethyl acetate, m.p. 226–227°.

Anal. Calcd. for $C_{21}H_{20}N_4O_6$: C, 58.25; H, 4.89. Found: C, 58.62; H, 5.09.

When lactone X (4.0 g., 0.017 mole) in 75 ml. of benzene was treated at ice temperatures with 5.8 g. (0.043 mole) of aluminum chloride and the complex stirred at room temperature overnight there was obtained after the usual workup 0.52 g. of unreacted lactone (X) and 4.5 g. (97% based on X consumed) of acid II, m.p. 95–100°. This acid was suitable for the reduction step described below and needed no further purification at this stage.

α-(β-**Methyl**-β-**phenylpropyl**)-γ-**phenylbutyric Acid** (IV). **a. From II.**—A solution of 5.0 g. (0.016 mole) of acid II dissolved in 70 ml. of absolute ethanol containing 1.0 g. of 10% palladium-on-charcoal was heated to 60° under 45 lb. of hydrogen. The theoretical uptake of hydrogen required about four hours at which time the catalyst was removed and the ethanol evaporated leaving 4.66 g. of acid IV as a colorless, mobile oil. The infrared and ultraviolet absorption spectra showed no detectable amount of unreduced ketone in the oil which was characterized as its *p*-**bromophenacyl ester**, fine colorless needles from alcohol, m.p. 93.5–94.5°.

Anal. Calcd. for $C_{28}H_{29}O_3Br$: C, 68.16; H, 5.92. Found: C, 68.12, 68.28; H, 6.17, 6.00.

b. From X.—A solution of 2.0 g. of X in 75 ml. of absolute alcohol was reduced catalytically as described in a above. The oily lactone (λ_{max} 5.66 μ, no absorption between 5.8–6.2 μ) was then condensed with benzene and aluminum chloride (2.0 g.) to give 1.4 g. (56%) of acid IV, identical in all respects to that prepared from II.

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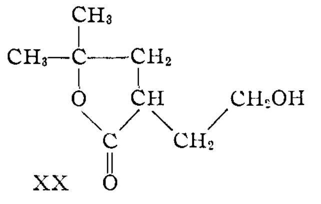
[19] Melting points and boiling points are both uncorrected. Ultraviolet absorption spectra were measured with a Beckman model DK automatic recording spectrophotometer in 95% ethanol as solvent. Infrared spectra were determined using a Perkin–Elmer model 21 double-beam spectrophotometer; the solid samples were pressed in potassium bromide. All distillations were through a 30-inch Podbielniak-type column with partial reflux head. Analyses are by Geller Labs., Hackensack, N. J.

c. **From Lactone XI.** α-(β-**Methallyl**)-γ-**butyrolactone** (**XI**) was prepared in 50% yield from diethyl β-methallyl malonate and ethylene oxide using typical conditions for the malonic ester synthesis[20]; b.p. 85–87° (2.25 mm.), $n^{26}D$ 1.4638.

Anal. Calcd. for $C_8H_{12}O_2$; C, 68.53; H, 8.63. Found: C, 68.16; H, 8.58.

Initially, we attempted to prepare XI using ethylene chlorohydrin as the alkylating agent, a reaction that is reportedly satisfactory for the lower homolog, α-allyl-γ-butyrolactone.[21] In our compound, however, lactonization with the double bond was the preferred reaction under these circumstances and α-(β-**hydroxyethyl**)-γ-**methyl**-γ-**valerolactone** (**XX**), b.p. 118–120° (0.6 mm.), $n^{23}D$ 1.4578, λ_{max} 2.90 and 5.70 μ, was the only product isolated.

Anal. Calcd. for $C_8H_{14}O_3$: C, 60.72; H, 8.92. Found: C, 60.88; H, 8.92.



XX

A solution of 17.5 g. (0,125 mole) of lactone (XI) in 75 ml. of benzene was cooled in ice and to it with stirring was added 44.5 g. (0.33 mole) of aluminum chloride. The complex was allowed to stand for 12 hr. at room temperature and then decomposed in ice and acid. The ethereal extract was shaken with carbonate solution and on acidification, approximately 0.5 g. of an oil precipitated, identical in all respects to the acid IV prepared from II. The neutral material (13 g.), which was different from the reduction product of X, proved to be the monoalkylation product, α-(β-**methyl**-β-**phenylpropyl**)-γ-**butyrolactone** (**XII**). A small sample crystallized from hexane as hexagonal plates, m.p. 57–58°.

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.00; H, 8.31. Found: C, 77.08; H, 8.22.

When this lactone XII was treated with excess benzene and aluminum chloride *at 80°* it could be converted almost quantitatively into acid IV, identified by its infrared spectrum and *p*-bromophenacyl ester, m.p. 93–94°.

2-(β-Methyl-β-phenylpropyl)-1-tetralone and 2-(β-Phenylethyl)-4,4-dimethyl-1-tetralone (V).—To 6.96 g. (0.033 mole) of phosphorus pentachloride was slowly added 8.9 g. (0.03 mole) of acid IV. After the initially vigorous reaction had subsided, the phosphorus oxychloride was codistilled with three 15-ml. portions of benzene. The crude acid chloride was then taken up in 30 ml. of dry benzene and added at ice temperatures over 20 minutes to 5.7 g. (0.043 mole) of aluminum chloride. After being stirred for five hr. at 20° the complex was decomposed in the usual fashion to give 7.4 g. (89% yield) of an oily mixture of tetralones (V), λ_{max} 246 mμ, log ε 4.04 and 292 mμ, log ε 3.19. **The 2,4-dinitrophenylhydrazone** formed orange felt-like needles from alcohol–ethyl acetate, m.p. 233–234°.

Anal. Calcd. for $C_{24}H_{26}N_4O_2$: C, 68.10; H, 5.72; N, 12.22. Found: C, 68.42; H, 5.68; N, 11.97.

The high yield and ready purification of this derivative suggests that one of the ketones is formed to a much larger extent than the other but no attempt was made to determine the composition of the mixture.

2-(β-Methyl-β-phenylpropyl)-1-tetralol and 2-(β-Phenylethyl)-4,4-dimethyl-1-tetralol.—A solution of 7.0 g. (0.025 mole) of tetralone (V) in 25 ml. of dry ether was added at room temperature to a slurry of 0.48 g. (0.0125 mole) of lithium aluminum hydride in 35 ml. of ether. The mixture was heated under reflux for two hours, decomposed with water and acid and the ether evaporated to 7.0 g. of an oil which crystallized from dilute ethanol as colorless needles, m.p. 94–95° and 99–100°. The infrared spectrum showed a strong alcohol peak at 3.00 μ and an aromatic peak at 6.25 μ but no absorption due to carbonyl. The ultraviolet absorption spectrum had λ_{max} 262 mμ, log ε 2.63 and 305 mμ, log ε 1.71.

Anal. Calcd. for $C_{20}H_{24}O$: C, 85.67; H, 8.63. Found: C, 85.65; H, 8.62.

3-(β-Methyl-β-phenylpropyl)-1,2-dihydronaphthalene and 3-(β-Phenylethyl)-1,1-dimethyl-1,2-dihydronaphthalene (XV).—A mixture of 1,36 g. of the tetralols (see experiment above) and 0.36 g. of phosphorus pentoxide was heated at 110° and 10 mm. of 25 minutes. Water was added and the crude hydrocarbons were extracted with ether and chromatographed on alumina (hexane eluent). There was obtained 0.76 g. (60%) of XV as a colorless oil, $n^{18}D$ 1.5820, λ_{max} 265 mμ, log ε 4.11. This material showed no alcohol absorption in the infrared and rapidly decolorized bromine water and permanganate, properties which are consistent with its formulation as a styrene XV.

5,5-Dimethyl-5,6,6a,7,8,13-hexahydrobenzo[*c*]phenanthrene (VI).—To 1.5 g. (5.3 mmoles) of the tetralol mixture was added dropwise at room temperature 2.0 ml. of concd. sulfuric acid. The dark solution was swirled for three minutes then poured quickly onto ice and water. The hydrocarbons were extracted into ether which was washed with water and carbonate solution, dried and evaporated. The crude residue was chromatographed on alumina to give 1.2 g. (80%) of an oily 4:1 mixture of VI and XV, λ_{max} 264 mμ, log ε 3.49 and 272 mμ, log ε 3.46. This mixture was normally dehydrogenated directly but could be separated into its components by careful chromatography in which case pure VI was obtained (λ_{max} 266 mμ, log ε 2.83 and 274 mμ, log ε 2.80) followed by the styrene (XV) (λ_{max} 265 mμ, log ε 4.11).

5,5-Dimethyl-5,6-dihydrobenzo[*c*]phenanthrene (XIII).—An intimate mixture of 0.51 g. of VI and XV and 70 mg. of 10% palladium-on-charcoal catalyst was heated to 300° for four hr. The melt was chromatographed on alumina in hexane solution to give 0.33 g. (70%) of XIII as a colorless fluorescent oil; λ_{max} (log ε): 230 mμ (4.5), 302 (3.9), 313 (4.0), 336 (3.9). Although it developed a color when mixed with 2,4,7-trinitrofluorenone, no derivative precipitated. Attempts to prepare a picrate were equally abortive.

5-Methylbenzo[*c*]phenanthrene (XVIII).—An intimate mixture of 0.56 g. (2.2 mmoles) of XIII and 0.11 g. of 30% palladium–charcoal catalyst was heated to 360° for two hours. The melt was taken up in hexane and chromatographed on alumina to give 0.30 g. of unreacted dihydro compound III followed by 0.21 g. of XVIII as a colorless, fluorescent oil with λ_{max} (log ε): 218.5 mμ (4.64), 224.3 (4.62), 230.2 (4.60), 244.6 (4.02), 254.8 (4.09), 264.0 (4.38), 273.7 (4.67), 283.7 (4.85), 296.0 (4.11), 304.5 (3.98), 317.7 (3,95), 329.5 (3.69). These figures are in excellent agreement with those reported for pure 5-methylbenzo[*c*]-phenanthrene.[22]

The picrate formed as orange needles from 95% ethanol, m.p. 125–126°. The mixed melting point with an authentic specimen[23] (m.p. 133–134°) was 126–133°. The large loss attending recrystallization of this picrate made extensive purification impractical.

The 2,4,7-trinitrofluorenone derivative precipitated as reddish-orange needles from acetic acid, m.p. 151–153°. The recorded[24] m.p. (cor.) is 158–158.5°.

γ-**Methyl**-γ-**valerolactone-2-acetic Acid (XVI).**—Ten grams (0.065 mole) of the anhydride I was heated in 50 ml. of 6 *N* hydrochloric acid until the solution became homogeneous (10 min.). From the cooled solution was obtained 7.8 g. (78%) of the lactone XVI as colorless crystals, m.p. 137–140°. This material was pure enough for the next step but for analytical purposes a small amount was crystallized from benzene, m.p. 141–143°.

Anal. Calcd. for $C_8H_{12}O_4$: C, 55.82; H, 6.98. Found: C, 55.92; H, 6.96.

3-Carboxy-5-methyl-5-phenylhexanoic Acid (XVII).—To a solution of 15 g. (0.087 mole) of lactone XVI in 175 ml. of benzene was added with stirring over 0.5 hour 29 g. (0.22 mole) of aluminum chloride. The mixture was allowed to warm up to about 50° and then stirred for seven hr. at room

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[20] We are grateful to Michael M. Martin who prepared this compound for us in connection with his senior research problem.

[21] K. Wiesner, Z. Valenta, A. J. Manson and F. W. Stonner, THIS JOURNAL, **77**, 680 (1955).

[22] G. M. Badger and I. S. Walker, *J. Chem. Soc.*, 3238 (1954),

[23] This material was made available to us through the kindness of Prof. M. S. Newman.

[24] K. H. Takemura, M. D. Cameron and M. S. Newman, THIS JOURNAL, **75**, 3280 (1953).

temperature. The usual work-up gave 19.7 g, (91%) of the dibasic acid XVII as a microcrystalline powder from water, m.p. 142–144°.

Anal. Calcd. for $C_{14}H_{18}O_4$: C, 67.22; H, 7.26. Found: C, 67.14; H, 7.44.

4,4-Dimethyl-1-tetralone-2-acetic Acid (III).—Ten grams (0.04 mole) of the dibasic acid XVII and 10.2 g. (0.1 mole) of acetic anhydride were heated under reflux for one hour and excess anhydride and acetic acid removed by distillation *in vacuo*. The crude anhydride was taken up in 90 ml. of benzene and to it at ice temperatures was added 11.2 g. (0.09 mole) of aluminum chloride over 0.5 hr. After 24 hr. at room temperature the complex was decomposed in the usual fashion to give 7.9 g. (85%) of acid III, m.p. 113–116°. A small sample crystallized from acetone–hexane had m.p. 120–122°, undepressed on admixture with the acid obtained from the direct Friedel–Crafts reaction between I and benzene.

Alkylation of 4,4-Dimethyl-1-tetralone.—To a cold solution of sodium ethoxide (from 0.15 mole of sodium) and 8.9 g. (0.12 mole) of ethyl formate in 150 ml. of dry ether was added at ice temperature with stirring 17.4 g. (0.1 mole) of 4,4-dimethyl-1-tetralone.[25] The resultant red solution was stirred for three hr. at room temperature and then ice and water were added. From the ether layer was recovered 6.3 g. of unreacted tetralone and from the acidified aqueous layer there was obtained 8.2 g. (63%) of the formyl derivative, b.p. 139.5–140° (4 mm.), n^{25}D 1.6020. To 5.0 g. (0.025 mole) of the formyl derivative was added in the cold with stirring 2.4 g. (0.035 mole) of dry sodium ethoxide in 100 ml. of dry benzene and the mixture was stirred at 25° for one hour. To this cooled solution was then added 7.0 g. (0.04 mole) of ethyl bromoacetate in 15 ml. of benzene. The resultant pink solution was stirred for two hr. at 25° and then heated under reflux for 20 hr. Water was added, excess solvent was removed and the crude oil was heated under reflux for four hr. with 100 ml. of 10% sodium hydroxide solution. From the acidified solution was isolated 2.7 g. of the alkylated formyl derivative and 1.4 g. of a tan solid which crystallized from acetone–hexane as colorless microneedles, m.p. 120–121°. The mixed melting point with a sample of III prepared above was 120–122°.

1-Phenyl-4,4-dimethyltetralin-2-acetic Acid (VIII).—To 10.0 g. (0.04 mole) of the methyl ester of III dissolved in 100 ml. of dry ether was added over one hour a solution of 0.04 mole of phenylmagnesium bromide in 50 ml. of ether. The solution was heated under reflux for 45 minutes and decomposed in the usual fashion to give 8.8 g. of a solid, m.p. 147–150°, which is probably a mixture of lactone VII and the corresponding hydroxy ester. This mixture was subjected to the Clemmensen reduction for 26 hours and from it was recovered 4.3 g. of neutral material VII and 3.2 g. (43% on the basis of lactone consumed) of acid VIII as a colorless oil.

Anal. Calcd. for $C_{20}H_{22}O_2$: neut. equiv., 294.4. Found: neut. equiv., 289.

5,5-Dimethyl-8-keto-5,6,6a,7,8,13-hexahydrobenzo[*c*]phenanthrene.—Acid VIII was cyclized according to Johnson and Glenn's[15] procedure exactly as described above for the preparation of V. The yield of oily ketone was 78% (after chromatography). Characterization was effected through the **2,4-dinitrophenylhydrazone**, orange, felt-like needles from ethyl acetate, m.p. 235–236°.

Anal. Calcd. for $C_{26}H_{24}N_4O_4$: N, 12.28. Found: N, 12.27.

Catalytic reduction of this ketone (as described above for II → IV) gave a 65% yield of pure VI, λ_{max} 266 mμ, log ϵ 2.83 and 274 mμ, log ϵ 2.80, uncontaminated by the styrene XV.

4,4-Dimethyl-1-tetralol-2-acetic Acid (IX).—A solution of 2.5 g. (0.011 mole) of keto acid III was dissolved in 50 ml. of 1:1 methanol–water and just neutralized to phenolphthalein with sodium hydroxide. To this mixture was added 0.14 g. (0.0037 mole) of sodium borohydride and the solution was heated to 60° for ten minutes. Decomposition with aqueous acid resulted in the formation of a tan solid which crystallized from benzene as colorless needles, m.p. 154–155°. The yield was 2.4 g. (90%), λ_{max} 3.07 and 5.86 μ.

Anal. Calcd. for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.78; H, 7.96.

The following conditions were ineffective in lactonizing this hydroxy acid: (a) two hr. reflux with 6 *N* hydrochloric or sulfuric acids, (b) refluxing for three hr. with 50% sulfuric acid, (c) refluxing the bromo acid with alcoholic sodium ethoxide solution for three hr. In all of these reactions, the broad absorption peak at 5.86 μ in the infrared spectrum of the product indicated the presence of acidic material.

1-Phenyl-4,4-dimethyltetralin-2-acetic Acid (VIII) **from IX.**—To 1.85 g. (0.013 mole) of phosphorus pentoxide in 20 ml. of refluxing benzene was added 5.2 g. (0.022 mole) of hydroxy acid IX in 30 ml. of benzene. The mixture was heated under reflux for two more hours, decomposed with water and extracted with ether to give 3.8 g. of an oil. Infrared analysis indicated the presence of anhydride in this material and it was consequently heated under reflux with 30 ml. of dilute hydrochloric acid to hydrolyze it to the corresponding olefin-acid. The crude product from this hydrolysis (3.6 g.) was dissolved in 75 ml. of dry benzene and to it with stirring was added 3.3 g. (0.025 mole) of aluminum chloride at ice temperatures. The complex was stirred at room temperature for four hr. and the usual workup gave 2.6 g. (40% yield) of acid VIII, identical in infrared spectrum to the acid prepared from III *via* lactone VII.

Methyl α-(β-Methallyl)-β-benzoylpropionate (**XIV**).—The method used for this reaction is that of Newman and Booth.[26] To a slurry of 30.6 g. (0.02 mole) of anhydride in 125 ml. of dry ether at −70° was added over two hr. a solution containing 0.02 mole of phenylmagnesium bromide in 75 ml. of dry ether. The mixture was stirred at −70° for three hr. and decomposed with saturated ammonium chloride solution. There was recovered 14.6 g. of anhydride and 11 g. of acidic material, 7.6 g. of which was esterified with diazomethane to give 4.75 g. of ester XIV as a colorless oil, b.p. 147–149° (1.3 mm.), n^{22}D 1.5188.

The **2,4-dinitrophenylhydrazone** crystallized from ethanol as yellow-orange needles, m.p. 113–114°.

Anal. Calcd. for $C_{21}H_{22}N_4O_6$: C, 59.14; H, 5.20; N, 13.14. Found: C, 59.13; H, 5.36; N, 13.23.

The infrared spectrum (λ_{max} 5.78, 5.93, 6.06, 6.26, 6.32, 11.20 μ) was quite different from that of fraction A obtained in the Friedel–Crafts reaction of I and benzene described above.

Ester XIV could be saponified and lactonized to give X and when alkylated with benzene and the product saponified, XIV gave ketoacid II in good yield, thus verifying its structure.

ITHACA, NEW YORK

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[25] R. T. Arnold, J. S. Buckley and J. Richter, THIS JOURNAL, **69**, 2322 (1947).

[26] M. S. Newman and W. T. Booth, Jr., *ibid.*, **67**, 154 (1945).