the heating was terminated, the solution turned cloudy. It was poured with stirring into crushed ice and water (100 g.) while still hot. A white, gummy material separated, but this hardened to a solid after several days of refrigeration. At this time the mixture was filtered, and the solid thus collected washed successively with water, 5% aqueous sodium bicarbonate and water. The air-dried crude product (0.71 g.) melted at 143–151°, a value that was not improved significantly by trituration with low-boiling petroleum ether. Crystallization from 83% ethanol, then twice from 55% ethanol gave a product of m.p. 154.5–156.3°. The mixed m.p. between this substance and authentic α-benzoyl-β-methylbutyranilide (m.p. 156.6–157.6°) was 153.5–157.2°, thus confirming its identity. The yield of crude product was 82%.

NEW YORK, N. Y.

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

Polynuclear Aromatic Hydrocarbons. VIII.[1] The Reaction between Allylsuccinic Anhydride and Benzene

BY DONALD D. PHILLIPS[2] AND TREVOR B. HILL[3]

RECEIVED FEBRUARY 20, 1958

The Friedel–Crafts reaction between allylsuccinic anhydride (I) and benzene afforded a complex mixture of acids from which, after esterification, it has been possible to isolate and characterize methyl α-phenacyl-γ-phenylvalerate (IV, R = CH_3), methyl 3-phenylcyclohexanone-5-carboxylate (III, R = CH_3) and a small amount of methyl 4-methyltetralone-2-acetate (II, R = CH_3). One of these (IV) has been converted to the carcinogenic hydrocarbon 5-methylbenzo[c]phenanthrene (VI). The contrasting results obtained with β-methallylsuccinic anhydride are discussed and a tentative explanation for the difference in behavior is suggested.

In a recent communication[4] we reported the use of β-methallylsuccinic anhydride as a convenient starting material for the preparation of substituted benzo[c]phenanthrenes. Although the synthetic scheme described in the earlier paper was particularly useful for the preparation of the *gem*-dimethyl derivatives of 5,6-dihydrobenzo[c]phenanthrene, the difficulties encountered in the final dehydrogenation step prompted us to investigate the use of allylsuccinic anhydride (I) in the original Friedel–Crafts condensation with benzene. Although some of the results paralleled those previously reported,[4] the principal product (III) of the reaction was of an entirely different structure than we had anticipated. Moreover, only trace amounts of the tetralone ester (II, R′ = H) could be isolated whereas the corresponding dimethyl compound (II, R′ = CH_3) was the *major* product when β-methallylsuccinic anhydride was employed as starting material.[4]

The condensation between allylsuccinic anhydride (I) and benzene resulted in the formation of a complex mixture of acids that was best separated by fractional distillation of the corresponding methyl esters. In this way it was possible to isolate from the highest boiling fractions about 14% of the acylated-alkylated product (IV) whose structure was established by its ultimate conversion to 5-methylbenzo[c]phenanthrene (VI). This was accomplished by saponification of IV (R = CH_3) followed by reduction of the carbonyl group to the corresponding methylenic derivative. This reduced acid then was cyclized to the tetralone (V, only one of two possible isomers) which was in turn reduced to the alcohol, cyclodehydrated with sulfuric acid and the resulting hexahydrobenzo[c]phenanthrene dehydrogenated to VI. Although the yield of IV was rather low, this sequence of reactions nevertheless provided a convenient synthesis of 5-methylbenzo[c]phenanthrene (VI), a hydrocarbon of interest because of its carcinogenic activity.[5]

From the fractions of intermediate boiling point there was isolated about 18% of a crystalline solid which initially was assumed to be the tetralone ester (II, R′ = H, R = CH_3) because some of its properties were similar to those of the corresponding compound (II, R = R′ = CH_3) isolated in the previous work.[4] The spectroscopic evidence[6] was not in favor of structure II, however, and it soon became evident that the compound contained an isolated carbonyl function. Moreover, permanganate oxidation afforded benzoic acid, an experimental fact that was incompatible with its formulation as II, R′ = H. The correct structure (III, R = CH_3) for this substance was deduced from several pieces of chemical and physical evidence. When the carbonyl group was removed by the Huang-Minlon modification of the Wolff–Kishner reduction and the product subsequently dehydrogenated, there was obtained a mixture of biphenyl and biphenyl-3-carboxylic acid, thus establishing the skeletal structure and the 1,3-relationship of the phenyl and carboxyl groups in III. Moreover, the reduction product was shown to be 3-phenylcyclohexanecarboxylic acid (Va, probably *cis*) by an independent synthesis. The important intermediates in this synthesis (VIa → VII → VIII (X = OH) → VIII (X = Br) → Va) are shown in Chart I but, because of the straightforward nature of these interconversions, the chemistry is discussed only in the Experimental section.

The position of the ketone group in III was readily established by catalytic and sodium borohydride reduction to the corresponding hydroxy ester

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[1] Paper VII, THIS JOURNAL, **78**, 5438 (1956).

[2] To whom inquiries regarding this article should be sent; Shell Development Co., Modesto, Calif.

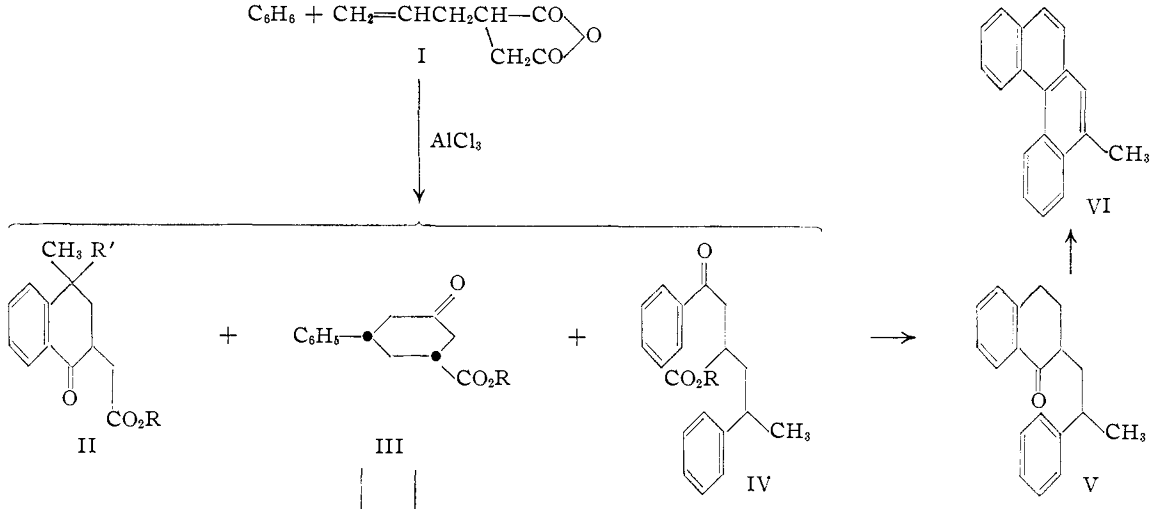
[3] From the thesis submitted by T. B. H. to Cornell University in partial fulfillment of the requirements for the Ph.D. degree, February, 1958.

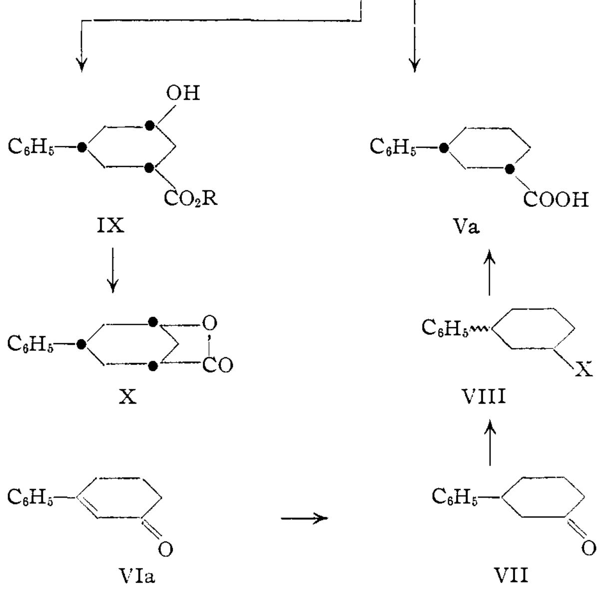
[4] D. D. Phillips and A. W. Johnson, THIS JOURNAL, **77**, 5977 (1955).

[5] W. E. Bachmann, *et al.*, *Proc. Roy. Soc.* (*London*), **B123**, 343 (1937); I. Berenblum, *Cancer Research*, **5**, 561 (1945).

[6] The Experimental section should be consulted for pertinent data in this respect.

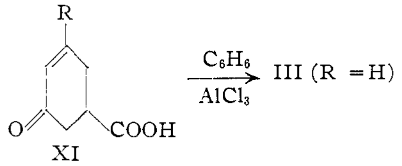
CHART I





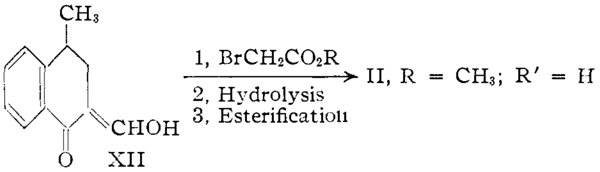
IX[7] which formed a lactone (X) when treated with *p*-toluenesulfonic acid in benzene. The five-membered nature of the lactone ring ($\lambda_{\max}^{\mathrm{KBr}}$ 5.64 μ) established the 1,3-relationship of the hydroxyl and the ester groups in IX and hence the same relationship must obtain in III.

Although a phenylcyclohexanone corresponding to III was not obtained from β-methallylsuccinic anhydride[4] its formation may be explained readily on the basis of the results obtained when the two anhydrides are treated with aluminum chloride in the *absence* of benzene.[8] Thus, β-methallylsuccinic anhydride formed the cyclohexenone (XI, R = CH_3) and allylsuccinic anhydride (I) was converted to the analogous derivative (XI, R = H) in the absence of an aromatic hydrocarbon. The conversion of XI (R = H) to III then becomes apparent as simply another example of the Friedel–Crafts alkylation of benzene by an α,β-unsaturated ketone.[9] The failure to obtain a similar product from the methylcyclohexenone (XI, R = CH_3) may well be a result of steric hindrance although this aspect of the problem was not studied in detail.



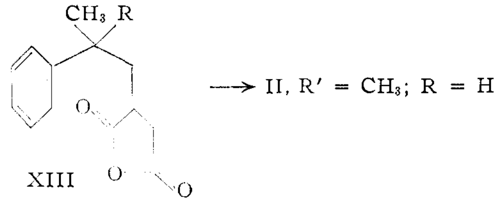
XI

When the mother liquors from the crystallization of III (R = CH_3) were chromatographed on alumina there was obtained a small amount of an oil with an infrared absorption spectrum that was characteristic of a conjugated carbonyl compound. This material was identified as the tetralone ester (II, R = CH_3, R′ = H) by comparison of its 2,4-dinitrophenylhydrazone with that of a synthetic specimen, prepared by the alkylation of 2-hydroxymethylene-4-methyltetralone (XII) with ethyl bromoacetate.



XII

The rather marked difference in the behavior of allylsuccinic (I) and β-methallylsuccinic anhydrides in the Friedel–Crafts reaction is apparent from these and our earlier results.[4] One can speculate that the extra methyl on the double bond in the



XIII

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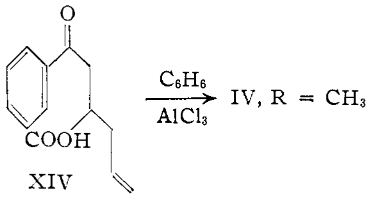
[7] In view of recent studies on the stereochemistry of complex metal hydride reductions (W. G. Dauben, G. J. Fonken and D. S. Noyce, THIS JOURNAL, **78**, 2579 (1956); S. Julia and Y. Bonnet, *Bull. soc. chim. France*, 1340 (1957)) it was expected that the hydroxyl and carbomethoxy groups would bear a *cis* relationship in the hydroxy ester. Because of the numerous opportunities for equilibration, all three large groups in IX probably have the *cis* configuration.

[8] D. D. Phillips and A. W. Johnson, *J. Org. Chem.*, **21**, 587 (1956).

[9] C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1941, pp. 479 *et seq.*

β-methallyl compound greatly increases the rate of alkylation to give XIII (R = CH_3) as a first intermediate. *Intra*molecular acylation of XIII would then be the preferred reaction path to afford the tetralone acid (II, R′ = CH_3, R = H) which is indeed the major product.[4] Because of the decreased electron density about the double bond, allylsuccinic anhydride (I) probably *acylates* benzene to give XIV as a first intermediate. In the presence of excess benzene and aluminum chloride,



XIV

XIV would be converted to IV (R = CH_3) which is one of the principal reaction products. The other possibility open to the less reactive (in an alkylating sense) allylsuccinic anhydride is the formation of the cyclohexenone (XI, R = H) which, because of its *intra*molecular nature, would probably be the preferred reaction course. The conversion of XI (R = H) to III (R = H) then would be expected in the presence of excess benzene and aluminum chloride, thus explaining the formation of III (R = H) as a major product.

The reactions of allylsuccinic and β-methallylsuccinic anhydride with other aromatic hydrocarbons are currently being studied and the results will be the subject of forthcoming publications.

Experimental[10]

Allylsuccinic Anhydride (I).—This material was prepared essentially by the method of Alder, *et al.*,[12] except for conditions of temperature. Considerable carbonization occurred at the suggested temperature of 250°, whereas at 200° the yields of I, b.p. 139–143° (17 mm.), ran as high as 73%.

Reaction between Allylsuccinic Anhydride and Benzene.—In a typical run, 111 g. (0.83 mole) of anhydrous aluminum chloride was added with stirring, over a period of 20 min., to a solution of 50.0 g. (0.36 mole) of allylsuccinic anhydride (I) in 300 ml. of anhydrous benzene. The addition and subsequent stirring for 36 hours were both carried out at room temperature.

The reaction mixture was worked up in the usual fashion to afford 55 g. of crude acids which were esterified by heating under reflux in 200 ml. of anhydrous methanol containing 2 ml. of concd. sulfuric acid. The esters were precipitated by pouring into excess water, extracted with ether and fractionally distilled to give 7.0 g. of forerun, b.p. 134–161° (0.3 mm.), 15.0 g. (18%) of **methyl 3-phenylcyclohexanone-5-carboxylate** (III, R = CH_3), b.p. 170–176° (0.2–0.4 mm.), $n^{20}D$ 1.5337, and 15.5 g. (14%) of **methyl α-phenacyl-γ-valerate** (IV, R = CH_3), b.p. 200–212° (0.3–0.4 mm.), $n^{20}D$ 1.5588, λ_{max} 5.78 and 5.92 μ.

The fractions containing III solidified on standing to give the ester as a waxy solid, m.p. 87–90°. An analytical sample crystallized from hexane as colorless plates, m.p. 91.5–92.5°; λ_{max} (log ε) 248 mμ (2.27), 252 (2.36), 258 (2.42), 264 (2.33), 269 (2.22) and 300 (1.66).

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.35; H, 6.96. Found: C, 72.61; H, 6.95.

The 2,4-dinitrophenylhydrazone of III (R = CH_3) crystallized from ethanol–ethyl acetate as orange needles, m.p. 162–163°, λ_{max} 364 mμ (log ε 4.39).

Anal. Calcd. for $C_{20}H_{20}O_6N_4$: C, 58.21; H, 4.87; N, 13.59. Found: C, 58.30; H, 5.00; N, 13.53.

α-(β-Phenethyl)-γ-phenylvaleric Acid.—A solution of 20.69 g. (0.066 mole) of methyl α-phenacyl-γ-phenylvalerate (IV, R = CH_3) and 12.1 g. (0.18 mole) of 85% potassium hydroxide in 100 ml. of absolute methanol was heated under reflux for 3.5 hr. The usual workup afforded 18.7 g. (95%) of crude acid (IV, R = H) which, without further purification, was dissolved in 100 ml. of 95% ethanol containing 3.5 g. of palladium-on-charcoal catalyst. The mixture was heated to 60° and subjected to a hydrogen pressure of 40 p.s.i. for 22 hr.

The catalyst was filtered and the solvent was evaporated to yield 17.0 g. of a colorless oil whose infrared absorption spectrum indicated the presence of some ester. The oil was consequently saponified to afford 16.2 g. (87% based on IV, R = CH_3) of **α-(β-phenethyl)-γ-phenylvaleric acid** as a colorless oil, λ_{max} 5.85 μ.

Anal. Calcd. for $C_{19}H_{22}O_2$: neut. equiv., 282.4. Found: neut. equiv., 284.0.

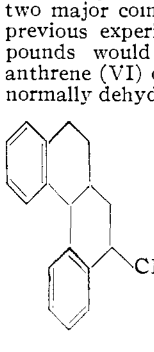
2-(β-Phenylpropyl)-1-tetralone (V) and/or 2-(β-Phenethyl)-4-methyl-1-tetralone.—The acid chloride from 8.6 g. (0.03 mole) of α-(β-phenethyl)-γ-phenylvaleric acid was prepared in benzene solution from 7.0 g. of phosphorus pentachloride and added with stirring, over 0.5 hour, to an ice-cooled suspension of 5.7 g. (0.043 mole) of aluminum chloride in 50 ml. of benzene. The complex was stirred for 4 hr. at room temperature and worked up as suggested[13] to afford 7.8 g. (97%) of the mixture of tetralones as a pale brown oil, λ_{max} 5.95 μ.

Attempts to form a derivative of this material were unsuccessful because of the mixture of diastereoisomers and structural isomers that it undoubtedly contained.

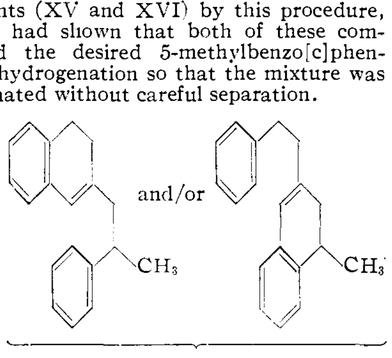
2-(β-Phenylpropyl)-1-tetralol and/or 2-(β-Phenethyl)-4-methyl-1-tetralol.—To an ethereal solution of 7.9 g. (0.014 mole) of the tetralone mixture was added, over 20 min., a solution of 0.6 g. (0.016 mole) of lithium aluminum hydride in 50 ml. of ether. The mixture was stirred at room temperature for 4 hr. and worked up in the usual fashion to afford 7.4 g. (93%) of the two tetralols as a viscous oil, λ_{max} 2.94 μ. This material would not form a derivative and was consequently used in the next step without further purification.

5-Methylbenzo[c]phenanthrene (VI).—A mixture of 7.4 g. (0.028 mole) of the tetralols (see above) in 10 g. of 95% sulfuric acid was stirred at room temperature for 3.5 min. The reaction was quenched by the addition of ice-water and the organic material was extracted into ether. After being washed with carbonate solution, water and saturated salt solution, the ether was evaporated and the organic residue was taken up in hexane and chromatographed on acid-washed alumina to yield 4.6 g. (67%) of oily hydrocarbons.

Although it was possible to separate the mixture into the two major components (XV and XVI) by this procedure, previous experience[4] had shown that both of these compounds would yield the desired 5-methylbenzo[c]phenanthrene (VI) on dehydrogenation so that the mixture was normally dehydrogenated without careful separation.



XV



XVI

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(10) 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 absorption spectra were determined using a Perkin-Elmer model 21 double-beam spectrophotometer; the solids were pressed in potassium bromide. All distillations were through a 30-inch Podbielniak-type column with partial reflux head.[11] Analyses are by Schwarzkopf Laboratories, Woodside 77, N. Y.

(11) J. Cason and H. Rapoport, "Laboratory Text in Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1950, p. 237.

(12) K. Alder, F. Pascher and A. Schmitz, *Ber.*, **76**, 27 (1943).

(13) W. S. Johnson and H. J. Glenn, THIS JOURNAL, **71**, 1092 (1949).

The dehydrogenation was effected by heating 1.6 g. (6.5 mmoles) of the chromatographed hydrocarbons with 0.2 g. of 10% palladium-on-charcoal for 1.5 hr. at 280–300°. The melt was chromatographed on alumina to give two principal fractions. The first (0.5 g.) was eluted with hexane and crystallized from ethanol as plates, m.p. 103–104°; λ_{max} 239 mμ (3.86, 272 (2.95) and 279 (2.79).

Anal. Calcd. for $C_{19}H_{18}$: C, 92.64; H, 7.36; mol. wt., 242. Found: C, 92.64; H, 7.45; mol. wt., 230.

This material has not been identified as yet.

The second fraction (0.7 g., 45%) was eluted with a 1:1 mixture of benzene and hexane and crystallized from hexane as colorless needles of **5-methylbenzo[c]phenanthrene** (VI), m.p. 71–72°, lit.[14] m.p. 70.4–71.0°.

Anal. Calcd. for $C_{19}H_{14}$: C, 94.18; H, 5.82. Found: C, 94.18; H, 5.97.

The ultraviolet absorption spectrum was superimposable on that reported.[15]

The **picrate** crystallized from ethanolic picric acid as orange microneedles, m.p. 136–138°, lit.[16] m.p. 132.5–133.5°.

Proof of Structure of Methyl 3-Phenylcyclohexanone-5-carboxylate (III, R = CH_3). a. **Oxidation.**—A mixture of 1.1 g. of potassium permanganate, 0.2 g. of III, R = CH_3, and 0.3 ml. of 10% sodium hydroxide solution was dissolved in 20 ml. of water and heated under reflux for 4 hr. The solution was acidified with concd. sulfuric acid and heated for another 0.5 hr.

The excess permanganate was reduced with sodium bisulfite and the clarified solution was extracted with benzene to afford on evaporation and subsequent sublimation 36 mg. (34%) of benzoic acid, identified by its characteristic infrared absorption spectrum and by a mixed m.p. determination with an authentic specimen.

b. **Wolff–Kishner Reduction.**—A solution containing 0.75 g. (3.2 mmoles) of III, R = CH_3, and 3 ml. of anhydrous hydrazine in 20 ml. of diethylene glycol was heated under reflux (140°) for 3 hr. To the hot solution was added 0.4 g. of potassium hydroxide and the mixture was heated slowly to 200° for 3 hr.

The cooled solution was poured into excess water and extracted with ether. The aqueous layer then was acidified and extracted with several small portions of benzene. Removal of the solvent afforded 0.61 g. of ***cis*-3-phenylcyclohexanecarboxylic acid** (Va) as a pale brown oil; λ_{max} 2.90, 3.10 and 6.05 μ.

Although this acid gradually solidified over a period of months, it was best characterized as the amide, long needles from dilute ethanol, m.p. 152.5–154.5°, undepressed on admixture with a synthetic specimen (see below).

Anal. Calcd. for $C_{13}H_{17}ON$: C, 76.79; H, 8.43. Found: C, 77.15; H, 8.72.

c. **Dehydrogenation.**—The product from the Wolff–Kishner reduction (part b above) was esterified with methanol and 0.45 g. (2.3 mmoles) of the ester was heated to 250–270° for 50 min. with 0.2 g. of 10% palladium-on-charcoal catalyst. During the heating period, 0.1 g. (29%) of a colorless hydrocarbon, m.p. 57–63°, sublimed onto the cold finger and this was subsequently identified as **biphenyl** by making the usual comparisons.

The melt was saponified and from the aqueous layer there was extracted 0.08 g. (19%) of **biphenyl-3-carboxylic acid**, colorless plates from dilute ethanol, m.p. 164–166°, lit.[17] m.p. 161–162°.

d. **Independent Synthesis of *cis*-3-Phenylcyclohexanecarboxylic Acid** (Va). 1. **1-Phenylcyclohexene-3-one** (VIa) was prepared from ethyl acetoacetate and phenyl β-piperidinoethyl ketone hydrochloride[18] essentially as described[19] and crystallized from hexane as colorless plates, m.p. 62–64°, lit.[19] m.p. 62–63°.

2. **3-Phenylcyclohexanone** (VII).—The phenylcyclohexanone VIa was hydrogenated at 60° to afford a quantitative yield of saturated ketone as a colorless oil, b.p. 144–146° (7.6 mm.), $n^{20}D$ 1.5428, lit.[20] b.p. 140° (6 mm.).

3. ***cis*-3-Phenylcyclohexanol (VIII, X = OH).**—The ketone VII was reduced by methanolic sodium borohydride in the usual fashion to afford a 65% yield of the alcohol as colorless needles from hexane, m.p. 79.0–81.5°, lit.[21] m.p. 79.5–80.5°.

4. **3-Phenylcyclohexyl Bromide** (VIII, X = Br).[22]—Anhydrous hydrogen bromide was bubbled through the molten alcohol at 80–100° and the product was worked up[21] to give the bromide as a colorless oil, b.p. 121–122° (1.4 mm.), $n^{20}D$ 1.5630, lit.[21] b.p. 186–187° (40 mm.).

5. ***cis*-3-Phenylcyclohexanecarboxylic Acid** (Va).—A Grignard complex was prepared in the usual manner from 4.5 g. (0.019 mole) of 3-phenylcyclohexyl bromide (VIII, X = Br) and 0.50 g. (0.021 mole) of magnesium turnings in 20 ml. of ether. The solution then was poured onto Dry Ice and worked up in the usual fashion to afford 1.3 g. (34%) of 3-phenylcyclohexanecarboxylic acid as a viscous oil that crystallized after several weeks. For comparison purposes, it was converted to the amide, as colorless needles from dilute ethanol, m.p. 150–152°, undepressed on admixture with the amide obtained from the Wolff–Kishner reduction of III, R = CH_3 (see above).

e. **Catalytic Reduction of III**, R = CH_3.—A solution containing 1.0 g. (4.3 mmoles) of the keto ester (III, R = CH_3) in 28 ml. of 95% ethanol was hydrogenated at atmospheric pressure in the presence of 0.1 g. of prereduced platinum catalyst. The uptake of the theoretical amount of hydrogen required 48 hr. after which time the solution was filtered and evaporated to leave the **methyl 3-phenyl-5-carbomethoxycyclohexanol** (IX, R = CH_3) as a viscous oil that failed to crystallize.

The ***p*-nitrobenzoate** crystallized from ethanol as colorless needles, m.p. 122–123°.

Anal. Calcd. for $C_{21}H_{21}O_6N$: C, 65.77; H, 5.52; N, 3.65. Found: C, 65.31; H, 5.30; N, 3.89.

Similar results sometimes could be obtained with sodium borohydride but the reaction often took an erratic course and the results were difficult to reproduce.

f. **Lactonization of IX**, R = CH_3.—A benzene solution of 1.5 g. (6.4 mmoles) of hydroxy ester (IX, R = CH_3) and 0.5 g. of *p*-toluenesulfonic acid was heated under reflux for 5 hr. The benzene was washed with carbonate solution, dried and evaporated to afford the lactone as a waxy solid. Crystallization from hexane yielded 0.7 g. (54%) of **3-phenyl-5-hydroxycyclohexanecarboxylic acid lactone** (X) as stout, colorless needles, m.p. 117.5–118.5°, λ_{max} 5.64 μ.

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.40; H, 6.80.

Methyl 4-Methyl-1-tetralone-2-acetate (II, R = CH_3, R′ = H).—When the residual oils from the crystallization of III (R = CH_3) were distilled and chromatographed on acid-washed alumina there appeared in the later fractions (1:1 benzene–chloroform eluent) an oil (0.1 g. from 2.0 g. of residual oil) with strong carbonyl absorption at 5.74 μ (ester) and 5.92 μ (aromatic ketone). The ultraviolet absorption spectrum (λ_{max} 246 mμ (log ϵ 3.92) and 286 mμ (3.28)) was very similar to that of the dimethyl derivative[4] (II, R = R′ = CH_3) and the compound was therefore assigned structure II, R = CH_3, R′ = H.

The **2,4-dinitrophenylhydrazone** crystallized from alcohol as a red powder, m.p. 150–174° dec., unchanged on recrystallization. Extensive purification of this derivative was not attempted, but the infrared and ultraviolet absorption spectra were compared directly with those of the synthetic specimen (see below).

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(14) M. S. Newman and L. M. Joshel, This Journal, **62**, 972 (1940).

(15) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, fig. 465.

(16) C. L. Hewett, *J. Chem. Soc.*, 596 (1936).

(17) F. Mayer, *Ber.*, **46**, 2587 (1913).

(18) C. Mannich and D. Lammering, *ibid.*, **55**, 3510 (1922).

(19) W. S. Johnson, J. S. Belew, L. J. Chinn and R. H. Hunt, This Journal, **75**, 4995 (1953).

(20) S. M. Mukherjee and B. K. Bhattacharyya, *J. Indian Chem. Soc.*, **23**, 451 (1946).

(21) A. J. Boyd, P. H. Clifford and M. E. Probert, *J. Chem. Soc.*, **117**, 1383 (1920); A. W. Crossley and N. Renouf, *ibid.*, **107**, 602 (1915). The stereochemistry of this alcohol was not established by either group, but the vigorous conditions employed (sodium and alcohol reduction of phenyldihydroresorcinol at 100°) would have provided ample opportunity for equilibration to a mixture in which the *cis*-alcohol would be expected to predominate (both large groups equatorial).

(22) The stereochemistry of this bromide was not determined although its mode of formation would suggest that it also has the *cis* configuration.

Independent Synthesis of II, R = CH_3, R′ = H.—4-Methyltetralone[23] was converted to the corresponding hydroxymethylene derivative XII which was alkylated with ethyl bromoacetate as previously described[4] for 4,4-dimethyltetralone to afford methyl 4-methyl-1-tetralone-2-acetate (II, R = CH_3, R′ = H) as a colorless oil, b.p. 129–135° (0.5–0.6 mm.), $n^{20}D$ 1.5576.

The 2,4-dinitrophenylhydrazone crystallized from ethanol-ethyl acetate as a red powder, m.p. 175–178° dec. The ultraviolet (λ_{max} 380 mμ, log ϵ 4.43) and infrared absorption spectra were superimposable on those from the ester separated by chromatography from the reaction between allylsuccinic anhydride and benzene.

ITHACA, NEW YORK

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[23] Prepared from benzene and γ-valerolactone by the procedure described for 1-tetralone; C. E. Olson and A. R. Bader, *Org. Syntheses*, **35**, 96 (1955).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

The Synthesis and Rearrangement of Some Benzonorbornenes[1a,1b]

BY J. MEINWALD AND G. A. WILEY[2]

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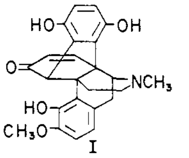
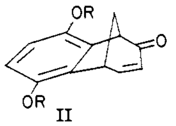
Techniques for the transformation of cyclopentadiene-quinone (VII) into 3′,6′-diacetoxybenzonorbornadiene (VIIIa), 3′,6′-dihydroxybenzonorbornadiene (VIIIb) and 3′,6′-dimethoxybenzonorbornadiene (VIIIc) are presented, and a variety of reactions of these compounds are described. *exo*-3′,6′-Diacetoxybenzonorbornadiene epoxide (XIa) was found to give rearranged derivatives of the corresponding 2,7-diol under either acidic or basic conditions. The base-induced rearrangement was unusually rapid, and the formation of an intermediary nortricyclyl dienone is suggested. Potassium permanganate oxidation of VIIIa yielded *cis-exo*-3′,6′-diacetoxybenzonorbornen-2,3-diol (XIVa), but lead tetraacetate oxidation of VIIIa in wet acetic acid gave rise to the rearranged 2,7-diol derivative XIIIa. *exo*-3′,6′-Dimethoxybenzonorbornadiene epoxide (XIc) gave the expected rearranged 2,7-acetoxy alcohol XIIc on acetolysis. Nucleophilic opening of the epoxide ring of XIa using sodium methoxide was slow, and gave rise to a product which is assigned the unrearranged structure XXI. Sodium permanganate and lead tetraacetate oxidations of VIIIc proceeded in strict analogy to the oxidations of VIIIa described above. A group of other transformation products of the above-mentioned compounds were prepared and characterized, of which the most interesting is probably *exo*-3′,6′-dimethoxybenzonorbornen-2-ol (XX), produced by lithium aluminum hydride reduction of XIc.

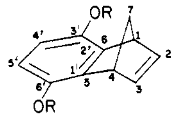
Recent studies of the chemistry of flavothebaone have led to the assignment of structure I to this compound.[3] Although this structure is in accord with all of the chemical and most of the physical data, it fails to provide a facile rationalization of the long wave length ultraviolet absorption maximum (λ_{max} 346, log ϵ 3.56) characteristic of flavothebaone. It has been suggested that the enone chromophore interacts with the non-conjugated hydroquinone system, and that this interaction is responsible for the "abnormal" spectrum.[3b] In attempting to test this hypothesis, a synthesis of the model compound II has been undertaken.[4] Although the synthesis has not been brought to completion at this time, a number of 3′,6′-disubstituted benzo-(1′,2′,5,6)-norbornene (III) derivatives have been prepared as possibly useful intermediates. At this moment the continuation of the synthesis from these compounds does not appear attractive. However, the chemistry of these compounds is of sufficient intrinsic interest to warrant independent treatment, and it is the purpose of the present paper to set forth some of the results of these studies.



I

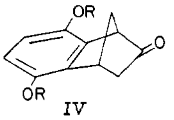


II

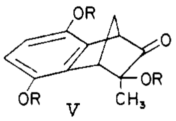


III

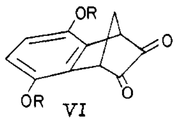
The desired key intermediates for the synthesis were compounds such as IV, V or VI, from which it is easy to imagine routes to II.



IV



V



VI

The starting material for these studies was the well known 1:1 cyclopentadiene-quinone adduct VII.[5] Early attempts to enolize VII to give derivatives of the hydroquinone VIII had been unsuccessful, presumably because of the reversibility of the initial diene addition.[5] Treatment of VII with acetic anhydride and pyridine has now been found to give the expected diacetate VIIIa in ex-

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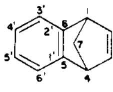
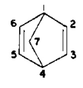
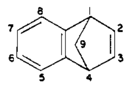
(1) (a) The ring system designated as "benzonorbornadiene" in this paper is shown below as i. The choice of this name was motivated by the authors' desire to relate this system to the parent compound norbornadiene ii, as well as to retain as simple a set of names as possible. The Ring Index would designate this system as 1,4-dihydro-1,4-methanonaphthalene, numbered as shown in iii. The authors are indebted to Mr. Leonard T. Capell for calling attention to this scheme of nomenclature. (b) See J. Meinwald, H. Nozaki and G. A. Wiley, THIS JOURNAL, **79**, 5579 (1957), for a preliminary Communication of some of the results described in this paper.



i



ii

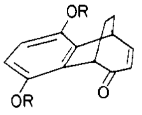


iii

(2) Opportunity Fellow, John Hay Whitney Foundation, 1955–1956; Allied Chemical and Dye Corp. Fellow, 1956–1957.

(3) (a) J. Meinwald and G. Wiley, *Chemistry & Industry*, 957 (1956); (b) J. Meinwald and G. Wiley, THIS JOURNAL, **79**, 2569 (1957); (c) K. W. Bentley, J. Dominguez and J. P. Ringe, *Chemistry & Industry*, 1353 (1956); (d) K. W. Bentley, J. Dominguez and J. P. Ringe, *J. Org. Chem.*, **22**, 418 (1957).

(4) A preliminary attempt to prepare the less exact model (iv) *via* a Diels–Alder reaction between tropone and benzoquinone was unsuccessful.



iv

(5) W. Albrecht, *Ann.*, **348**, 34 (1906); O. Diels and K. Alder, *Ber.*, **62**, 2337 (1929).