The decompositions were carried out in a specially constructed, 200-ml. round-bottom flask in which the reactants could be kept separated. The flask was connected to a jacketed gas buret, the mercury in which was covered with a layer of aqueous acetone of the same composition as the reaction mixture.[42] Mixing the components to start the reaction and agitation during the course of the reaction was achieved by a shaker (200 oscillations per minute) which was totally immersed in a constant temperature bath maintained at 35.00 ± 0.01°. Water from this bath was circulated through the jacket of the gas buret. The reaction vessel was charged by placing the required volumes of water, acetone and standard unsaturate, cupric chloride and DBC solutions into three separate compartments.

For runs in the absence of air the separated components were repeatedly degassed at -196° and 10^{-6} mm. pressure by standard procedures. The vessel was finally filled with purified nitrogen, allowed to come to temperature equilibrium in the constant temperature bath, and the reaction was started. Volume readings at constant pressure were taken at regular time intervals. For runs in the presence of air the degassing operation was omitted and the charged reaction flask was immediately placed in the water-bath.

The pre-formed cuprous chloride was determined in separate experiments by treating the unmixed reactants with excess ferric ammonium sulfate solution immediately after the degassing operation and titrating with standard ceric ammonium sulfate solution.

Acknowledgment.—The authors wish to thank Mr. Martin Gottesman for his assistance with some of the experimental work.

NEW YORK 53, N. Y.

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[42] No vapor pressure correction is necessary for gases measured under these conditions. See R. Livingston in "The Technique of Organic Chemistry," Vol. 8, "Investigations of Rates and Mechanisms of Reactions," Interscience Publishers, Inc., New York, N. Y., 1953, p. 53.

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

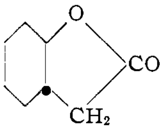
The Friedel–Crafts Condensation of *trans*-2-Hydroxycyclohexaneacetic Acid Lactone with Aromatic Hydrocarbons. II. *p*-Xylene, Tetralin and α-Methylnaphthalene

BY DONALD D. PHILLIPS AND D. N. CHATTERJEE[1]

RECEIVED DECEMBER 16, 1957

The lactone I in the title afforded a complex mixture of isomeric acids when treated with *p*-xylene in the presence of aluminum chloride. The products included the three position isomers of *p*-xylylcyclohexaneacetic acid (II, III and IV, R = *p*-xylyl) as well as the *cis* isomer of IV. Tetralin also yielded II, III and IV (R = β-$C_{10}H_{11}$) although no *cis* isomers were obtained. The reaction between lactone I and 1-methylnaphthalene afforded cyclohexaneacetic acids but of undetermined orientation. Two of these acids have been converted to ketones (XIII and XIV), one of which (XIV) suggests that, at least to some extent, abnormal orientation occurred. The use of some of these arylcyclohexaneacetic acids in the synthesis of several polynuclear aromatic hydrocarbons is discussed.

In a recent communication[2] we reported the abnormal Friedel–Crafts condensation of lactone I with benzene and naphthalene, a reaction that afforded minor amounts of the expected *o*-arylcyclohexaneacetic acids (II, R = C_6H_5 and β-$C_{10}H_7$) and major amounts of the *meta* (III, R = C_6H_5 and β-$C_{10}H_7$) and *para* (IV, R = C_6H_5 and β-$C_{10}H_7$) isomers. The formation of these products was rationalized[2] on the basis of equilibration among three of the possible carbonium ion intermediates (*cf.* V) before attack on the aromatic hydrocarbon took place.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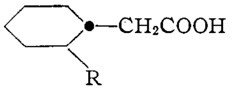
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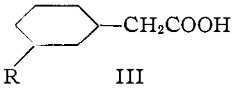
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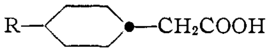
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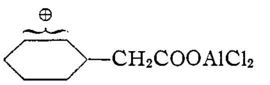
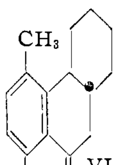
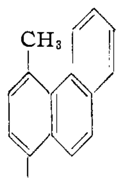
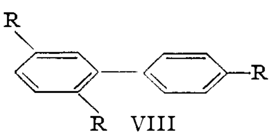

V

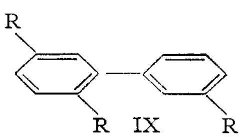
To gain further insight into the scope and mechanism of this reaction we have examined the behavior of three more aromatic hydrocarbons and, although the results were similar to those with benzene and naphthalene, some important qualitative differences were observed. For example, the reaction between the lactone I and *p*-xylene afforded a complex mixture of acids from which it was possible to separate about 10% of pure crystalline *trans*-*p*-acid IV (R = *p*-xylyl) by direct crystallization. The *o*-isomer (*ca.* 10%) was removed from the mother liquor as the ketone VI by hydrogen fluoride cyclization. Its constitution was established by reduction, dehydration and dehydrogenation to 1,4-dimethylphenanthrene (VII).


VI


VII

When the residual acidic oil from the cyclization experiment was distilled and allowed to stand in hexane there was deposited a second crystalline acid (*ca.* 9% yield), m.p. 124–125°, which afforded the same hydrocarbon (VIII, R = CH_3) on decarboxylative dehydrogenation as did the *trans*-*p*-acid (IV, R = *p*-xylyl). This observation sug-


VIII


IX

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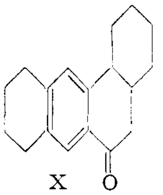
[1] Fulbright Scholar, 1956–1958; permanent address, Krishnagar College, West Bengal, India.

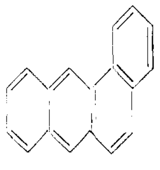
[2] D. D. Phillips and D. N. Chatterjee, THIS JOURNAL, **80**, 1360 (1958).

gested that the 124–125° acid was the *cis* isomer of IV, R = *p*-xylyl, a postulate that was confirmed by an independent synthesis. The isolation of the thermodynamically less stable *cis* isomer is difficult to rationalize on the basis of simple carbonium ion intermediates and suggests the possible intervention of a stereospecific reaction mechanism in which kinetic control is of considerable importance. We have not been able to isolate the *cis* isomer from the reaction of any other aromatic hydrocarbon with the lactone I because of the complexity of the mixtures obtained, but it is highly unlikely that *p*-xylene is unique in this respect.

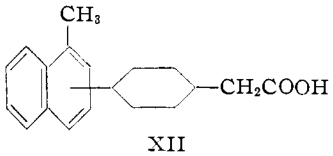
About 60% of the reaction product from *p*-xylene and lactone I remained as an uncrystallizable oil. Dehydrogenation and oxidation experiments established that this oil contained the *m*- and *p*-isomers (III and IV, R = *p*-xylyl) as major constituents with the *m*-isomer predominating as had been observed in the benzene and naphthalene series.[2] The presence of the *m*-isomer was confirmed by the isolation of methyl biphenyl-2,3′,5-tricarboxylate (IX, R = CO_2CH_3) on dehydrogenation and subsequent oxidation of the resultant trimethylbiphenyl. The concomitant formation of methyl biphenyl-2,4′,5-tricarboxylate (VIII, R = CO_2CH_3) from the *p*-isomer IV (R = *p*-xylyl) made the separation difficult and quantitative estimates of the composition of this oil were not possible by this method.

The results from the reaction between tetralin and the lactone I were very similar to those obtained from naphthalene. The mixture of acids (41% yield) afforded the *trans-p*-acid IV (R = β-$C_{10}H_{11}$) by direct crystallization and an oily mixture from which the *o*-isomer (II, R = β-$C_{10}H_{11}$) was separated by hydrogen fluoride cyclization. The constitution of the ketone so obtained (X) was established by conversion to 1,2-benzanthracene (XI). The acid mixture that resisted cyclization was shown to contain the *m*- and *p*-isomers (III and IV, R = β-$C_{10}H_{11}$) by dehydrogenation to the corresponding tolylnaphthalenes and β-naphthylphenylacetic acids as described for the naphthalene case.[2]

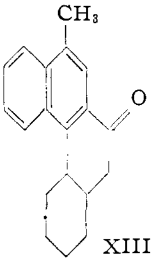

X


XI

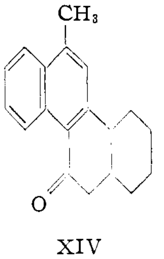
The results from the α-methylnaphthalene reaction were interesting in that an unexpected orientation was observed in at least one of the products. The crude reaction mixture afforded by direct crystallization an acid (XII) to which the *para* structure was assigned by analogy with our previous results. The orientation of the entering group was not established with certainty although the ultraviolet absorption spectrum of the dehydrogenation product was very similar to that of β-phenylnaphthalene and agreed well with either a 1,3- or 1,7-disubstituted naphthalene. The hydrogen fluoride cyclization of the residual oil from this crystallization afforded a mixture of two ketones, one of which (XIII) was shown to be the product of expected[3] orientation by conversion to 5-methylbenzo[c]phenanthrene. The other ketone afforded 6-methylchrysene (XV) on reduction and dehydrogenation, an observation that strongly suggests that the original point of attachment of the cyclohexaneacetic acid moiety was carbon 3.[4] Examples of this abnormal orientation in the electrophilic substitution of an α-alkylnaphthalene are very rare, if indeed they are known at all.[5]



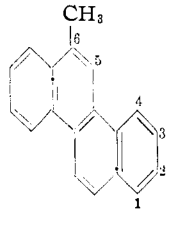
XII



XIII



XIV



XV

It must be concluded that the Friedel–Crafts condensation of the lactone I with aromatic hydrocarbons is a complex reaction affording the *o*-, *m*- and *p*-arylcyclohexaneacetic acids (probably both *cis* and *trans* isomers) by at least two different mechanisms. Whether or not these results can be expected of other lactones in the Friedel–Crafts reaction will be the subject of further investigations.

Acknowledgments.—The senior author (D.D.P.) is grateful to the Alfred P. Sloan Foundation for their generous support of this work. D.N.C. is indebted to the Damon Runyon Memorial Cancer Research Fund for a postdoctoral fellowship.

Experimental[6]

Condensation of the Lactone I with *p*-Xylene.—A solution of 14 g. (0.1 mole) of the lactone I in 60 ml. of dry *p*-xylene was added dropwise over a 30-minute period to a well-stirred suspension of 14.6 g. (0.11 mole) of aluminum chloride in 50 ml. of *sym*-tetrachloroethane held at ice temperature. The dark brown mixture was stirred at 0° for two hr. and then at room temperature for 8 hr.

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[3] "Elsevier's Encyclopedia of Organic Chemistry," Vol. 12B, Elsevier Publishing Co., Inc., New York, N. Y., 1948, pp. 96–97.

[4] It is obviously possible to rationalize this result by postulating rearrangements of the methyl group during the original Friedel–Crafts condensation and/or during the dehydration–dehydrogenation step. We prefer the simpler explanation offered above, although the possibility of rearrangements is by no means excluded. It should be noted, however, that positions 2, 4, 5 and 8 are highly unlikely as sites of attack in 1-methylnaphthalene as the resultant products could not give rise to a chrysene on cyclization. Substitution at C_6 would require a methyl migration from C_1 to C_6 (chrysene numbering, see XV) while substitution at C_7 would require a migration from C_4 to C_6, both of which seem highly unlikely.

[5] For a summary of *m*-alkylations in the Friedel–Crafts condensations of toluene see N. K. Bhattacharyya, *J. Indian Chem. Soc.*, **32**, 711 (1955); see also, however, D. D. Phillips, THIS JOURNAL, **77**, 3658 (1955). A thorough search of ref. 3 failed to reveal an example of electrophilic substitution at carbon 3 of a 1-substituted naphthalene.

[6] Melting points and boiling points are both uncorrected. Ultraviolet absorption spectra were measured in isoöctane on a Beckman model DK automatic recording spectrophotometer. Analyses are by Schwarzkopf Labs., Woodside 77, N. Y.

After decomposition of the complex by ice and hydrochloric acid, the organic layer was separated, washed with water and finally extracted with 5% sodium carbonate solution. Acidification of the alkaline solution gave 20 g. of acidic material in the form of a viscous oil. This oil was converted to the methyl ester in the usual fashion to afford 17 g. (65%) of an isomeric mixture of **methyl *p*-xylylcyclohexaneacetate** as a colorless oil, b.p. 140–142° (0.5 mm.), $n^{25}\mathrm{D}$ 1.5195.

Anal. Calcd. for $C_{17}H_{24}O_2$: C, 78.46; H, 9.23. Found: C, 78.49; H, 8.96.

Saponification of the methyl esters yielded 16 g. (62% based on lactone I) of a mixture of isomeric *p*-xylylcyclohexaneacetic acids as a viscous oil which was dissolved in hexane. After several days there was deposited 1.8 g. of ***trans*-4-*p*-xylylcyclohexaneacetic acid** (IV, R = *p*-xylyl). Recrystallization from hexane and finally from methanol gave the pure acid as rectangular plates, m.p. 128–129°, undepressed on admixture with a synthetic specimen (see below).

Anal. Calcd. for $C_{16}H_{22}O_2$: C, 78.05; H, 8.94. Found: C, 78.23; H, 9.11.

The amide crystallized from methanol in long silky needles, m.p. 176–177°, undepressed on admixture with the synthetic amide (see below).

After separation of the *trans*-acid IV (R = *p*-xylyl), the mother liquor afforded 14 g. of a viscous oil which was freed of the *o*-isomer II (R = *p*-xylyl) by cyclization with hydrogen fluoride (see below). The acidic material that resisted cyclization was distilled to give 11.5 g. of a viscous liquid, b.p. 180–182° (0.1 mm.). This was dissolved in hexane and, after several days, the solution deposited 1.4 g. of colorless solid, m.p. 118–120°. After crystallization from hexane and finally from methanol, the acid separated as fine colorless needles, m.p. 124–125°. The mixed m.p. with the *trans*-acid IV (R = *p*-xylyl) was 90–95°. This acid was identified as ***cis*-4-*p*-xylylcyclohexaneacetic acid** (*cis*-IV, R = *p*-xylyl) by comparison with a synthetic specimen and by its dehydrogenation and subsequent oxidation to biphenyl-2,4′,5-tricarboxylic acid (VIII, R = COOH).

Anal. Calcd. for $C_{16}H_{22}O_2$: C, 78.05; H, 8.94. Found: C, 78.15; H, 9.12.

The amide crystallized from methanol in short needles, m.p. 188–189°, undepressed on admixture with synthetic amide (see below).

The acidic matter (9.5 g.) left after separation of the *cis*-acid was a viscous liquid from which no further solid could be isolated. It was shown to be a mixture of the *m*- and *p*-acids (III and IV, R = *p*-xylyl) by dehydrogenation and oxidation experiments.

Palladium Dehydrogenations. a. The 128–129° Acid IV (R = *p*-Xylyl).—One gram of the acid was heated for 4 hr. at 280–300° with 0.1 g. of 10% palladium-on-charcoal catalyst. The melt was cooled and extracted with ether. Removal of the solvent left 0.6 g. of a colorless, mobile oil, b.p. 112–115° (1 mm.), $n^{25}\mathrm{D}$ 1.5745; λ_{max} 239 mμ, log ϵ 4.04, characteristic of an *o*-substituted biphenyl derivative.[7a] The infrared and ultraviolet absorption spectra of this hydrocarbon were identical with those of synthetic 2,4′,5-trimethylbiphenyl (VIII, R = CH_3, see synthesis below).

Anal. Calcd. for $C_{15}H_{16}$: C, 91.83; H, 8.17. Found: C, 91.84; H, 8.07.

The hydrocarbon (0.5 g.) was oxidized by heating under reflux for 48 hr. with an excess of 5% potassium permanganate solution. The usual workup gave 0.15 g. of a colorless solid that was converted to the methyl ester. The ester crystallized from hexane in stout prisms, m.p. 105–106°, undepressed on admixture with a synthetic sample of *trimethyl* **2,4′,5-biphenyltricarboxylate** (VIII, R = CO_2CH_3).

b. The 125° Acid IV (R = *p*-Xylyl).—One-half gram of the acid on dehydrogenation with 0.1 g. of 10% palladium-on-charcoal (as described above) gave 0.3 g. of a liquid hydrocarbon, b.p. 112–115° (1 mm.), showing identical ultraviolet and infrared absorption spectra as the hydrocarbon from the 128–129° acid. Oxidation of this hydrocarbon with neutral permanganate and subsequent esterification gave 50 mg. of trimethyl biphenyl-2,4′,5-tricarboxylate (VIII, R = CO_2CH_3) as stout prisms, m.p. 105–106°.

c. The Uncrystallizable Oil.—One gram of the uncrystallizable oil left after separation of the *o*- and *p*-isomers (II and IV, R = *p*-xylyl) on dehydrogenation as described above afforded 0.6 g. of a hydrocarbon, b.p. 112–115° (1 mm.), λ_{max} 240 mμ, log ϵ 4.08, characteristic of *o*-substituted biphenyl derivative.[7a]

Anal. Calcd. for $C_{15}H_{16}$: C, 91.83; H, 8.17. Found: C, 91.75; H, 8.31.

Oxidation of 0.5 g. of the hydrocarbon with excess of neutral permanganate, as described above, gave 0.2 g. of solid acid which was converted to the methyl ester. This was dissolved in hexane and the solution slowly deposited 40 mg. of colorless prisms, m.p. 105–106°, undepressed on admixture with an authentic sample of trimethyl 2,4′,5-biphenyltricarboxylate (VIII, R = CO_2CH_3). From the mother liquor was isolated 60 mg. of soft silky needles, m.p. 91–92°, identical with a synthetic sample of **trimethyl 2,3′,5-biphenyltricarboxylate** (IX, R = CO_2CH_3; see synthesis below).

10-Keto-5,6,7,8,9,10,13,14-octahydro-1,4-dimethylphenanthrene (VI).—Fourteen grams of the oily mixture of isomeric *p*-xylylcyclohexaneacetic acids left after removal of the *p*-isomer IV (R = *p*-xylyl) was treated in a polyethylene bottle with 150 ml. of anhydrous hydrogen fluoride at 0°. After standing for 10 min. at ice temperature (with frequent shaking), the mixture was freed of hydrogen fluoride by evaporation and the residue was poured into a solution of potassium carbonate. Extraction of the neutral material with ether followed by removal of the solvent gave 2.2 g. of oily ketone which was taken up in hexane and chromatographed on acid-washed alumina. Elution of the column with 15% benzene in hexane gave 1.5 g. of an oil which solidified on cooling. It crystallized from hexane in long colorless needles, m.p. 74–75°.

Anal. Calcd. for $C_{16}H_{20}O$: C, 84.21; H, 8.77. Found: C, 84.45; H, 8.97.

The semicarbazone crystallized from aqueous ethanol in short needles, m.p. 196–197°.

Anal. Calcd. for $C_{17}H_{23}ON_3$: N, 14.73. Found: N, 14.65.

The 2,4-dinitrophenylhydrazone crystallized from benzene in short red plates, m.p. 231–232° dec.

Anal. Calcd. for $C_{22}H_{24}O_4N_4$: C, 64.70; H, 5.88. Found: C, 64.56; H, 5.95.

1,4-Dimethylphenanthrene (VII).—A solution of 0.23 g. (0.006 mole) of lithium aluminum hydride in 25 ml. of dry ether was added to 0.45 g. (0.002 mole) of the ketone VI in 25 ml. of dry ether. The mixture was heated under reflux for 2 hr. and the usual workup afforded 0.38 g. of an oily alcohol which was dehydrogenated by heating for 2 hr. at 300–320° with 0.1 g. of 10% palladium-on-charcoal catalyst. The melt was dissolved in ether which, on evaporation, left 0.25 g. of oily hydrocarbon. This material was converted to the **picrate** which separated from methanol as orange needles, m.p. 142–143°, undepressed on admixture with an authentic sample of **1,4-dimethylphenanthrene picrate**.[8]

The hydrocarbon was regenerated from the picrate by passing a benzene solution through a column of alumina. It crystallized from methanol in colorless needles, m.p. 47–48°, undepressed on admixture with an authentic sample of **1,4-dimethylphenanthrene (VII)**.

Synthesis of *cis*- and *trans*-4-*p*-Xylylcyclohexaneacetic Acid (IV, R = *p*-Xylyl). a. 1-*p*-Xylylcyclohexene-4-acetic Acid.—A Grignard reagent prepared from 3.7 g. of 2-bromo-*p*-xylene, 0.48 g. of magnesium and 25 ml. of ether was added slowly, at −5°, to a well-stirred solution of 3.8 g. of ethyl cyclohexanone-4-acetate[2] in 25 ml. of dry ether. The colorless complex was stirred at room temperature for 4 hr. and then was decomposed with ice and dilute sulfuric acid. The organic layer was extracted with ether and the crude alcohol was dehydrated by heating for 1 hr. at 160–170° with 4 g. of powdered potassium bisulfate. The unsaturated ester was distilled to give 1.8 g. of a colorless oil, b.p. 170–190° (1 mm.).

Saponification of this material afforded 1.1 g. (23%) of a colorless, viscous liquid which slowly solidified. It crystallized from hexane in colorless needles, m.p. 70–72°.

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[7] R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Hydrocarbons," John Wiley and Sons, New York, N. Y., 1951; a, chart 162; b, chart 12; c, chart 297; d, charts 200, 204; e, chart 465; f, chart 451.

[8] J. Colonge and R. Domenech, *Bull. soc. chim. France*, 289 (1953), report m.p. 50° for 1,4-dimethylphenanthrene and m.p. 144° for its picrate.

Anal. Calcd. for $C_{16}H_{20}O_2$: C, 78.68; H, 8.20. Found: C, 78.45; H, 8.35.

b. *cis*- and *trans*-**4-*p*-Xylylcyclohexaneacetic Acid** (IV, R = *p*-Xylyl).—The foregoing unsaturated acid was hydrogenated in absolute ethanol at atmospheric pressure in the presence of 0.1 g. of 5% palladium-on-charcoal catalyst. The theoretical amount of hydrogen was absorbed in 15 minutes. The solution was filtered and the solvent was removed to leave a semisolid mass that slowly deposited from hexane 0.2 g. of crystalline solid, m.p. 122–125°. Recrystallization of this solid from hexane and finally from methanol gave *trans*-**4-*p*-xylylcyclohexaneacetic acid** as colorless rectangular plates, m.p. 128–129°.

Anal. Calcd. for $C_{16}H_{22}O_2$: C, 78.05; H, 8.94. Found: C, 78.13; H, 9.20.

The amide crystallized from methanol in fine needles, m.p. 176–177°.

Anal. Calcd. for $C_{16}H_{23}ON$: C, 78.36; H, 9.38. Found: C, 78.21; H, 9.52.

The mother liquor, after separation of the *trans*-acid, was concentrated and another crop (0.1 g.) of crystals, m.p. 90–100°, was obtained. From this crop, 30 mg. of the *trans*-acid was isolated by fractional crystallization. The combined mother liquors slowly deposited 50 mg. of colorless needles, m.p. 120–122°. Recrystallization from hexane and finally from methanol afforded *cis*-**4-*p*-xylylcyclohexaneacetic acid** as fine silky needles, m.p. 124–125°. The mixed m.p. with the *trans*-acid was 88–90°.

Anal. Calcd. for $C_{16}H_{22}O_2$: C, 78.05; H, 8.94. Found: C, 78.24; H, 9.05.

The amide crystallized from methanol in fine plates, m.p. 188–189°.

Anal. Calcd. for $C_{16}H_{23}ON$: C, 78.36; H, 9.38. Found: C, 78.49; H, 9.45.

Synthesis of Trimethyl Biphenyl-2,4′,5-tricarboxylate (VIII, R = CO_2CH_3). **a. 2,4′,5-Trimethylbiphenyl** (VIII, R = CH_3).—A Grignard reagent prepared from 9.3 g. (0.05 mole) of 2-bromo-*p*-xylene, 1.2 g. of magnesium and 50 ml. of dry ether was added with stirring to an ice-cooled solution of 5.6 g. (0.05 mole) of 4-methylcyclohexanone in 25 ml. of ether. The complex was stirred for 4 hr. at room temperature and then was heated under reflux for 2 hr. Decomposition by ice and sulfuric acid, then by dehydration (potassium bisulfate) and distillation gave 7 g. (70%) of the corresponding **cyclohexene** derivative, b.p. 105–108° (1 mm.), $n^{25}\text{D}$ 1.5225.

Dehydrogenation of 3 g. of the above cyclohexene derivative by heating for 4 hr. at 220–250° with 1 g. of sulfur gave 1.5 g. of **2,4′,5-trimethylbiphenyl**, b.p. 120–122° (1 mm.), $n^{25}\text{D}$ 1.5735, λ_{max} 237 mμ, log ϵ 4.14.

Anal. Calcd. for $C_{15}H_{16}$: C, 91.83; H, 8.17. Found: C, 91.75; H, 8.05.

b. Trimethyl Biphenyl-2,4′,5-tricarboxylate.—One gram of the foregoing biphenyl derivative was oxidized by heating under reflux for 48 hr. with an excess of 5% potassium permanganate solution. The usual workup yielded 0.3 g. of solid acid. Esterification of this acid by methanol and sulfuric acid gave 0.2 g. of **trimethyl biphenyl-2,4′,5-tricarboxylate** (VIII, R = CO_2CH_3), which crystallized from hexane in colorless prisms, m.p. 105–106°; λ_{max} 237 mμ, log ϵ 4.51.

Anal. Calcd. for $C_{18}H_{16}O_6$: C, 65.85; H, 4.87. Found: C, 66.15; H, 5.03.

Trimethyl Biphenyl-2,3′,5-tricarboxylate (IX, R = CO_2CH_3).—A Grignard reagent prepared from 9.3 g. of 2-bromo-*p*-xylene, and 1.2 g. of magnesium in 50 ml. of ether when treated with 5.6 g. of 3-methylcyclohexanone as described above gave 5 g. (50%) of the **cyclohexene** derivative, b.p. 105–106° (1 mm.), $n^{25}\text{D}$ 1.5230. Dehydrogenation of 3 g. of this compound by 1 g. of sulfur yielded 2 g. of **2,3′,5-trimethylbiphenyl** (IX, R = CH_3), b.p. 114–116° (1 mm.), $n^{25}\text{D}$ 1.5750; λ_{max} 235 mμ, log ϵ 4.04.

Oxidation of the foregoing biphenyl derivative (0.7 g.) with neutral potassium permanganate, as described above, gave 0.2 g. of solid acid which was esterified by heating with methanol and sulfuric acid. Chromatographic purification and then crystallization from hexane gave 0.1 g. of **trimethyl biphenyl-2,3′,5-tricarboxylate** (IX, R = CO_2CH_3) as soft silky needles, m.p. 91–92°; λ_{max} 293 mμ, log ϵ 3.54; 232 mμ, log ϵ 4.48.

Anal. Calcd. for $C_{18}H_{16}O_6$: C, 65.85; H, 4.87. Found: C, 65.62; H, 4.68.

Condensation of the Lactone I with Tetralin.—Sixteen grams of anhydrous aluminum chloride was added over 1 hr. at 0–5° to a well-stirred solution of 14 g. (0.1 mole) of the lactone I and 35 ml. of purified tetralin in 100 ml. of *sym*-tetrachloroethane. The dark brown mixture was stirred at room temperature for 6 hr. and then was heated at 40–45° for 2 hr. The usual workup gave 15 g. of semisolid acidic material which, on esterification, afforded 12 g. (44%) of isomeric **methyl β-tetralylcyclohexaneacetates** as a colorless, fluorescent oil, b.p. 160–165° (0.1 mm.), $n^{25}\text{D}$ 1.5341.

Anal. Calcd. for $C_{19}H_{26}O_2$: C, 79.70; H, 9.09. Found: C, 79.84; H, 9.18.

The ultraviolet absorption spectrum of this ester (λ_{max} 278 mμ, log ϵ 2.75; 270 mμ, log ϵ 2.65; 264 mμ, log ϵ 2.45) was identical with the spectrum of β-methyltetralin.[7b]

Saponification of the ester gave 11.2 g. of a semisolid acid mixture which was dissolved in hexane. The solution slowly deposited 3.8 g. (14% based on the lactone) of a solid, m.p. 143–145°. Crystallization from methanol afforded **4-β-tetralylcyclohexaneacetic acid** (IV, R = β-$C_{10}H_{11}$), m.p. 149–150°; λ_{max} 278 mμ, log ϵ 2.70; 270 mμ, log ϵ 2.68; 264 mμ, log ϵ 2.48.

Anal. Calcd. for $C_{18}H_{24}O_2$: C, 79.41; H, 8.82. Found: C, 79.25; H, 8.59.

The amide crystallized from methanol in short needles, m.p. 203–204°.

Anal. Calcd. for $C_{18}H_{25}ON$: C, 79.70; H, 9.22. Found: C, 79.58; H, 9.41.

Palladium Dehydrogenations. a. The 149–150° Acid IV (R = β-$C_{10}H_{11}$).—One gram of the acid, on heating for 4 hr. at 280–300° with 0.1 g. of 10% palladium-on-charcoal, yielded 0.8 g. of solid hydrocarbon which crystallized from hexane in needles, m.p. 93–94°, and was identified as **β-*p*-tolylnaphthalene** by comparison with a synthetic specimen.[2]

b. The Uncrystallizable Oil.—The uncrystallizable oil left after separation of the *trans-p*-isomer IV (R = β-$C_{10}H_{11}$) and the *o*-isomer II (R = β-$C_{10}H_{11}$) (by cyclization with hydrogen fluoride, see below), was dehydrogenated under similar conditions to yield 0.55 g. of a liquid hydrocarbon. This material was taken up in hexane and chromatographed on alumina. Elution with hexane afforded 0.35 g. of a liquid hydrocarbon which possessed an ultraviolet absorption spectrum (λ_{max} 285 mμ, log ϵ 4.12 and 251 mμ, log ϵ 4.75) characteristic of an unhindered β-phenylnaphthalene derivative.[7c]

Anal. Calcd. for $C_{17}H_{14}$: C, 93.58; H, 6.42. Found: C, 93.41; H, 6.38.

The analysis and ultraviolet absorption spectrum suggested that it was **β-*m*-tolylnaphthalene**[2] derived from the *m*-acid III (R = β-$C_{10}H_{11}$).

Elution of the chromatographic column with 5% benzene in hexane yielded 0.11 g. of β-*p*-tolylnaphthalene, m.p. 94–95°.

Sulfur Dehydrogenations. a. The 149–150° Acid IV (R = β-$C_{10}H_{11}$).—One gram of the methyl ester of this acid was dehydrogenated by heating for 5 hr. at 220–250° with 0.7 g. of sulfur. The melt was cooled, dissolved in benzene and passed through a column of alumina. Saponification of the eluate gave 0.3 g. of solid acidic material which crystallized from glacial acetic acid in needles, m.p. 185–186°, undepressed on admixture with an authentic[2] sample of **4-β-naphthylphenylacetic acid.**

b. The Uncrystallizable Oil.—One gram of the methyl ester of the uncrystallizable oil on dehydrogenation with sulfur, as described above, gave a large amount of tarry product. However, by chromatographic purification of the dehydrogenated ester and then saponification and fractional crystallization from methanol, it was possible to separate it into two fractions: (1) 50 mg. of **4-β-naphthylphenylacetic acid,** m.p. 185–186°, and (2) 80 mg. of short plates, m.p. 146–147°, probably **3-β-naphthylphenylacetic acid.** This acid was identical with the acid, m.p. 146°, obtained[2] from the sulfur dehydrogenation of the uncrystallizable oil from the lactone I–naphthalene condensation.

trans-**4-Keto-1′,2′,3′,4′,1,2,3,4,5,6,7,8-dodecahydro-1,2-benzanthracene (X).**—To 6.8 g. (0.025 mole) of the uncrystallizable oil left after separation of the *trans-p*-acid IV (R = β-$C_{10}H_{11}$) in a polyethylene bottle was added, at 0°, 100 ml. of anhydrous hydrogen fluoride. The mixture was stirred for 10 min. and the dark red homogeneous solution was decomposed and worked up in the usual fashion to give 0.8 g. of neutral material which was dissolved in hexane and chromatographed on acid-washed alumina. Elution with 25% benzene in hexane gave 0.4 g. of the ketone X which readily solidified. After vacuum sublimation followed by crystallization from hexane it was obtained as colorless needles, m.p. 118–120°. An analytical sample obtained by recrystallization from methanol had m.p. 122–123°; λ_{max} 302 mμ, log ε 3.45; 263 mμ, log ε 4.15.

Anal. Calcd. for $C_{18}H_{22}O$: C, 85.04; H, 8.66. Found: C, 84.78; H, 8.36.

The 2,4-dinitrophenylhydrazone crystallized from pyridine in red needles, m.p. 272–273° dec.

Anal. Calcd. for $C_{24}H_{26}N_4O_4$: C, 66.35; H, 6.00. Found: C, 65.91; H, 5.87.

***trans*-4-Hydroxy-1′,2′,3′,4′,1,2,3,4,5,6,7,8-dodecahydro-1,2-benzanthracene.**—To a slurry of 0.12 g. of lithium aluminum hydride in 15 ml. of dry ether was added a solution of 0.25 g. of the ketone X in 15 ml. of dry ether. The mixture was heated under reflux for 2 hr., after which the usual workup gave 0.2 g. of solid alcohol which crystallized from pentane as fine granules, m.p. 140–141°.

Anal. Calcd. for $C_{18}H_{24}O$: C, 84.37; H, 9.37. Found: C, 84.12; H, 9.25.

1,2-Benzanthracene (XI).—The foregoing alcohol (0.1 g.) was intimately mixed with 50 mg. of 10% palladium-on-charcoal catalyst and the mixture was heated for 2 hr. at 300–350° during which time a part of the hydrocarbon sublimed into the condenser. Extraction of the melt with hot benzene and then chromatography gave 50 mg. of solid hydrocarbon which crystallized from methanol in colorless plates, m.p. 161–162°, lit.[9] m.p. 160.5–161°. The hydrocarbon showed the characteristic color reactions and ultraviolet absorption spectrum of 1,2-benzanthracene.

The picrate crystallized from benzene–methanol in red needles, m.p. 143–144°, lit.[10] m.p. 141.5–142.5°.

Condensation of the Lactone I with α-Methylnaphthalene.—The condensation of 14 g. (0.1 mole) of the lactone I with 32 g. of α-methylnaphthalene and 16 g. (0.12 mole) of aluminum chloride in 100 ml. of tetrachloroethane, as described above, gave 20 g. of crude acidic material. This was esterified to yield 12.5 g. (42%) of isomeric **methyl α-methylnaphthylcyclohexaneacetates** as a colorless viscous oil, b.p. 170–175° (0.05 mm.), $n^{30}\text{D}$ 1.5745.

Anal. Calcd. for $C_{20}H_{24}O_2$: C, 81.08; H, 8.10. Found: C, 81.42; H, 8.03.

The ultraviolet absorption spectrum of this ester (λ_{max} 321 mμ, log ε 2.60; 305 mμ, log ε 2.82; 278 mμ, log ε 3.75; 228 mμ, log ε 4.99) was similar to those of 1,3- and 1,7-dimethylnaphthalene.[7c]

Saponification of the ester gave a semisolid acid that deposited from hexane 3.5 g. of a crystalline solid, m.p. 145–150°. After one crystallization from benzene and finally from methanol, it separated as colorless plates, m.p. 159–160°. The ultraviolet absorption spectrum of this acid was identical with that of the original mixture of esters.

Anal. Calcd. for $C_{19}H_{22}O_2$: C, 80.85; H, 7.80. Found: C, 80.58; H, 7.56.

The amide crystallized from methanol in colorless plates, m.p. 200–201°.

Anal. Calcd. for $C_{19}H_{23}ON$: C, 81.13; H, 8.18. Found: C, 80.95; H, 8.25.

Palladium Dehydrogenation of the Acid, M.p. 159–160°.—One gram of the methyl ester of the acid, when dehydrogenated by heating with 0.1 g. of 10% palladium-on-charcoal according to the conditions described earlier, gave 0.5 g. of a hydrocarbon, b.p. 178–180° (1 mm.), $n^{25}\text{D}$ 1.6605.

Anal. Calcd. for $C_{18}H_{16}$: C, 93.10; H, 6.90. Found: C, 92.86; H, 7.14.

The ultraviolet absorption spectrum of this compound (λ_{max} 287 mμ, log ε 4.04 and 253 mμ, log ε 4.70) was very similar to that of β-phenylnaphthalene[7c] and has tentatively been assigned the structure of **3-(or 7)-*p*-tolyl-1-methylnaphthalene.**

The dehydrogenation of 1 g. of the methyl ester of the uncrystallizable oil left after separation of the 159–160° acid furnished a hydrocarbon, b.p. 180–185° (1 mm.), showing the same ultraviolet absorption spectrum as the hydrocarbon obtained from the 159–160° acid.

These experiments suggest that the condensation of the lactone I with α-methylnaphthalene takes place predominantly in one of the β-positions rather than in the expected[3] 4-position.

Cyclization Experiments. a. The 159–160° Acid.—Attempted cyclization of the acid by hydrogen fluoride gave back the original acid exclusively.

b. The Uncrystallizable Oil.—Cyclization of 7 g. of the uncrystallizable oil by 100 ml. of anhydrous hydrogen fluoride, as described above, gave 0.9 g. of neutral material which was taken up in hexane and chromatographed on alumina. Elution with hexane gave 0.45 g. of a semisolid ketone and 25% benzene in hexane afforded 0.35 g. of a semisolid ketone. Both fractions seemed to be a mixture of ketones which could not be separated by chromatography. This postulate was verified by the isolation of two different 2,4-dinitrophenylhydrazones; red plates, m.p. 170–175°, and red needles, m.p. 286–288° dec.

Reduction of 0.2 g. of the ketone mixture with lithium aluminum hydride and then dehydrogenation according to the conditions described earlier gave a semisolid mass which was taken up in hexane and chromatographed on alumina. Elution with hexane gave a trace of undehydrogenated oil followed by 20 mg. of **5-methylbenzo[c]phenanthrene** in the form of an oil which was converted to the picrate. After one crystallization from methanol this picrate was obtained as reddish-orange needles, m.p. 129–130°. The mixed m.p. with an authentic sample (m.p. 133°) of the picrate of 5-methylbenzo[c]phenanthrene was not depressed.[11]

The hydrocarbon regenerated from the picrate was an oil which did not solidify. However, its ultraviolet absorption spectrum (λ_{max} 372, 355, 330, 318, 304, 282, 274, 254, 244, 230 and 218 mμ) was in good agreement with that reported.[7e]

Elution of the chromatographic column with 25% benzene in hexane gave 50 mg. of a solid which crystallized from methanol in colorless needles, m.p. 148–149°. After two crystallizations from methanol it was obtained as short needles, m.p. 158–160°, and was identified as **6-methylchrysene (XV).** The mixed m.p. with an authentic sample[12] (m.p. 160–161°) was 158–160°. The ultraviolet absorption spectrum of the hydrocarbon (λ_{max} 362, 354, 346, 323, 308, 296, 283, 269, 259, 244 and 222 mμ) was in excellent agreement with that reported for 6-methylchrysene.[7f]

The picrate crystallized from benzene–hexane in red needles, m.p. 162–163°.

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[9] L. F. Fieser and H. J. Creech, THIS JOURNAL, **61**, 3502 (1939).

[10] J. W. Cook, *J. Chem. Soc.*, 2524 (1931).

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

[12] Made available through the courtesy of Prof. M. S. Newman who records m.p. 160.2–161.2° for the hydrocarbon and 170–170.6° for its picrate (THIS JOURNAL, **60**, 2947 (1938)).