gave the analytical sample, m.p. 185–187°. Using these conditions, B-triisopropyl-N-triphenylborazole was obtained in 20% yield.

4. **Hexaphenylborazole. a. From Phenylmagnesium Bromide.**—Phenylmagnesium bromide prepared from magnesium (2.36 g., 0.097 g. atom) and bromobenzene (15.2 g., 0.097 mole) in 100 ml. of ether was added to a suspension of I (10 g., 0.024 mole) in ether (100 ml.) as described in 1. At the end of a 2-hour reflux period, the reaction mixture contained solid material. A filter stick was used to remove the supernatant solution and the solid residue, after being washed with several fresh portions of ether, was dried, ground in a mortar and continuously extracted with $CHCl_3$ for a period of 4 hours. After being decolorized with charcoal, the solution was concentrated and the crystalline hexaphenylborazole was collected in three crops; weight 8.5 g., yield 65%. The analytical sample was obtained by two further recrystallizations from chloroform, m.p. 413–415°.

The following alternate procedure for isolating hexaphenylborazole gave lower yields: The reaction mixture was cautiously decomposed with 5% HCl solution. The solid material which was insoluble in both the organic and aqueous layers was collected and recrystallized from chloroform to give a 29% yield of hexaphenylborazole.

b. From Phenyllithium.—To a 500-ml. flask containing a solution of phenyllithium, prepared from 1.46 g. (0.21 g. atom) of lithium shot in 25 ml. of dry benzene and 15.7 g. (0.1 mole) of bromobenzene in 50 ml. of dry ether, was added with stirring a suspension of I (10.3 g., 0.025 mole) in 100 ml. of dry benzene and 200 ml. of dry ether over a period of 45 minutes. A very gentle exothermic reaction ensued causing the separation of a finely-divided solid from a peach-colored solution. The quantity of solid increased with further addition of I. After being refluxed overnight, the reaction mixture was cooled and filtered. During this operation the solid assumed a purple color and the filtrate became blood red. Working up this filtrate in the usual manner furnished a viscous, red residue which was not further investigated. The solid was washed with hot water to remove LiCl and the water-insoluble solid, after air-drying, was recrystallized from $CHCl_3$ to give 2.45 g. (18%) of hexaphenylborazole. Two further recrystallizations from $CHCl_3$ furnished the analytical sample, m.p. 413–415°.

C. Kuivala's Method.[14]—To 187 ml. of a solution of *n*-butyllithium (0.3 molar) in ligroin (b.p. 60–90°) was added with stirring a solution of aniline (4.72 g., 0.054 mole) in 50 ml. of ligroin followed by the dropwise addition of a solution of di-*n*-butyl phenylboronate[19] (0.054 mole) in 50 ml. of ligroin. No temperature change was observed. After another 187 ml. of a solution of *n*-butyllithium (0.3 molar) in ligroin was added, the reaction mixture was stirred at room temperature overnight, followed by a 24-hour reflux. The cooled reaction mixture was filtered and the filtrate refluxed for 24 hours longer without depositing additional solid material. The precipitate was digested with water and the water-insoluble material was collected, dried and recrystallized from $CHCl_3$ to give 0.517 g. (5.3%) of hexaphenylborazole. The infrared and ultraviolet spectra of this material were identical with those of the hexaphenylborazole prepared above.

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(19) K. Torsell, *Acta Chem. Scand.*, **8**, 1779 (1954).

STAMFORD, CONN.

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

The Friedel–Crafts Condensation of *trans*-2-Hydroxycyclohexaneacetic Acid Lactone with Aromatic Hydrocarbons. I. Benzene and Naphthalene

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

RECEIVED OCTOBER 21, 1957

The lactone I in the title has been condensed with benzene to give an 87% yield of an isomeric acid mixture from which *trans*-4-phenylcyclohexaneacetic acid (II, R = C_6H_5) and a solid mixture of II (R = C_6H_5), 3-phenylcyclohexaneacetic acid (III, R = C_6H_5) and *trans*-2-phenylcyclohexaneacetic acid (IV, R = C_6H_5) have been isolated. The latter has been cyclized and reduced to the octahydrophenanthrol (VII). A similar condensation between lactone I and naphthalene afforded a 45% yield of the corresponding β-naphthylcyclohexaneacetic acids (II, III and IV, R = β-$C_{10}H_7$). The latter (IV) has been cyclized, reduced and dehydrogenated to yield chrysene. A possible mechanism for this abnormal Friedel–Crafts reaction is discussed.

The lactone of *trans*-2-hydroxycyclohexaneacetic acid (I), conveniently prepared[2] from the commercially available cyclohexene oxide, seemed to be particularly suitable[3] as a starting material for the synthesis of polynuclear aromatic hydrocarbons. With this view in mind, we have studied the Friedel–Crafts condensation of this lactone with several hydrocarbons and, in every instance, we have found the reaction to take an unexpected course.

From the aluminum chloride-catalyzed reaction between lactone I and benzene there was isolated an 87% yield of isomeric phenylcyclohexaneacetic acids. By fractional crystallization, this mixture has afforded approximately 15% of pure *trans*-4-phenylcyclohexaneacetic acid (II, R = C_6H_5) and 85% of a mixture of acids, m.p. 70–71°. Although the exact composition of this latter mixture has not been determined, we have been able to show that it contains a small amount of II, R = C_6H_5, about 15% of the *trans-ortho* isomer IV (R = C_6H_5) and a *major* amount of the *meta* isomer III (R = C_6H_5), of unknown stereochemistry.

The structure of the *para* condensation product II (R = C_6H_5) was established both by a comparison with authentic material[4] as well as by dehydrogenation to *p*-phenylphenylacetic acid (V, R = C_6H_5) which was independently synthesized. Although it was not possible to obtain a pure specimen of the *o*-acid IV (R = C_6H_5), its relative concentration in the mixture was established by cyclization to the known octahydrophenanthrone (VIII). The determination of the relative amount of the *meta* isomer (III, R = C_6H_5) in the 70–71° acid mixture was more difficult although its presence in substantial concentrations was clearly indicated by dehydrogenation and oxidation where-

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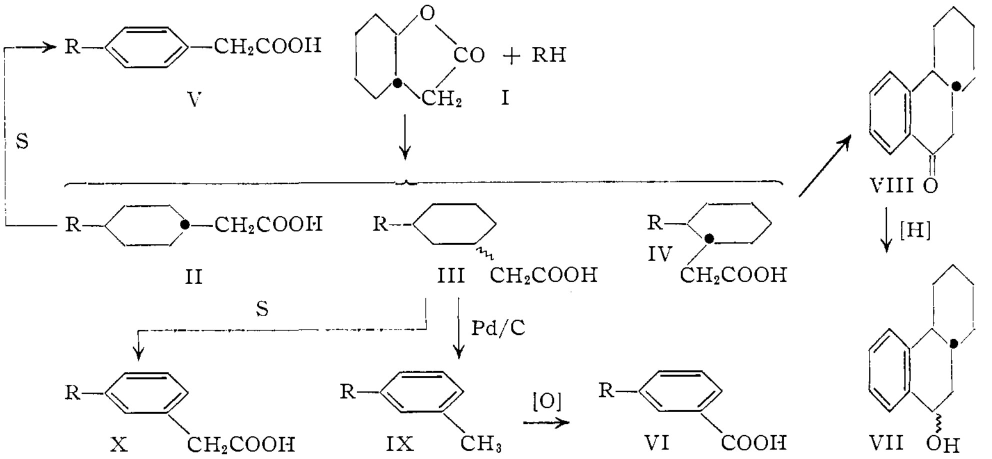
[1] Fulbright Scholar, 1956–1958; permanent address, Krishnagar College, West Bengal, India.

[2] M. S. Newman and C. A. VanderWerf, THIS JOURNAL, **67**, 235 (1945).

[3] A preliminary report of the use of this lactone in the synthesis of chrysene has been published recently; D. D. Phillips, *Chemistry & Industry*, 54 (1956).

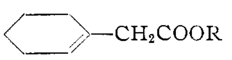
[4] L. F. Fieser, *et al.*, THIS JOURNAL, **70**, 3190 (1948). We are grateful to Dr. H. E. Zaugg of Abbott Laboratories for a sample of this acid.

Chart I

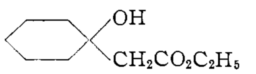


by biphenyl-3-carboxylic acid (VI, R = C_6H_5) was obtained. Dehydrogenation of the low melting acid with sulfur afforded both V and X (R = C_6H_5), the latter in preponderant amounts, thus establishing unequivocally the formation of III (R = C_6H_5) in the original condensation.

The formation of acids II and III (R = C_6H_5) in amounts greater than that of the expected *ortho* IV was surprising although there is some precedent for abnormal products in the Friedel–Crafts condensation of closely related compounds. For instance Nenitzescu and Gavat[5] have obtained the *p*-acid, II (R = C_6H_5) from the reaction between benzene and cyclohexylideneacetic acid in the presence of aluminum chloride. The same acid is formed[6] from Δ^1-cyclohexenylacetic acid (XI, R = H) and benzene, but neither group[5,6] isolated the *meta* isomer from the reaction. More recently, the *p*-acid II (R = C_6H_5) has been obtained from the Friedel–Crafts reaction between benzene and ethyl 1-hydroxycyclohexaneacetate (XII) along with a small amount of the *trans-o*-acid IV (R = C_6H_5).[7] Similar results also have been obtained



XI



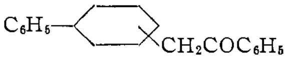
XII

from XI (R = C_2H_5), although in this instance, the *trans-o*-acid and the *trans-p*-acid were obtained in essentially equal amounts.[8a] The French workers also have reported the condensation between lactone I and benzene, but once again they record the isolation of only the *o*- and *p*-acids.[8b]

Zaugg[9] has repeated the work cited previously[5,6] and has demonstrated a certain stereospecificity in the reaction by his isolation of pure *trans*-acid II (R = C_6H_5) uncontaminated by the *cis* isomer, crystals of which were available for seeding. The *trans* configuration of the two acids isolated (II and IV, R = C_6H_5) plays a significant role in the mechanism postulated by Zaugg in which bridged ion intermediates are suggested.[10] The *absence* of *meta* product in Zaugg's experiments was rationalized by the steric requirements of the bridged ions, but the mechanism must be reconsidered in view of our findings that the *meta* isomer is a *major* product.

Although it is tempting to invoke bridged ions as a rationalization of the results mentioned above, we prefer to adopt the simpler explanation that the three products II, III and IV (R = C_6H_5) are formed as a result of a series of 1,2-hydrogen shifts, analogies for which are legion. The *trans* stereochemistry observed in the *ortho* and *para* compounds II and IV may then be ascribed simply to thermodynamic control of the reaction in which the more stable products would be expected. It would be instructive to know the stereochemistry of the *meta* product III (R = C_6H_5), but we have not been able to determine it as yet, although work along these lines is continuing.

Since the *o*-acid IV (R = C_6H_5) or its cyclization product VIII was the desired compound at the outset of this research, we investigated ways in which the yield of IV might be increased. One attempt involved the use of a large excess of aluminum chloride with the hope that the desired acid would be removed from the mixture as the ketone VIII.[11] The yield of ketone was substantially the same, however, and a mixture of II and III (R = C_6H_5) was obtained as before. The reaction was further complicated by the formation of intermolecular products (*cf.* XIII) so that this method was abandoned. Even in the presence of anhydrous hydrogen fluoride, the yields of ketone



XIII

VIII were approximately the same and the ubiquitous *m*- and *p*-phenylcyclohexaneacetic acids were once more obtained.

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[5] C. D. Nenitzescu and J. Gavat, *Ber.*, **70**, 1883 (1937).

[6] J. W. Cook and F. Goulden. *J. Chem. Soc.*, 1559 (1937).

[7] E. B. Carton, H. F. Lederle, L. F. Schwartzman and G. F. Woods, This Journal, **74**, 5126 (1952).

[8] (a) F. Winternitz, M. Mousseron and J. Vinas, *Bull. soc. chim. France*, 1035 (1952); (b) F. Winternitz, M. Mousseron and G. Rouzier, *ibid.*, 316 (1954).

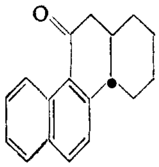
[9] We are grateful to Dr. H. E. Zaugg for communicating his results to us. In view of the duplication of effort, Dr. Zaugg's results will not be published but will be discussed briefly in this paper.

[10] D. S. Noyce and H. I. Weingarten, This Journal, **79**, 3098 (1957), have invoked similar bridged ions to explain the formation of *trans*-methyl 3- and 4-acetoxycyclohexanecarboxylate in the reaction between the corresponding *cis*-alcohols and acetic anhydride.

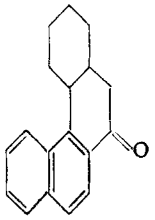
[11] Compare the synthesis of 1-tetralone from benzene and butyrolactone; C. E. Olson and A. R. Bader, *Org. Syntheses*, **35**, 95 (1955).

Our results in the naphthalene series are substantially the same and will therefore be discussed only briefly. The condensation of the lactone I with naphthalene in the presence of aluminum chloride afforded a 45% yield of the analogous acids II, III and IV (R = β-$C_{10}H_7$) along with a 20% of a dicondensation product. From the mixture it was possible to isolate by fractional crystallization a pure sample of the ***trans-para*** product II (R = β-$C_{10}H_7$), m.p. 145–147°, whose identity was established by dehydrogenation to V (R = β-$C_{10}H_7$) and by independent synthesis. The mother liquor then was separated into a mixture of solid acids, m.p. 95–98°, and an uncrystallizable oil.

By techniques similar to those described for the 70–71° acid obtained in the benzene series,[12] we were able to confirm the presence of substantial quantities of the *m*-acid III (R = β-$C_{10}H_7$) in the 95–98° mixture. Moreover, the uncrystallizable oil was found to be relatively rich in the ***ortho*** isomer IV (R = β-$C_{10}H_7$) by cyclization to the octahydrochrysene derivative XIV. The constitution of this ketone was established by reduction, dehydration and dehydrogenation to afford chrysene. Moreover, it was possible to isolate from the ketonic mixture the product from α-alkylation in the form of the ketoöctahydrobenzo[c]phenanthrene (XV), the constitution of which was established by conversion to benzo[c]phenanthrene.



XIV



XV

We have also examined in detail the reaction between the lactone I and *p*-xylene, 1-methylnaphthalene and tetralin and the results will be the subject of a forthcoming publication. Moreover, we have been able to use XIV as an intermediate in a convenient preparation of the potent carcinogen, 3,4-benzpyrene, and we hope to communicate details of this synthesis in the near future.

Acknowledgment.—The senior author (D. D. P.) is grateful to the Lalor Foundation for their initial support of this program during the summer of 1955, and to the Alfred P. Sloan Foundation for their generous support since that time. D. N. C. wishes to thank the Damon Runyon Memorial Cancer Fund for a post-doctoral fellowship.

Experimental[13]

Condensation of Lactone I with Benzene: The Synthesis of the Isomeric Phenylcyclohexaneacetic Acids.—A solution of 28 g. (0.2 mole) of the lactone I in 70 ml. of dry benzene was added dropwise during 15 min. to a well-stirred suspension of 29.2 g. (0.22 mole) of anhydrous aluminum chloride in 80 ml. of benzene held at ice temperature. The mixture was allowed to stand at 0° for 4 hours and then at room temperature for 4 hours after which it was heated to 40–45° for one hour.

The light brown complex was decomposed with ice and hydrochloric acid and the aqueous solution was extracted with 500 ml. of ether. The combined ether–benzene solution was washed with water and then extracted with 10% sodium carbonate solution. The acid fraction was esterified and distilled to yield 40 g. of an isomeric mixture of **methyl phenylcyclohexylacetate**, b.p. 116–118° (0.1 mm.), $n^{25}D$ 1.5165.

Anal. Calcd. for $C_{15}H_{20}O_2$: C, 77.58; H, 8.62. Found: C, 77.32; H, 8.55.

Saponification of the above ester gave 38 g. (87%) of an isomeric mixture of phenylcyclohexaneacetic acids which slowly solidified. It was dissolved in acetic acid and the clear solution was diluted in the cold with water until a permanent turbidity appeared. After standing for several days with occasional stirring, the solution deposited 6 g. (13%) of ***trans*-4-phenylcyclohexaneacetic acid** (II, R = C_6H_5) which after recrystallization from aqueous acetic acid and finally from aqueous methanol, melted at 113–114°. The mixed m.p. of this acid with an authentic sample[9] was not depressed.

The amide crystallized from aqueous ethanol in fine plates, m.p. 195–196°, lit.[4] m.p. 194–195.5°.

The acetic acid mother liquor on dilution gave about 30 g. of an oily acid which slowly solidified. It crystallized from hexane in fine needles, m.p. 70–71°.

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.06; H, 8.25. Found: C, 76.81; H, 8.20.

Dehydrogenation of the Acid (M.p. 70–71°) with Palladium.—One gram of the acid was heated for 4 hours with 0.1 g. of 10% palladium-on-charcoal catalyst at 300–330°. The melt was extracted with ether and washed with aqueous sodium carbonate, but no acidic material resulted on acidification of the alkaline solution. Removal of the solvent and distillation of the neutral residue gave 0.7 g. (90%) of a colorless mobile liquid with a characteristic odor, b.p. 90–92° (1 mm.), $n^{25}D$ 1.6020. The ultraviolet absorption spectrum of this compound ($\lambda_{max}^{isooctane}$ 250 mμ, log ε 4.22) was identical with that of **4-methylbiphenyl**, prepared according to Gomberg.[14]

Anal. Calcd. for $C_{13}H_{12}$: C, 92.85; H, 7.15. Found: C, 92.68; H, 7.08.

The liquid nature of this hydrocarbon as compared to synthetic solid material (m.p. 45–46°) may be attributed to contamination with substantial amounts of 3-methylbiphenyl, but attempted separation of the two by chromatography was unsuccessful.

This hydrocarbon (0.5 g.) was oxidized by heating under reflux for 6 hours with 100 ml. of 5% potassium permanganate solution. Excess of the oxidant was destroyed by sodium bisulfite. Filtration from the sludge of manganese dioxide followed by concentration, acidification and ether extraction gave 0.3 g. of acid which, after two crystallizations from aqueous methanol, separated as colorless needles, m.p. 218°. Mixed m.p. of this acid with an authentic sample of ***p*-phenylbenzoic acid** was not depressed.

The mother liquor on dilution gave another crop of acid which, after several crystallizations from aqueous methanol, melted sharply at 160°. The mixed m.p. of this acid with an authentic sample of ***m*-phenylbenzoic acid** was not depressed. Because of the large losses that attended the recrystallizations, it was not possible to determine the relative composition of the mixture by oxidation.

Dehydrogenation of the Acid (M.p. 70–71°) with Sulfur.—One gram of the acid was heated for 4 hours with 0.5 g. of powdered sulfur at 220–230°. The temperature then was slowly raised to 250° during one hour. The product was taken up in ether and extracted with sodium bicarbonate solution. Acidification of the alkaline extract yielded 0.45 g. of solid acid which crystallized from benzene in fine plates, m.p. 120–122°. This acid seems to be *p*-phenylphenylacetic acid contaminated with some of the *meta* isomer. Although several crystallizations of the acid from benzene afforded a small amount of *p*-phenylphenylacetic

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(12) The experimental section should be consulted for details of the dehydrogenations, oxidations, etc.

(13) Melting points and boiling points are uncorrected. Ultraviolet absorption spectra were measured in 95% ethanol (unless otherwise indicated) with a Beckman model DK automatic recording spectrophotometer. Infrared absorption spectra were obtained on a Perkin-Elmer model 21 double-beam spectrophotometer. Analyses were performed by Schwarzkopf Labs., Woodside 77, N. Y.

(14) M. Gomberg and J. C. Pernert, THIS JOURNAL, **48**, 1378 (1926).

acid (V, R = C_6H_5), m.p. 162–163° (identified by comparison with an authentic specimen prepared according to Schwenk and Papa[15]), no pure *ortho* isomer could be isolated from the mother liquor. The acid isolated from the filtrate after several crystallizations from a benzene–hexane mixture melted at 135°. It showed an ultraviolet absorption spectrum (λ_{max} 249 mμ, log ε 4.12) quite characteristic of an unhindered biphenyl derivative and was identified as ***m*-phenylphenylacetic acid** (X, R = C_6H_5) by comparison with an authentic sample.[16]

Once again, the substantial losses that resulted in each recrystallization made it virtually impossible to determine the relative amounts of the *para* and *meta* isomers in this mixture. This was accomplished more satisfactorily by conversion to the amides (see below).

Separation of the 70–71° Acid by Amide Formation.—The acid, m.p. 70–71° (0.65 g.), after being freed of *ortho* isomer by cyclization (described below) was converted in the usual fashion to the amide (0.65 g.). This amide was dissolved in methanol from which 0.15 g. of the amide from the *para* isomer II (R = C_6H_5), m.p. 190°, separated. The filtrate was diluted with water and 0.25 g. of **3-phenylcyclohexaneacetamide**, m.p. 118–119°, was collected.

Anal. Calcd. for $C_{14}H_{19}ON$: C, 77.42; H, 8.75; N, 6.45. Found: C, 77.31; H, 8.52; N, 6.28.

A second crop (0.05 g., m.p. 115–116°) separated from the mother liquor on concentration. From these data it was possible to estimate the relative amounts of *para* and *meta* isomers in the mixture as 40 and 60%, respectively.

Cyclization Experiments on the 70–71° Acid. (a) **Sulfuric Acid.**—The acid (2.2 g., 0.01 mole) was heated with stirring for 1.5 hr. on the steam-bath with a mixture of 9 ml. of concd. sulfuric acid and 3 ml. of water. The reaction mixture was poured onto crushed ice and the ketone was extracted with ether. The ether solution was washed with aqueous ammonia and water and was dried over sodium sulfate. The neutral product left after removal of the ether (0.2 g., 10%) readily solidified. It crystallized from hexane to give 0.15 g. of ***trans*-9-keto-1,2,3,4,9,10,11,12-octahydrophenanthrene** (VIII) as fine needles, m.p. 96°.[17,18]

The 2,4-dinitrophenylhydrazone crystallized from ethyl acetate in fine, deep orange needles, m.p. 258°, lit.[8b,17] 246–248°, 260–263°.

The semicarbazone crystallized from ethanol in fine plates, m.p. 256° dec.

Anal. Calcd. for $C_{15}H_{19}ON_3$: C, 70.03; H, 7.39. Found: C, 70.15; H, 7.25.

(b) **Hydrogen Fluoride.**—The 70–71° acid (3.3 g., 0.015 mole) was added with shaking to 40 ml. of anhydrous hydrogen fluoride contained in a polyethylene bottle and immersed in ice. The acid quickly dissolved giving a dark red solution. After 5 minutes standing in the ice-bath, the reaction mixture was freed from hydrogen fluoride by evaporation and the residue was poured into a concentrated solution of potassium carbonate. Extraction of the neutral matter with ether gave 0.85 g. of an oily material which was taken up in hexane and chromatographed on acid-washed alumina. Elution with hexane gave 0.1 g. of a colorless oil which showed the characteristic infrared absorption peak of a conjugated ester ($\lambda_{max.}$ 5.84 μ). The compound was completely saponifiable to an acid, m.p. 200°, and identified as phthalic acid. In view of the limited amount at our disposal, it was not examined further.[19] Elution of the chromatographic column with 10% benzene in hexane gave 0.4 g. (13%) of the ketone which slowly solidified. Vacuum sublimation followed by crystallization from hexane gave the pure ketone VIII, m.p. 96°.

The alkaline solution on acidification afforded 2 g. of acid that slowly solidified. This acid could be degraded to *p*-phenylphenylacetic acid or *p*-phenylbenzoic acid and a relatively smaller amount of *m*-phenylphenylacetic acid or *m*-phenylbenzoic acid according to the conditions described earlier. Attempted fractional crystallization from methanol or hexane led to the separation of a small quantity of the *p*-acid II (R = C_6H_5) followed by a second crop, m.p. 70°, consisting of the mixed crystals of the acids II and III (R = C_6H_5). Treatment of the acid chloride with gaseous ammonia in benzene solution gave an amide which crystallized from methanol to give the amide of acid II (R = C_6H_5), m.p. 193°. From the mother liquor the amide of the *meta* isomer III (R = C_6H_5) was isolated, m.p. 119–120°.

(c) **Inverse Friedel–Crafts Method.**[20]—The acid chloride from 3.3 g. (0.015 mole) of the acid (m.p. 70–71°) and 3.5 g. (0.016 mole) of phosphorus pentachloride was dissolved in 10 ml. of dry benzene and added at 5° with stirring to a suspension of 2 g. (0.015 mole) of aluminum chloride in 10 ml. of benzene. The dark red complex was stirred for 5 hours at room temperature and decomposed in the usual fashion to give 2 g. of oily ketonic material which was taken up in hexane and chromatographed on alumina.

Elution with hexane gave 1.1 g. of an oil followed by elution with 15% benzene in hexane when 0.33 g. (11% of the desired ketone VIII was isolated. This crystallized from hexane to give the pure ketone VIII, m.p. 95°.

The hexane eluent seems to be ketone formed by reaction with the benzene solvent (*cf.* XIII). It showed an intense carbonyl peak in the infrared spectrum, but could not be dehydrogenated to a phenanthrene. It readily formed a **2,4-dinitrophenylhydrazone**, but attempted crystallization from the usual solvents led to the separation of an oil which did not solidify. However, by chromatography on acid-washed alumina, using benzene and finally benzene–ethyl acetate as solvent, it was possible to separate it into three different products: (1) bright orange needles from methanol, m.p. 149–150°, which analyzed fairly well for **ω-(phenylcyclohexyl)-acetophenone** and was probably the ketone derived from the *meta* isomer (*m*-XIII). *Anal.* Calcd. for $C_{26}H_{26}N_4O_4$: C, 68.12; H, 5.67. Found: C, 69.05; H, 6.06. (2) Orange needles from ethyl acetate, m.p. 170–171°, found to be identical with the 2,4-dinitrophenylhydrazone of ω-(*trans*-4-phenylcyclohexyl)-acetophenone (*p*-XIII) unequivocally synthesized (see below) from the acid II (R = C_6H_5). (3) Deep orange needles from ethyl acetate, m.p. 258°, identical with the 2,4-dinitrophenylhydrazone derivative of the cyclic ketone VIII.

ω-(*trans*-4-Phenylcyclohexyl)-acetophenone (*p*-XIII).—An acid chloride prepared from 0.4 g. of the acid II (R = C_6H_5) and 0.4 g. of phosphorus pentachloride was taken up in 10 ml. of dry benzene and added at 5° with stirring to a suspension of 0.3 g. of aluminum chloride in 5 ml. of benzene. It was stirred at room temperature for 2 hr. and then at 50–60° for 1 hour. The usual workup gave 0.3 g. of a semi-solid mass which, after chromatographic purification, solidified. It crystallized from hexane in fine needles, m.p. 84–85°.

Anal. Calcd. for $C_{20}H_{22}O$: C, 86.30; H, 7.90. Found: C, 86.40; H, 8.21.

The 2,4-dinitrophenylhydrazone crystallized from ethyl acetate as orange needles, m.p. 170–171°.

Anal. Calcd. for $C_{26}H_{26}N_4O_4$: C, 68.12; H, 5.67; N, 12.22. Found: C, 68.41; H, 5.49; N, 12.35.

***trans*-9-Hydroxy-1,2,3,4,9,10,11,12-octahydrophenanthrene (VII).**—A solution of 0.46 g. (0.012 mole) of lithium aluminum hydride in 25 ml. of ether was added to 0.8 g. (0.004 mole) of the ketone VIII dissolved in 25 ml. of ether. The solution was heated under reflux for 2 hours and worked up in the usual manner to give 0.7 g. (87%) of the alcohol which crystallized from hexane in soft silky needles, m.p. 90–91°, lit. m.p. 90–91°,[21] 89–91°.[22]

Condensation of the Lactone I with Benzene in the Presence of Hydrogen Fluoride.—A solution of the lactone (3.5 g.) in benzene (15 ml.) was added slowly to anhydrous hydrogen fluoride (100 ml.) contained in a polyethylene bottle and immersed in crushed ice. It was kept at 0° for 24 hours and then at 15–18° for 24 hours during which period it was necessary to shake it occasionally to bring the organic layer into intimate contact with the hydrofluoric acid. The

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[15] E. Schwenk and D. Papa, *J. Org. Chem.*, **11**, 799 (1946).

[16] Made available through the courtesy of Dr. D. L. Turner who records a m.p. of 135–137° for this isomer (THIS JOURNAL, **72**, 3283 (1950)).

[17] E. Buchta and H. Ziener, *Ann.*, **601**, 155 (1956).

[18] W. E. Bachmann and E. J. Fornefeld, THIS JOURNAL, **72**, 5529 (1950).

[19] A small amount of this ester was isolated from all cyclization experiments and even pure 4-phenylcyclohexaneacetic acid (II, R = C_6H_5) yielded a small amount when treated with hydrogen fluoride.

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

[21] R. P. Linstead, R. R. Whetstone and P. Levine, *ibid.*, **64**, 2020 (1942).

[22] C. Buchanan and A. C. Ritchie, *J. Chem. Soc.*, 4523 (1954).

dark red solution was concentrated by evaporating most of the hydrogen fluoride and the residue was poured into a concentrated solution of potassium carbonate.

Extraction with ether gave 1.5 g. of neutral matter which showed infrared absorption at $\lambda_{max.}$ 5.65 and 5.95 μ, indicating the presence of some unreacted lactone. This was hydrolyzed by heating under reflux with alcoholic potassium hydroxide solution. The alkaline solution on acidification gave an acid from which 0.5 g. of unreacted lactone was recovered by distillation. The neutral material was taken up in ether. Removal of the solvent furnished 0.75 g. (17%) of solid ketone VIII, m.p. 95–96°.

The acidic product from the above condensation consisted of 1.8 g. of a semi-solid that was converted to the methyl ester and purified by distillation. The first fraction (0.5 g., b.p. 110–120° (0.1 mm.)) was saponified to give an acid which was predominantly the *para* isomer II (R = C_6H_5). It formed an amide which, after several crystallizations from aqueous methanol, melted at 192–193°. The rest of the material distilled above 190° (0.1 mm.) as a viscous oil. Saponification of this material gave an amorphous solid which could not be crystallized. However, the neutralization equivalent of the acid showed that it was probably a dimolecular condensation product of the lactone and benzene.

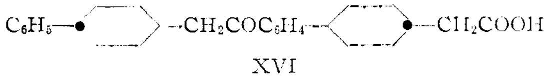
Anal. Calcd. for $C_{22}H_{30}O_4$: neut. equiv., 179. Found: neut. equiv., 180.

Condensation of the Lactone I with Benzene in the Presence of Excess Aluminum Chloride.—To a solution of 7 g. (0.05 mole) of the lactone in 50 ml. of dry benzene was added, over 0.5 hr. at room temperature, 23.2 g. (0.175 mole) of aluminum chloride. The dark red complex was stirred at room temperature for 2 hours and then heated on the steam-bath with continued stirring for 8 hours. After cooling to room temperature, the complex was decomposed with ice and hydrochloric acid. Extraction of the organic matter by ether and then washing with sodium carbonate solution gave 4 g. of an oily ketone which was taken up in hexane and chromatographed on acid-washed alumina. After a forerun of 1.5 g. of an oil (hexane eluent), 1.1 g. (11%) of the ketone VIII, m.p. 96°, was eluted with 25% benzene in hexane.

The hexane eluent (1.1 g.) showed an intense conjugated carbonyl peak in the infrared spectrum, but it could not be converted to a phenanthrene derivative. It readily formed an oily 2,4-dinitrophenylhydrazone derivative which solidified after chromatography, and from which, except for a small amount of the 2,4-dinitrophenylhydrazone of ketone VIII, no sharp melting product could be isolated. The analysis of the material that melted over a wide range corresponded to that of a ketone derived from reaction of the phenylcyclohexaneacetic acids with benzene (*cf.* XIII).

Anal. Calcd. for $C_{26}H_{26}N_4O_4$: C, 68.12; H, 5.67. Found: C, 67.65; H, 5.83.

The acidic material from the condensation amounted to 3 g. of a semi-solid material. Esterification of this acid followed by vacuum distillation gave 1 g. of ester corresponding to II (R = C_6H_5), identified by the formation of its characteristic amide, m.p. 193°. The rest of the material showed infrared absorption at $\lambda_{max.}$ 5.85 and 5.95 μ indicating that it was a ketoacid. Repeated purification through the sodium salt gave a creamy solid which had a neutralization equivalent roughly corresponding to the self-condensation product of phenylcyclohexylacetic acid (XVI). *Anal.* Calcd. for $C_{28}H_{34}O_3$: neut. equiv., 418. Found: neut. equiv., 398.



XVI

Condensation of the Lactone I with Naphthalene: Synthesis of the Isomeric β-Naphthylcyclohexaneacetic Acids (II, III, IV, R = β-$C_{10}H_7$).—To a mixture of 28 g. (0.2 mole) of the lactone I, 64 g. (0.5 mole) of naphthalene and 200 ml. of purified tetrachloroethane was added over 1 hr. at 0–5°, 29.2 g. (0.22 mole) of aluminum chloride. The dark red complex that formed was stirred at room temperature for 6 hours and then was warmed to 40–45° for 2 hours. The complex was decomposed by ice and hydrochloric acid and the aqueous layer was extracted with 200 ml. of benzene. The combined organic layers were washed with water and the acidic material was extracted with 10% sodium carbonate solution which was subsequently steam distilled to remove traces of naphthalene and tetrachloroethane. Acidification of the alkaline solution afforded 44 g. of solid acidic material which was converted to the methyl ester. Distillation of the ester gave 25 g. (45%) of isomeric methyl **β-naphthylcyclohexane acetates** as a colorless oil, b.p. 168–170° (0.05 mm.), $n^{30}D$ 1.5738.

Anal. Calcd. for $C_{19}H_{22}O_2$: C, 80.85; H, 7.80. Found: C, 80.64; H, 7.68.

The ultraviolet absorption spectrum of this ester ($\lambda_{max.}$ 225 mμ, log ϵ 4.92; 275 mμ, log ϵ 3.68; 304 mμ, log ϵ 2.66; 311 mμ, log ϵ 2.50 and 318 mμ, log ϵ 2.59) was identical to the spectrum of β-methylnaphthalene.[23a]

The rest of the material distilled above 210° (0.05 mm.) and yielded 10 g. of a highly viscous oil. Saponification followed by repeated purification through the sodium salt gave a colorless solid which softened at 100° and melted completely at 115°. Attempted crystallization of the solid from the usual solvents led to the separation of oil. However, the analysis of the solid was in good agreement with that required by the condensation of two moles of lactone with naphthalene.

Anal. Calcd. for $C_{26}H_{32}O_4$: C, 76.41; H, 7.90; neut. equiv., 204. Found: C, 75.81; H, 7.72; neut. equiv., 208.

Although this dimolecular condensation product was practically the exclusive result when equimolar ratios of lactone and naphthalene were used, the yield of the monomolecular condensation product could not be improved beyond 45% by using larger proportions of naphthalene or by varying the reaction conditions.

The first fraction consisting of 25 g. of isomeric esters was saponified to give 23.5 g. of a semi-solid acid mixture which was dissolved in benzene. The crystals that separated after one day (6 g., 11% based on lactone I) had m.p. 145–147°. After one crystallization from benzene and finally from methanol, the acid separated as stout colorless plates, m.p. 153–154°. It was identified as ***trans*-4-β-naphthylcyclohexaneacetic acid** (II, R = β-$C_{10}H_7$) by comparison with a synthetic specimen (see below).

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.60; H, 7.46. Found: C, 80.82; H, 7.51.

The amide crystallized from absolute ethanol as colorless plates, m.p. 234–235°. The mixed m.p. of this sample with the amide derived from the synthetic acid was 234–235°.

The benzene mother liquor after separation of the *trans*-*p*-acid II (R = β-$C_{10}H_7$) was diluted with hexane. The crystals that separated after several days (10.5 g., 20%) had m.p. 95–98°. After several crystallizations from benzene–hexane, the product had m.p. 105–106°. This material, as well as the uncrystallizable oil (7 g., 13%) from the combined mother liquors, had ultraviolet absorptions that were the same as II (R = β-$C_{10}H_7$), and they were shown by dehydrogenation and cyclization experiments to be the acid II (R = β-$C_{10}H_7$) contaminated with a small amount of *trans*-2-β-naphthylcyclohexaneacetic acid (IV, R = β-$C_{10}H_7$) and a relatively large amount of the *meta* isomer III (R = β-$C_{10}H_7$).

Dehydrogenation with Palladium. (a) The 145–147° Acid II (R = β-$C_{10}H_7$).—One gram of the methyl ester of the acid, m.p. 145–147°, was heated for 4 hours at 270–280° with 0.1 g. of 10% palladium-on-charcoal catalyst. The temperature then was raised slowly to 300° during one hour. The melt was extracted with ether, and removal of the solvent left 0.8 g. of an oil that readily solidified. It crystallized from hexane in stout needles, m.p. 94–95°, and was identified as **β-*p*-tolylnaphthalene** by comparison with a synthetic specimen.

(b) The 95–98° Acid.—One gram of the methyl ester of the acid, m.p. 95–98°, when dehydrogenated with 0.1 g. of 10% palladium-on-charcoal catalyst as above, gave 0.6 g. of a liquid hydrocarbon which was taken up in hexane and chromatographed on alumina. Elution with hexane gave 0.35 g. of a liquid hydrocarbon which possessed an ultraviolet absorption spectrum ($\lambda_{max}^{isooctane}$ 285 mμ, log ϵ 4.1;

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(23) (a) R. A. Friedel and M. Orchin, "Ultraviolet Absorption Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, Chart No. 197; (b) Chart No. 298; (c) Chart No. 464.

250 mμ, log ϵ 4.7) very similar to that of β-*p*-tolylnaphthalene and significantly different from β-*o*-tolylnaphthalene.[23b]

Anal. Calcd. for $C_{17}H_{14}$: C, 93.58; H, 6.42. Found: C, 93.38; H, 6.75.

The hydrocarbon is evidently β-*p*-tolylnaphthalene largely contaminated with β-*m*-tolylnaphthalene (IX, R = β-$C_{10}H_7$).

Elution of the chromatographic column with 10% benzene-in-hexane gave 0.15 g. of solid material which crystallized from hexane in needles, m.p. 95°. This was identified as β-*p*-tolylnaphthalene.

Dehydrogenation with Sulfur. (a) The 145–147° Acid.—One gram of the methyl ester of the acid, m.p. 145–147°, was heated to 220–230° for 4 hours with 0.4 g. of sulfur. The temperature then was raised gradually to 250° during 2 hours and the melt was cooled, taken up in benzene and boiled for a few minutes with copper powder to remove traces of sulfur. Removal of the solvent followed by saponification gave 0.5 g. of solid acidic material which crystallized from glacial acetic acid in fine needles, m.p. 185–186°, undepressed by admixture with an authentic sample (see synthesis below) of 4-β-naphthylphenylacetic acid (V, R = β-$C_{10}H_7$).

(b) **The 95–98° Acid.**—One gram of the methyl ester of the acid, m.p. 95–98°, when dehydrogenated by sulfur as described above, gave 0.2 g. of the acid, m.p. 185–186° (V, R = β-$C_{10}H_7$). From the acetic acid mother liquor another crop of crystals (0.1 g.) was isolated which, after several crystallizations from methanol, melted at 146°. It possessed an ultraviolet absorption spectrum ($\lambda_{max.}$ 287 and 251 mμ; log ϵ 4.2 and 4.72, respectively) identical to that of V (R = β-$C_{10}H_7$) and is evidently **3-β-naphthylphenylacetic acid** (X, R = β-$C_{10}H_7$), derived from the *meta* isomer III (R = β-$C_{10}H_7$).

Anal. Calcd. for $C_{18}H_{14}O_2$: C, 82.44; H, 5.34; neut. equiv., 262. Found: C, 82.34; H, 5.31; neut. equiv., 261.4.

The relative amounts of the *para* and *meta* isomers in the 95–98° acid were determined, as in the benzene case, by conversion to the amides.

Separation of the 95–98° Acid by Amide Formation.—One gram of the acid, m.p. 95–98°, after being freed of the *ortho* isomer by cyclization (described below) was converted to the amide (1 g.). Crystallization of the amide from absolute ethanol afforded 0.3 g. of the amide from the *para* isomer II (R = β-$C_{10}H_7$), m.p. 233–234°. The mother liquor, on dilution, gave another crop of crystals which after two crystallizations from aqueous methanol gave 0.4 g. of **3-β-naphthylcyclohexaneacetamide**, m.p. 145–146°, derived from the *meta* isomer III (R = β-$C_{10}H_7$).

Anal. Calcd. for $C_{18}H_{21}ON$: C, 80.90; H, 7.86; N, 5.24. Found: C, 80.75; H, 7.58; N, 5.21.

From these data, the relative amounts of the *para* and *meta* isomers were estimated as 43 and 57%, respectively.

Cyclization of the 95–98° Acid with Hydrogen Fluoride.—Ten grams (0.037 mole) of the acid was added slowly to 150 ml. of anhydrous hydrogen fluoride contained in a polyethylene bottle. The dark red solution was kept at 0° for 20 minutes and most of the hydrogen fluoride was allowed to evaporate in a current of air. The residue was poured into a concentrated solution of potassium carbonate. Extraction with ether gave 0.5 g. of neutral material which was taken up in hexane and chromatographed on alumina. Elution with 15% benzene in hexane gave 0.35 g. of an oily material which partly solidified. It crystallized from hexane in fine plates to give 0.22 g. of ***trans*-11-keto-1,2,3,4,-11,12,13,14-octahydrochrysene (XIV)**, m.p. 115–117°. Vacuum sublimation followed by crystallization from methanol gave the analytical sample as fine needles, m.p. 119–120°, lit.[17] m.p. 118–119°.

The 2,4-dinitrophenylhydrazone crystallized from a pyridine-alcohol mixture as deep red needles, m.p. 230–232°, lit.[17] m.p. 222–225°.

The alkaline solution on acidification gave 9 g. of acidic material which slowly solidified. Attempted separation of the components by fractional crystallization led to the formation of mixed crystals of acids II and III (R = β-$C_{10}H_7$).

Cyclization of 7 g. of the uncrystallizable oil from the condensation of lactone I and naphthalene with 100 ml. of anhydrous hydrogen fluoride as described above gave 2.5 g. of neutral material which was taken up in hexane and allowed to stand overnight. The crystals that separated (0.35 g.) had m.p. 140–145°. After one crystallization from benzene-hexane, pure **6-keto-1,2,3,4,4a,5,6,15-octahydrobenzo-[c]phenanthrene (XV)**, was obtained as clusters of needles, m.p. 154–155°; $\lambda_{max.}$ 342, 288, 276, 253; log ϵ 3.35, 3.91, 3.73 and 4.67, respectively.

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.40; H, 7.20. Found: C, 86.28; H, 7.35.

The 2,4-dinitrophenylhydrazone crystallized from benzene in deep red plates, m.p. 273° dec.

Anal. Calcd. for $C_{24}H_{22}O_4N_4$: N, 13.02. Found: N, 12.88.

The mother liquor, after separation of the ketone XV, was chromatographed on alumina. Elution with 15% benzene in hexane gave 0.9 g. of the ketochrysene XIV which, after crystallization from hexane, showed a m.p. of 119–120°. Elution with 25% benzene in hexane afforded an additional 50 mg. of ketone XV, m.p. 152–153°.

6-Hydroxy-1,2,3,4,4a,5,6,15-octahydrobenz[c]phenanthrene.—A solution of 0.25 g. (0.001 mole) of the ketone XV in 15 ml. of dry ether was added at room temperature to a slurry of 0.12 g. (0.003 mole) of lithium aluminum hydride in 15 ml. of dry ether. The mixture was heated under reflux for 2 hr., decomposed with water and dilute sulfuric acid and the ether evaporated. The residual solid crystallized from ethanol to give 0.2 g. (80%) of soft silky needles, m.p. 215–217°.

Anal. Calcd. for $C_{18}H_{20}O$: C, 85.71; H, 7.93. Found: C, 85.42; H, 7.97.

Dehydrogenation.—This alcohol (0.1 g.) was intimately mixed with 50 mg. of 10% palladium-on-charcoal catalyst and heated for 0.5 hr. to 300–320° and then for 1 hr. at 320–350°. Extraction of the melt with benzene followed by chromatography gave 50 mg. of liquid hydrocarbon which was converted to the picrate by warming with a methanolic solution of picric acid. The separated **picrate** had m.p. 122–124° and after one crystallization from methanol, it was obtained as vermilion needles, m.p. 126°, lit.[24] m.p. 126°.

The hydrocarbon, regenerated from the picrate by passing a benzene solution through a column of alumina, was obtained in the form of an oil which did not readily solidify. However, its characteristic ultraviolet absorption spectrum ($\lambda_{max.}$ 370, 348, 325, 313, 301, 280, 270, 229, 218 mμ) was the same as that reported for benzo[c]phenanthrene.[23c]

Reduction and Dehydrogenation of XIV.—When 0.25 g. of the ketone XIV was reduced with lithium aluminum hydride as described above for XV, there was obtained, in essentially quantitative yield, the corresponding alcohol. Without purification, this alcohol was simultaneously dehydrated and dehydrogenated at 320–350° to afford chrysene, m.p. 250–253°, identified by its characteristic ultraviolet absorption spectrum and by a mixed m.p. determination with an authentic specimen.

Condensation of the Lactone I with Naphthalene in the Presence of Hydrogen Fluoride.—The lactone (21 g., 0.15 mole) was added slowly, with frequent shaking, to a suspension of finely pulverized naphthalene in 250 ml. of anhydrous hydrogen fluoride contained in a polyethylene bottle and kept at 0°. The reaction mixture was held at 0° for 24 hr. and then at 15–18° for 24 hr. During this period it was necessary to shake the mixture occasionally to keep the organic phase in intimate contact with the acid. Excess hydrogen fluoride then was evaporated by a current of air and the concentrated residue was poured into a large volume of potassium carbonate solution. Extraction of the organic matter followed by concentration led to the separation of a large amount of naphthalene. The rest of the naphthalene was removed by distillation below 85° (0.5 mm.).

The neutral matter (15 g.) after removal of naphthalene showed infrared absorption peaks at 5.65 and 5.95 μ, indicating the presence of some unreacted lactone. Hydrolysis of this material by alcoholic potassium hydroxide followed by acidification of the alkaline filtrate and distillation of the semi-solid mass gave 8.5 g. of unreacted lactone. The remaining neutral material (2.5 g.) was chromatographed on alumina. Hexane eluted a small amount of naphthalene and elution with 15% benzene in hexane gave 1.1 g. of the

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(24) J. W. Cook, *J. Chem. Soc.*, 2524 (1931).

ketone XIV which partly solidified. It crystallized from hexane in fine needles, to give 0.8 g. of the ketone XIV, m.p. 116–118°.

Synthesis of β-*p*-Tolylnaphthalene. (a) **4-Methyl-1-β-naphthyl-Δ^1-cyclohexene.**—A solution of β-naphthyllithium (prepared according to Gilman and Moore[25] from 0.38 g. of lithium wire and 5.2 g. of β-bromonaphthalene in 20 ml. of dry ether) was added slowly with stirring, at ice temperature, to a solution of 2.8 g. of *p*-methylcyclohexanone in 20 ml. of ether. The reaction mixture was stirred at room temperature during 2 hr. and then heated under reflux for 1 hour. After decomposition with ice and dilute sulfuric acid the reaction mixture was thoroughly extracted with ether.

Removal of the solvent afforded 4.5 g. of crude material which was dehydrated by heating for one hour at 160–170° with 3 g. of powdered potassium bisulfate. Extraction from the inorganic material and then distillation gave a small forerun containing naphthalene and 2.5 g. of an oil, b.p. 145–150° (0.5 mm.), which slowly solidified. This solid was taken up in hexane and chromatographed on alumina. Elution with hexane gave a small amount of naphthalene and 2 g. of a colorless material which readily solidified. Crystallization from hexane yielded the cyclohexene derivative as fine needles, m.p. 65–66°.

Anal. Calcd. for $C_{17}H_{18}$: C, 91.89; H, 8.11. Found: C, 91.81; H, 8.05.

(b) **β-*p*-Tolylnaphthalene.**—One gram of the cyclohexene derivative was heated for 2 hr. at 320–330° with 0.1 g. of 10% palladium-on-charcoal catalyst. The product was extracted with ether and distillation of the residue, after removal of the solvent, gave 0.8 g. of material which readily solidified. It crystallized from hexane as stout needles, m.p. 94–95°. Recrystallization from methanol gave pure β-*p*-tolylnaphthalene as colorless needles, m.p. 96°; $\lambda_{max}^{isooctane}$ 287 mμ, log ε 4.12 and 251 mμ, log ε 4.71.

Anal. Calcd. for $C_{17}H_{14}$: C, 93.54; H, 6.46. Found: C, 93.50; H, 6.52.

Synthesis of *cis*- and *trans*-4-β-Naphthylcyclohexaneacetic Acid (II, R = β-$C_{10}H_7$). (a) **Cyclohexanone-4-acetic Acid.**—This was prepared from *p*-hydroxyphenylacetic acid essentially as described.[26] The yield of the keto acid was greatly improved by the use of bromine and magnesium hydroxide[27] as an oxidizing agent.

To a mechanically stirred solution of 15 g. (0.1 mole) of 4-hydroxycyclohexaneacetic acid in 75 ml. of 5 *N* sodium hydroxide solution was added slowly a hot solution of magnesium sulfate (40 g. of the heptahydrate in 30 ml. of water). The flask was cooled below 10° and stirring was continued while bromine (5.5 ml.) was added over a period of 1 hr. The reaction mixture was stirred at 10–15° for 6 hr. and allowed to stand overnight.

The solution then was acidified with 10 *N* sulfuric acid and an oily layer separated. The aqueous layer was concentrated on a steam-bath, extracted with ether and combined with the oil. Removal of the solvent left 12 g. of a sirup which distilled at 150° (0.1 mm.) to give 7.4 g. (50%) of a colorless, viscous oil which readily solidified. It crystallized from benzene in stout hexagonal plates, m.p. 68–70°, lit.[26] m.p. 67–68°.

The semicarbazone crystallized from methanol in needles, m.p. 176–177°, lit. m.p.[26] 175–176°.

Esterification of this acid by the usual methods led to the formation of a self-condensation product. However, it was esterified in 80% yield by refluxing the sodium salt with ethyl bromide in absolute ethanol for 10 hr. The ethyl ester had b.p. 95–96° (0.1 mm.).

Anal. Calcd. for $C_{10}H_{16}O_3$: C, 65.21; H, 8.70. Found: C, 65.05; H, 8.62.

(b) **1-β-Naphthyl-Δ^1-cyclohexene-4-acetic Acid.**—A solution of β-naphthylmagnesium bromide (prepared from 4.5 g. of β-bromonaphthalene and 0.52 g. of magnesium in 20 ml. of ether) was added slowly at −5° to a stirred solution of 3.8 g. of ethyl cyclohexanone-4-acetate in 20 ml. of dry ether. The yellow crystalline complex was stirred at 0° for 2 hr. and then the temperature was raised to 25° during 2 hr. The usual workup gave 5 g. of a semi-solid material which was dehydrated by heating for 0.5 hr. at 160–170° with 3 g. of powdered potassium bisulfate.

Extraction with ether and then distillation gave a forerun (2 g.) distilling below 100° (0.1 mm.) consisting of unreacted keto ester and a small amount of naphthalene from which 1.5 g. of the keto ester was recovered by chromatography. The second fraction distilled at 170–190° (0.1 mm.) as semi-solid mass (1.5 g.). Saponification of this material by alcoholic potassium hydroxide solution gave 0.3 g. of neutral material which, after crystallization from benzene, melted at 181–182° and was identified as β,β-dinaphthyl. The alkaline solution on acidification gave 0.9 g. of the desired acid which crystallized from methanol in colorless plates, m.p. 140–141°.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.20; H, 6.76. Found: C, 81.10; H, 6.86.

(c) ***cis*- and *trans*-4-β-Naphthylcyclohexaneacetic Acid** (II, R = β-$C_{10}H_7$).—At atmospheric pressure, 0.53 g. (0.002 mole) of the unsaturated acid described above, dissolved in 15 ml. of absolute ethanol, was reduced in the presence of 0.1 g. of 5% palladium-on-charcoal catalyst. About 90% of the theoretical amount of hydrogen was absorbed in the course of 15 min. After an hour at room temperature, the solution was filtered and concentrated. The last trace of ethanol was removed by azeotropic distillation with benzene. The benzene solution was concentrated, diluted with a little hexane and allowed to stand overnight, during which time the *cis*-acid separated as crystals, m.p. 135–142°. After two crystallizations from benzene, 0.25 g. of pure ***cis*-acid** was obtained as stout colorless needles, m.p. 151–152°; $\lambda_{max.}$ 318, 311, 304, 275, 226 mμ; log ε 2.58, 2.41, 2.64, 3.69, 5.09, respectively.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.60; H, 7.46. Found: C, 80.73; H, 7.56.

The amide crystallized from aqueous ethanol as fine plates, m.p. 198–199°.

Anal. Calcd. for $C_{18}H_{21}ON$: C, 80.90; H, 7.86; N, 5.24. Found: C, 80.75; H, 7.62; N, 5.13.

The benzene mother liquors were combined and diluted with hexane. The separated crystals, after several recrystallizations from a benzene–hexane mixture and finally from ethanol, gave 50 mg. of pure ***trans*-acid** as fine colorless plates, m.p. 153–154°; $\lambda_{max.}$ 318, 311, 304, 275, 226 mμ; log ε 2.65, 2.48, 2.71, 3.70 and 5.16, respectively. The mixed m.p. with the *cis*-acid was depressed.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.60; H, 7.46. Found: C, 80.56; H, 7.52.

The amide crystallized from absolute ethanol as colorless plates, m.p. 233–234°.

Anal. Calcd. for $C_{18}H_{21}ON$: C, 80.90; H, 7.86; N, 5.24. Found: C, 80.68; H, 7.78; N, 5.08.

4-β-Naphthylphenylacetic Acid (V, R = β-$C_{10}H_7$).—The methyl ester (0.5 g.) of 1-β-naphthyl-Δ^1-cyclohexene-4-acetic acid was dehydrogenated by heating for 4 hr. at 220–230° with 0.25 g. of powdered sulfur and then at 230–250° for 1 hour. This melt was taken up in benzene and excess sulfur was removed by warming with copper powder. Removal of the solvent and then saponification of the oily residue gave 0.25 g. of solid acid which crystallized from glacial acetic acid in fine needles, m.p. 186–187°.

Anal. Calcd. for $C_{18}H_{14}O_2$: C, 82.44; H, 5.34. Found: C, 82.21; H, 5.15.

The amide crystallized from absolute ethanol as fine plates, m.p. 258°.

Anal. Calcd. for $C_{18}H_{15}ON$: C, 82.76; H, 5.74. Found: C, 82.54; H, 5.82.

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(25) H. Gilman and T. Moore, THIS JOURNAL, **62**, 1843 (1940).

(26) H. E. Ungnade and F. V. Morriss, *ibid.*, **70**, 1898 (1948).

(27) J. A. McRae, E. H. Charlesworth and D. S. Alexander, *Can. J. Research*, **21B**, 6 (1943).