bon was obtained by reduction of the radical with sodium and boiling amyl alcohol.

An excess of a carbon tetrachloride solution of chlorine decolorized the radical after 30 minutes; hydrogen chloride was evolved and no crystalline product could be isolated. When the radical (0.5 g.) in 20 ml. of carbon tetrachloride was mixed with 0.2 g. of bromine and allowed to stand for 12 hours, the color became noticeably lighter. Distillation of the solvent at room temperature left a brown gum which was partly dissolved by 35 ml. of boiling alcohol. Cooling this solution gave 0.15 g. of α,γ-bisdiphenylene-β-phenylallyl ethyl ether.

A solution of 0.4 g. of the radical in 25 ml. of benzene was boiled for 6 hours while a stream of oxygen was passed through. The solution was then distilled to a small volume and cooled, giving 0.1 g. of unchanged radical. No other crystalline substance could be isolated.

A hot solution of 0.5 g. of the radical in 25 ml. of acetic acid was treated with 1 g. of chromic acid in a little water. After the vigorous reaction was over the solution was boiled for five minutes. There was obtained 0.1 g. of benzoic acid and 0.3 g. of steam distilled fluorenone.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON UNIVERSITY]

The Cyclodehydration of 2-(γ-Phenylpropyl)-cycloheptanone[1,2]

BY C. DAVID GUTSCHE, N. N. SAHA[3] AND HERBERT E. JOHNSON

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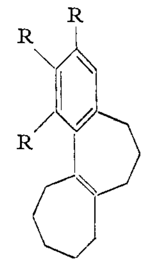
The cyclodehydration of 2-(γ-phenylpropyl)-cycloheptanone has been found to give, instead of the expected olefin Ia, a mixture containing 1-cyclohexyltetralin, 2-cyclohexyltetralin, 1-cyclohexylnaphthalene, 2-cyclohexylnaphthalene and other unidentified products. These materials were characterized by isolation from the cyclization mixture followed by comparison with authentic samples, the syntheses for which are described.

The work described in this communication had its inception in an attempt to synthesize octahydrodemethoxydeoxydeacetamidocolchicine (Ib)[4] by cyclization of 2-[(γ-3′,4′,5′-trimethoxyphenyl)-propyl]-cycloheptanone (IVb). The reaction, however, did not take the desired course. In the hope of elucidating the actual events, the same reaction with the un-methoxylated analog IVa was investigated in considerable detail.



Ia, R = H
Ib, R = OCH_3

The ketones IVa and IVb were prepared in 60 and 68% over-all yield, respectively, from the corresponding γ-arylbutylamines IIa and IIb by cathylation to IIIa and IIIb followed by nitrosation and treatment with cyclohexanone under the usual ring-enlargement conditions.[5] In view of the known efficacy of polyphosphoric acid as a cyclizing agent for systems containing methoxyl groups,[6] this was the reagent of choice in the case of IVb and, for comparative purposes, in the case of IVa also. In both instances, somewhat more strenuous conditions than are usually employed were necessary to effect complete disappearance of the ketone, and it is this fact which may be responsible for the wayward course of the cyclization. Ketone IVb required contact with polyphosphoric acid at 125° for 30 minutes; ketone IVa required contact with polyphosphoric acid at 100° for 24 hr. or 200° for 2.5 hr. In each case a volatile fraction (30–45%) was obtained which boiled in the range expected for the cyclodehydration product. It is these materials, principally that derived from IVa, which is the subject of this discussion.

The cyclization product from IVb consisted of an oil possessing an analysis in approximate agreement with a $C_{19}H_{26}O_3$ formula (although a methoxyl determination indicated some demethylation). The ultraviolet spectrum, however, showed strong absorption bands at 235 mμ 41,500) and 278 mμ (5000) with a minimum at 254 mμ (3580), whereas Ib has a maximum at 254 mμ (7760) and a minimum at 243 mμ (6030).[4] Similarly, the cyclization product from IVa consisted of an oil possessing an analysis in close agreement with a $C_{16}H_{20}$ formula but an ultraviolet spectrum quite different from that expected for Ia.[7]

Cyclization into the benzene nucleus was indicated by the infrared spectrum of the product from IVa which showed a pattern of bands in the 1650–2000 cm.$^{-1}$ region characteristic of 1,2-disubstituted benzenes.[8] The virtual absence of an olefinic linkage in the product was indicated by the

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[1] This work was supported, in part, by: (a) a grant-in-aid from the American Cancer Society upon recommendation of the Committee on Growth of the National Research Council, and (b) a grant-in-aid from the National Science Foundation.

[2] A preliminary account of this work was presented at the 126th Meeting of the American Chemical Society, New York, N. Y., 1954, Abstracts, p. 33-O.

[3] Postdoctoral research associate, 1955–1956.

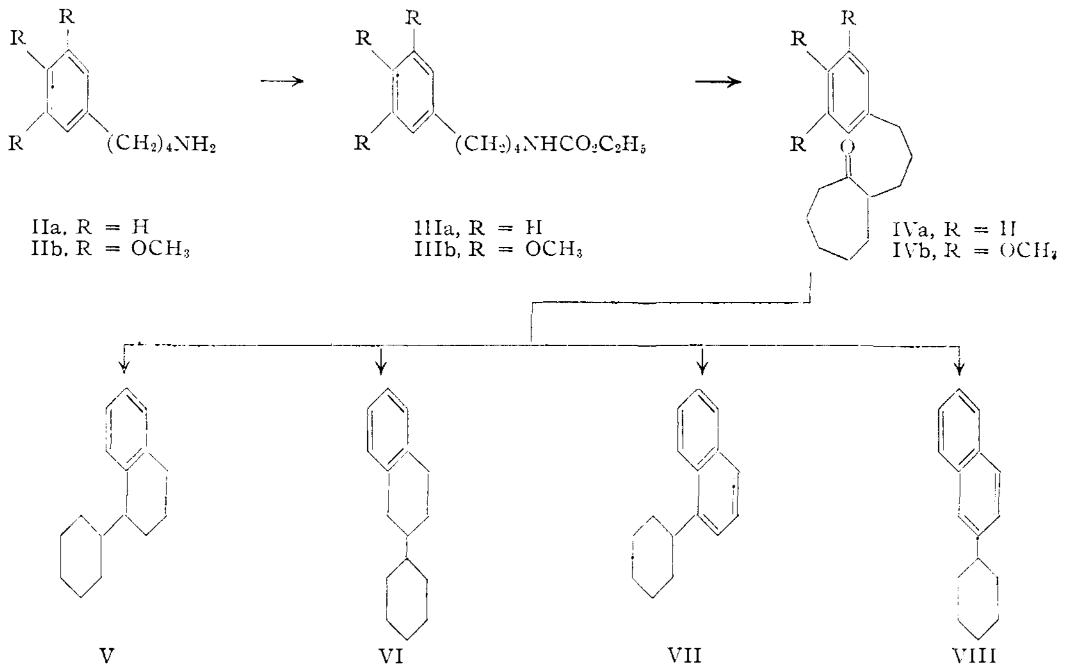
[4] H. Rapoport, A. R. Williams, J. E. Campion and D. E. Pack, THIS JOURNAL, **76**, 3693 (1954).

[5] C. D. Gutsche, "Organic Reactions," Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 364.

[6] *Cf.* for example, A. Koebner and R. Robinson, *J. Chem. Soc.*, 1994 (1938); W. E. Bachmann and W. J. Horton, THIS JOURNAL, **69**, 58 (1947); R. C. Gilmore and W. J. Horton, *ibid.*, **73**, 1411 (1951); J. Koo, *ibid.*, **75**, 1891 (1953).

[7] Compounds containing a double bond in conjugation with a phenyl group ordinarily have an absorption maximum in the 245–265 mμ region. Thus, styrene has a maximum at 245 mμ (16,000)—M. Pestemer and L. Willigut, *Monatsh.*, **66**, 119 (1935); 2-phenylcyclohexene has a maximum at 247 mμ (12,000)—A. C. Cope, F. S. Fawcett and G. Munn, THIS JOURNAL, **72**, 3399 (1950); 1,2-dihydronaphthalene has a maximum at 262 mμ (10,000)—R. A. Morton and A. J. A. de Gouveia, *J. Chem. Soc.*, 916 (1934). The cyclization product from IVa has maxima at 218 mμ (13,800), 224 mμ (30,000), 268 mμ (1820) and 274 mμ (1900).

[8] C. W. Young, R. B. DuVall and N. Wright, *Anal. Chem.*, **23**, 709 (1951).



IIa, R = H
IIb, R = OCH_3

IIIa, R = H
IIIb, R = OCH_3

IVa, R = H
IVb, R = OCH_3

V VI VII VIII

failure to absorb hydrogen in the presence of a palladium catalyst and by the failure to react with potassium permanganate, nitrosyl chloride, ozone or perbenzoic acid.[9] At first, these facts were difficult to reconcile with a $C_{16}H_{20}$ formula. It was eventually ascertained, however that the cyclization product is not a single entity but a mixture of at least five compounds including 1-cyclohexyltetralin (V), 2-cyclohexyltetralin (VI), 1-cyclohexylnaphthalene (VII) and 2-cyclohexylnaphthalene (VIII).[10] The evidence for this conclusion is detailed in the following section.

Identification of 1-Cyclohexyltetralin (V).—When the cyclization product from IVa was fractionated, either by distillation through a spinning band column or by chromatography on alumina, a lower-boiling, less strongly adsorbed material was obtained which had an analysis in close agreement with a $C_{16}H_{22}$ formula. The infrared spectrum of this compound was characteristic of a 1,2-disubstituted benzene derivative,[8] and the ultraviolet spectrum showed only the bands characteristic of the phenyl nucleus. When dehydrogenated with 10% palladium-on-charcoal, 1-phenylnaphthalene was produced, suggesting that the $C_{16}H_{22}$ compound is 1-cyclohexyltetralin. However, since migration of phenyl groups between the 1- and 2-positions of naphthalene is known to occur[11] and since even more drastic events are known to take place under conditions of dehydrogenation,[12] a more secure identification was sought through comparison with the product from an unequivocal synthesis of 1-cyclohexyltetralin. Hexahydrobenzophenone (IX) was subjected to a Reformatsky reaction with ethyl α-bromoacetate, and the resulting hydroxy ester was dehydrated, hydrolyzed and reduced to the acid X. An Arndt–Eistert sequence applied to X yielded XI[13] which was then cyclized to 4-cyclohexyltetralone-1 (XII). Removal of the keto group of XII yielded 1-cyclohexyltetralin (V) in 41% over-all yield from IX. The infrared and ultraviolet spectra of the authentic sample of V were identical with those of the sample obtained from the cyclization product of IVa. Further identification was obtained through a comparison of the 2,4-dinitrophenylhydrazones (two isomers formed) of the acetyl derivative of authentic V and that derived from IVa.

Identification of 2-Cyclohexyltetralin (VI).—When the cyclization product from IVa was fractionated by chromatography on alumina, a material was obtained in exceedingly small amount which had an infrared spectrum different from that of 1-cyclohexyltetralin and almost identical with that of 2-cyclohexyltetralin (VI). An authentic sample of VI was prepared from cyclohexylsuccinic anhydride by condensation with benzene followed by reduction to XIX and XVI, cyclization to 2-cyclohexyltetralone-1 (XIX) and 3-cyclohexyltetralone-1 (XVII) and reduction to 2-cyclohexyltetralin (VI). The structural assignment of XIX and XVI is based on the premise that mono-alkyl-substituted succinic anhydrides usually react with benzene to yield the α-alkyl-β-benzoylpropionic

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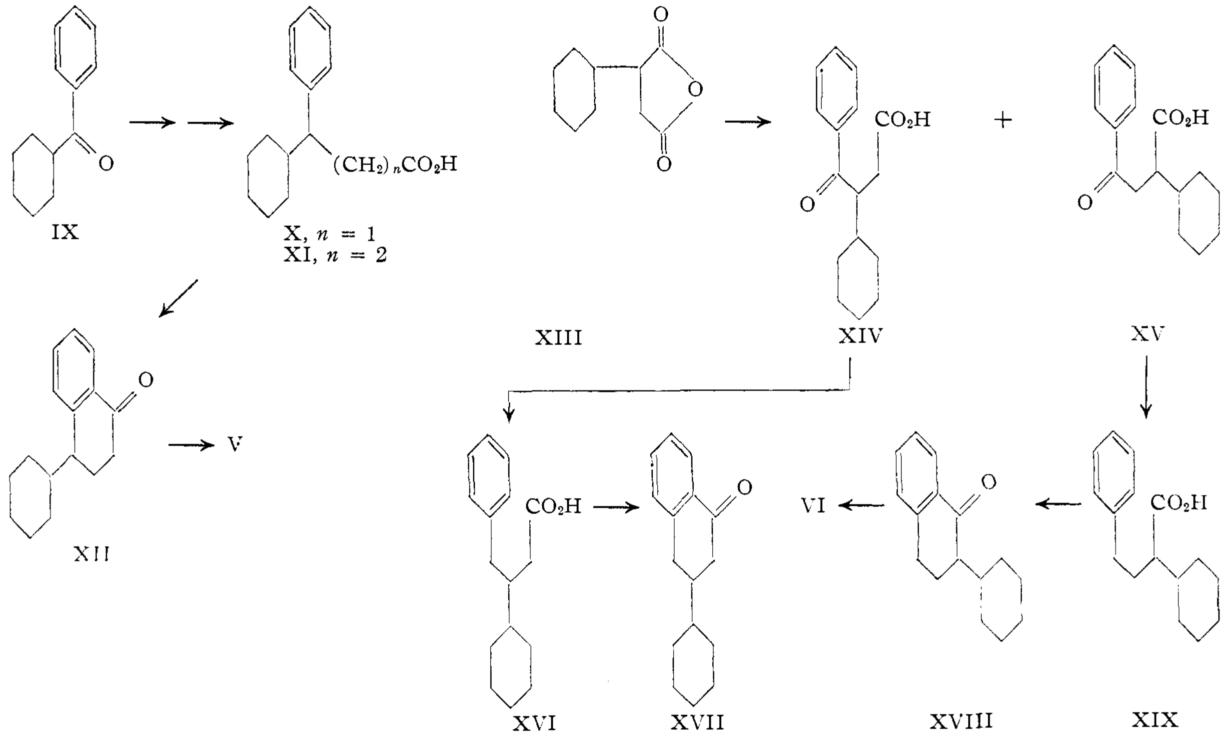
[9] Ozone and perbenzoic acid, however, were not completely without action. Ozonolysis produced a very small amount of carbonyl-containing material, and perbenzoic acid oxidation showed a 25% consumption of oxidant in 24 hr. and another 25% in 14 days.

[10] In addition to these four compounds, an unidentified solid was isolated in small quantity. It had an analysis compatible with a $C_{16}H_{16}$ formula and an ultraviolet spectrum very similar to that of a naphthalene but shifted somewhat to the visible. Dehydrogenation yielded a hydrocarbon with a $C_{16}H_{12}$ or a $C_{16}H_{10}$ formula.

[11] F. Mayer and R. Schiffner, *Ber.*, **67**, 67 (1934).

[12] P. A. Plattner in "Newer Methods of Preparative Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1948, pp. 36–51.

[13] An alternate synthesis of XI from IX was attempted *via* the Stobbe condensation. Difficulties were encountered, however, (*cf.* Experimental section) and the route was abandoned. Also attempted was the condensation of cyclohexylmagnesium bromide and α-tetralone as reported by J. W. Cook and C. A. Lawrence, *J. Chem. Soc.*, 1434 (1936). 1-Cyclohexyl-3,4-dihydronaphthalene was formed in low yield (Cook and Lawrence do not report a yield) and was contaminated with difficultly separable starting ketone.



acid in larger amount.[14] Thus, the higher-melting product from XIII and benzene, obtained in 73% yield, is assigned structure XV; the lower-melting product, obtained in 13% yield, is assigned structure XIV. 2-Cyclohexyltetralin, like the 1-isomer, forms two 2,4-dinitrophenylhydrazones of the acetyl derivative.

Identification of 1-Cyclohexylnaphthalene (VII).—From one of the middle fractions obtained from the distillation of the product from IVa 1-cyclohexylnaphthalene (VII) could be isolated *via* the picrate. Authentic VII was prepared by controlled dehydrogenation of 1-cyclohexyltetralin.

Identification of 2-Cyclohexylnaphthalene (VIII). When the cyclization product from IVa was fractionated, either by distillation through a spinning band column or by chromatography on alumina, a higher-boiling, more strongly adsorbed material was obtained which had an analysis in close agreement with a $C_{16}H_{18}$ formula. The ultraviolet spectrum of this fraction was identical with that of authentic VIII, it formed a trinitrobenzene complex which gave no depression in m.p. when admixed with the trinitrobenzene complex of authentic VIII, and it could be dehydrogenated to 2-phenylnaphthalene. Authentic VIII was prepared by reduction of 2-cyclohexenylnaphthalene, obtained from 2-naphthylmagnesium bromide and cyclohexanone.[15]

No accurate quantitative data as to the relative amounts of V, VI, VII and VIII present in the mixture were obtained. However, on the basis of the ultraviolet spectrum of the crude material, the yields of dehydrogenation products and the yields from chromatographic separation, it appears that the mixture contains *ca.* 65% of V, 25% of VIII and 10% of VI, VII and unidentified products.[16]

Discussion of Results

The rearrangement of alicyclic rings under the influence of various catalysts is a well-known and extensively-studied phenomenon. For instance, Pines, *et al.*,[17] have found that cycloheptanol reacts with benzene under the influence of aluminum chloride or sulfuric acid to give a mixture containing appreciable amounts of methylphenylcyclohexanes. In the course of the present work an intramolecular counterpart to this reaction was discovered when it was found that the alcohol XX yields 1-cyclohexyltetralin (V) under the influence of Friedel–Crafts catalysts.[18] This conversion

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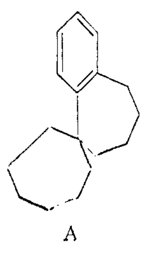
[14] E. Berliner, "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 242.

[15] F. Bergmann and E. Bergmann, THIS JOURNAL, **62**, 1699 (1940).

[16] These figures apply only to the volatile portion of the product (30–45%). The non-volatile portion has not been investigated.

[17] H. Pines, A. Edeleanu and V. N. Ipatieff, THIS JOURNAL, **67**, 2193 (1945).

[18] The product from XX contains other materials in addition to V, possibly the spiran A which, on the basis of other published data (*cf.* R. O. Roblin, D. Davidson and M. T. Bogert, *ibid.*, **57**, 151 (1935); R. A. Barnes, *ibid.*, **76**, 3004 (1953)) would be expected to be the major product. On the basis of the infrared and ultraviolet spectra of the product and on the basis of its dehydrogenation products, 2-cyclohexyltetralin does not appear to be present.



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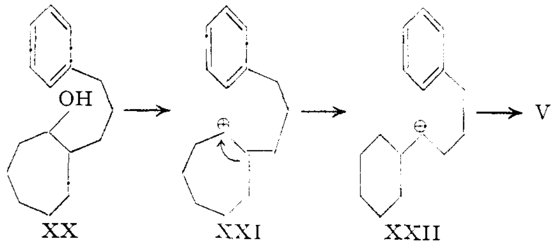
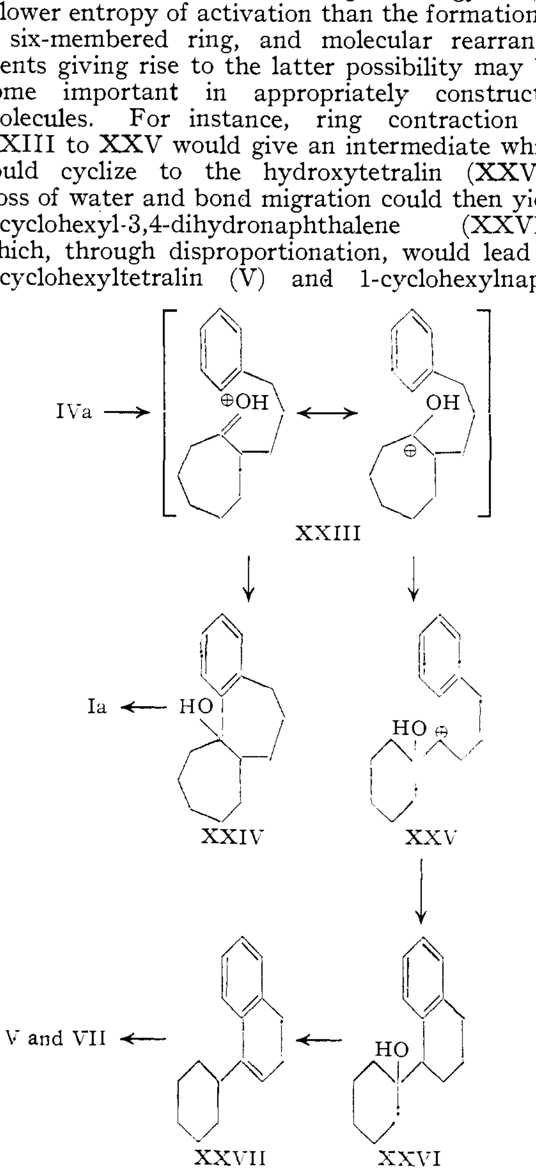
can be rationalized as



A similar rationalization can be invoked to explain the formation of 1-cyclohexyltetralin and 1-cyclohexylnaphthalene from IVa. Addition of a proton to IVa would give the cation XXIII which, although more stable and less reactive than an oxonium ion derived from an alcohol (*e.g.*, the intermediate between XX and XXI), has several possibilities for further reaction. Direct cyclization would yield the alcohol XXIV and from it the olefin Ia. The formation of a seven-membered ring, however, is a process with a higher energy and/or a lower entropy of activation than the formation of a six-membered ring, and molecular rearrangements giving rise to the latter possibility may become important in appropriately constructed molecules. For instance, ring contraction of XXIII to XXV would give an intermediate which could cyclize to the hydroxytetralin (XXVI). Loss of water and bond migration could then yield 1-cyclohexyl-3,4-dihydronaphthalene (XXVII) which, through disproportionation, would lead to 1-cyclohexyltetralin (V) and 1-cyclohexylnaphthalene (VII). Failure to find equivalent amounts of V and VII might indicate a more obscure mechanism, but in any event there is ample precedent for hydrogen transfer reactions under comparable conditions, particularly from the work of Pines, Ipatieff and co-workers.[19,20] A rationalization for the formation of 2-cyclohexyltetralin and 2-cyclohexylnaphthalene is less obvious, and speculation on this point has not been particularly productive.



Although cyclodehydration reactions have been extensively studied in certain series,[21] there are only a few examples of reactions analogous to the one under discussion, and all but one of these involve cyclodehydration to form six-membered rings.[22] The one exception is the attempt by Nunn and Rapson[23] to effect the cyclization of 2-[γ-(p-methoxyphenyl)-propyl]-cyclopentanone with phosphorus pentoxide in refluxing xylene. The cyclization required 50 hr., and the product, obtained in 32% yield, consisted of an oil with the correct analysis for $C_{15}H_{18}O$ but with properties different from those expected. It is probable that their product has a structure resulting from molecular rearrangements. Similarly, it is supposed that the material resulting from the cyclization of IVb contains products of molecular rearrangement, probably cyclohexyltrimethoxytetralins and cyclohexyltrimethoxynaphthalenes.

Experimental[24–26]

2-Arylcycloalkanones (IV). γ-(3,4,5-Trimethoxyphenyl)-butyronitrile.—Following a previously described procedure[27] a mixture of 53.0 g. (0.217 mole) of 1-chloro-3-(3′,4′,5′-trimethoxyphenyl)-propane (b.p. 135–144° (0.5 mm.); $n^{25}D$ 1.5305), 31.8 g. (0.49 mole) of potassium cyanide, 1.5 g. of potassium iodide, 210 ml. of 95% ethanol and 80 ml. of water was refluxed for 14 hr. The reaction mixture was then concentrated to half of its original volume, poured into 400 ml. of water and worked up in the usual fashion to yield 45.0 g. (88%) of a colorless liquid with b.p. 150–160° (mainly 156°) at 0.4 mm., $n^{25}D$ 1.5263. A middle cut was taken for analysis.

Anal. Calcd. for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28. Found: C, 66.75; H. 7.31.

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[19] C. Mentzer and Dat Xuong, *Bull. soc. chim. France*, 885 (1947), found that anisole and cyclohexanone react in the presence of aluminum chloride to give a mixture of p-methoxyphenylcyclohexene and p-methoxyphenylcyclohexane, the latter apparently predominating. R. F. Evans and J. C. Smith, *J. Chem. Soc.*, 798 (1954), have described a reaction in which a compound of the dihydronaphthalene type undergoes disproportionation in the presence of polyphosphoric acid.

[20] H. Pines, A. Weizmann and V. N. Ipatieff, This Journal, **70**, 3589 (1948); V. N. Ipatieff, H. Pines and R. C. Olberg, *ibid.*, **70**, 2123 (1948); R. C. Olberg and V. N. Ipatieff, *ibid.*, **74**, 4872 (1952).

[21] *Cf.* C. K. Bradsher, *Chem. Revs.*, **38**, 447 (1938), for a review of cyclodehydration reactions leading to aromatic systems. *Cf.* E. C. Horning and J. Koo, This Journal, **73**, 5830 (1951), for a recent and typical example of the Bougault type of cyclodehydration (J. Bougault, *Compt. rend.*, **159**, 745 (1915)).

[22] H. France, S. H. Tucker and J. Forrest, *J. Chem. Soc.*, 7 (1945); J. Colonge and F. Collomb, *Bull. soc. chim. France*, 285 (1951).

[23] J. R. Nunn and W. S. Rapson, *J. Chem. Soc.*, 1051 (1951).

[24] All melting points are corrected; all boiling points are uncorrected.

[25] The microanalyses were performed by Mrs. Charlotte Thompson, Washington University, and by Drs. Weiler and Strauss, Oxford, England.

[26] The ultraviolet spectra were determined with a Beckman model DU spectrophotometer and a Cary recording spectrophotometer; the infrared spectra were determined with a Perkin-Elmer model 21 spectrophotometer.

[27] H. Rapoport and J. E. Campion, This Journal, **73**, 2239 (1951).

δ-(3,4,5-Trimethoxyphenyl)-butylamine (IIb).—A solution of 45.0 g. of γ-(3,4,5-trimethoxyphenyl)-butyronitrile in 250 ml. of ethanol and 60 ml. of 28% ammonium hydroxide was treated with 3 half-teaspoonsful of Raney nickel and hydrogenated at 2.5 atmospheres in a Parr-type apparatus. After 5 hr. the uptake of hydrogen ceased, and the reaction mixture was worked up to yield 38.5 g. (84%) of a colorless liquid with b.p. 137–139° (0.3 mm.), $n^{25}\text{D}$ 1.5292. A lithium aluminum hydride reduction of the nitrile resulted in only a 51% yield of the amine.

Anal. Calcd. for $C_{13}H_{21}NO_3$: C, 65.24; H, 8.85. Found: C, 65.65; H, 8.79.

The picrate of IIc was obtained as yellow-green needles after several recrystallizations from hot water; m.p. 172–173°.

Anal. Calcd. for $C_{19}H_{24}N_4O_{10}$: C, 48.72; H, 5.16. Found: C, 48.76; H, 5.11.

Ethyl N-[δ-(3,4,5-Trimethoxyphenyl)-butyl]-carbamate (IIIb).—Using previously described procedures,[28] 51.6 g. of the amine IIb was converted with ethyl chlorocarbonate at 0–5° to 67.0 g. (100%) of a viscous, colorless liquid with $n^{25}\text{D}$ 1.5150.

Anal. Calcd. for $C_{16}H_{25}NO_5$: C, 61.61; H, 8.09. Found: C, 61.73; H, 8.28.

2-[γ-(3′,4′,5′-Trimethoxyphenyl)-propyl]-cycloheptanone (IVb).—Ethyl N-nitroso-N-[δ-(3,4,5-trimethoxyphenyl)-butyl]-carbamate was obtained in 98% yield by nitrosation of IIIb at 15–20° for 6 hr. using standard procedures.[29] In a 500-ml. three-necked flask fitted with a dropping funnel and a stirrer was placed 30 g. (0.306 mole) of cyclohexanone, 80 ml. of absolute methanol and 5 g. of finely powdered potassium carbonate. The flask was placed in a water-bath maintained at 25°, and to the stirred mixture was added 67.0 g. (0.212 mole) of the nitroso compound over a period of 45 minutes. The yellowish mixture was allowed to stand at room temperature for 4 hr. and was then filtered. The filtrate was evaporated by heating under reduced pressure, and the residue was distilled to give 41.6 g. (62%) of a yellow liquid with b.p. 190–220° (0.5–1.5 mm.). Redistillation gave 36.0 g. (54%) of almost colorless product, b.p. 172–175° (0.2 mm.), $n^{25}\text{D}$ 1.5286.

Anal. Calcd. for $C_{19}H_{28}O_4$: C, 71.22; H, 8.81. Found: C, 71.05; H, 8.59.

The 2,4-dinitrophenylhydrazone of IVb was obtained as dull red needles from petroleum ether (b.p. 63–69°), m.p. 140–141°.

Anal. Calcd. for $C_{25}H_{32}N_4O_7$: C, 59.99; H, 6.44. Found: C, 60.13; H, 6.45.

Ethyl N-(δ-Phenylbutyl)-carbamate (IIIa).—Using previously described procedures, 49.0 g. of δ-phenylbutylamine (IIIa) (prepared by catalytic reduction of γ-phenylbutyronitrile) was converted to 66.3 g. (91%) of IIIa, obtained as a colorless liquid, b.p. 120–122° (0.2 mm.), n^{25}_{D} 1.5060.

Anal. Calcd. for $C_{13}H_{19}NO_2$: C, 70.55; H, 8.65. Found: C, 70.34; H, 8.81.

2-(γ-Phenylpropyl)-cycloheptanone (IVa).—Ethyl N-nitroso-N-(δ-phenylbutyl)-carbamate was obtained in 100% yield by nitrosation of IIIa at 18–25° for 5.5 hr. using standard procedures. A 73.0-g. sample of the nitroso compound was treated with 40 g. of cyclohexanone, 100 ml. of methanol and 10 g. of potassium carbonate as described above to yield 50.6 g. (74.5%) of a colorless liquid with b.p. 124–125°(0.3 mm.), $n^{25}\text{D}$ 1.5212.

Anal. Calcd. for $C_{16}H_{22}O$: C, 83.43, H, 9.63; N, 0.00. Found: C, 83.64; H, 9.63; N, 0.00.

The 2,4-dinitrophenylhydrazone of IVa was obtained as bright orange needles from ethanol; m.p. 120–121°.

Anal. Calcd. for $C_{22}H_{26}N_4O_4$: C, 64.37; H, 6.39. Found: C, 64.65; H, 6.18.

Redistillation of the forerun obtained in the preparation of IVa gave a colorless liquid with b.p. 55°(0.3 mm.), $n^{25}\text{D}$ 1.4917. This material appears to be **ethyl δ-phenylbutyl ether.**

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.92; H, 9.82.

Polyphosphoric Acid Cyclizations. Cyclization of 2-[γ-(3′,4′,5′-Trimethoxyphenyl)-propyl]-cycloheptanone (IVb).—The polyphosphoric acid was prepared by dissolving, with heating, 40 g. of phosphorus pentoxide in 25 ml. of 85% phosphoric acid.[6] A 2.00-g. sample of IVb was treated with 30 ml. of polyphosphoric acid and was heated, with swirling, for 30 minutes at 120–130°. The brownish-red mixture was poured onto chopped ice and allowed to stand overnight. The organic material was then extracted into ether, the ether solution was dried and the ether was evaporated to leave a yellow residue. The residue was taken up in petroleum ether (b.p. 63–69°) and passed through a column of alumina. The fraction removed with petroleum ether–benzene (1:10) was distilled to give 0.56 g. (30%) of an oil, b.p. 160–163° (0.1 mm.), $n^{25}\text{D}$ 1.5713; $\lambda_{\text{max}}^{\text{EtOH}}$ mμ (ε): 235 (37,700), 278 (5350); $\lambda_{\text{min}}^{\text{EtOH}}$ (ε): 254 mμ (3280); $\bar{\gamma}_{\text{max}}^{\text{liquid}}$ in cm.$^{-1}$: 707, 738, 760, 782, 838, 878, 922, 943, 969, 1003, 1042, 1065, 1097, 1121, 1146, 1158, 1190, 1227, 1248, 1280, 1324, 1350, 1390, 1421, 1445, 1490, 1602, 2630, 2810, 2880, 3460(weak) and 4300.

Anal. Calcd. for $C_{19}H_{26}O_3$: C, 75.46; H, 8.67; CH_3O, 30.7. Found: C, 76.75; H, 8.85; CH_3O, 25.3.

Cyclization of 2-(γ-Phenylpropyl)-cycloheptanone (IVa).—A mixture of 75 g. of IVa and 900 ml. of polyphosphoric acid was heated with stirring for 2.5 hr. at 200°. The product was distilled in a Claisen flask and yielded 1.8 g. of naphthalene[30] as a forerun and 31 g. (45%) of material with b.p. 109–126° (0.4 mm.); $\lambda_{\text{max}}^{\text{EtOH}}$ mμ (ε): 218 (13,800), 224 (30,000), 268 (1820), 274 (1900). A second distillation through a Claisen flask of a 4-g. sample of this material gave 2.6 g. of a colorless oil, b.p. 96–98° (0.2 mm.), $n^{25}\text{D}$ 1.5548.

Anal. Calcd. for $C_{16}H_{20}$: C, 90.50; H, 9.50. Found: C, 90.61; H, 9.82.

The remaining 27 g. of material was distilled through a Piros–Glover spinning band column, and 25 fractions were collected at arbitrary intervals. These could be roughly classified into four groups: (a) fractions 5–10 containing 7.5 g. with b.p. 104–108° (0.7 mm.), $n^{25}\text{D}$ 1.5490–1.5510; (b) fractions 17–20 containing 4.2 g. with b.p. 115–117° (0.8 mm.), $n^{25}\text{D}$ 1.5600–1.5810; (c) fractions 23–24 containing 2.9 g. with b.p. 124–126° (0.8 mm.), $n^{25}\text{D}$ 1.5970–1.5980; (d) fraction 25 containing 2.3 g. with b.p. 127–128° (0.3 mm.), $n^{25}\text{D}$ 1.6215. Further information on these fractions is given in succeeding sections of the Experimental section.

From another comparable experiment, a 3.91-g. sample of once-distilled material was subjected to chromatographic separation on a column 2 cm. × 30 cm. containing 173 g. of alumina (Fisher adsorption grade). The column was eluted with petroleum ether (b.p. 63–69°), and 45 fractions of 15 ml. each were collected. These could be classified into three groups: (a) fractions 8–18 containing 2.80 g., $n^{25}\text{D}$ 1.5490; (b) fraction 20 containing 0.03 g.; (c) fractions 27–45 containing 0.37 g., $n^{25}\text{D}$ 1.5980.

Cyclization also could be effected by heating for longer periods at 100°. A reaction carried out at 100° for 2.5 hr. showed *ca.* 80% of unreacted IVa; after 10 hr., *ca.* 30% of unreacted IVa remained; after 24 hr., *ca.* 5% of unreacted IVa remained. The infrared spectrum of the material obtained from the 24-hr. run at 100° was identical in every respect with that of the material obtained from a 2.5 hr. run at 200°, and it is presumed that the products are very similar in nature. The identification of V, VI, VII and VIII as described below involved material obtained from the 200° runs. In a number of instances, however, similar experiments with similar results were performed on material from 100° runs

1-Cyclohexyltetralin (V). (A) Synthesis from Hexahydrobenzophenone *via* Reformatsky and Arndt–Eistert Sequence.—Ethyl β-hydroxy-β-phenyl-β-cyclohexylpropionate was prepared by the reaction of 28 g. (0.148 mole) of hexahydrobenzophenone[31] with a total of 37 g. (0.22 mole) of ethyl α-bromoacetate and 14.6 g. (0.22 gram atom) of zinc according to previously described methods.[32] The product consisted of 38 g. (93%) of solid material, m.p. 55–56.5°,

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[28] W. W. Hartman and M. R. Brethen, *Org. Syntheses*, **12**, 38 (1932).

[29] W. W. Hartman and R. Phillips, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 464.

[30] The genesis of naphthalene is uncertain, but it is believed to arise through cyclization of ethyl δ-phenylbutyl ether, a probable contaminant of IVa, to tetralin followed by dehydrogenation.

[31] V. Meyer and W. Scharvin, *Ber.*, **30**, 1940 (1897).

[32] *Cf.*, for example, J. W. Cook, C. L. Hewett and C. A. Lawrence, *J. Chem. Soc.*, 71 (1936); C. D. Gutsche, THIS JOURNAL, **73**, 786 (1951).

from which an analytical sample was obtained as colorless needles by recrystallization from ethanol; m.p. 57–57.5°.

Anal. Calcd. for $C_{17}H_{24}O_3$: C, 73.88; H, 8.75. Found: C, 73.22; H, 8.56.

The hydroxy ester was dehydrated by the thionyl chloride–pyridine method[32] to yield a mobile, yellow oil with b.p. 155–158° (0.9 mm.). Reduction with hydrogen at two atmospheres of pressure in the presence of 10% palladium-on-charcoal catalyst followed by saponification by refluxing for 7 hr. with 30% aqueous potassium hydroxide produced **β-phenyl-β-cyclohexylpropionic acid (X)** in 80% over-all yield from the hydroxy ester, m.p. 96–98°. An analytical sample was obtained as fine needles by two recrystallizations from aqueous ethanol; m.p. 99–100°.

Anal. Calcd. for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.20; H, 8.55.

γ-Phenyl-γ-cyclohexylbutyric acid (XI) was obtained from X by application of the Arndt–Eistert sequence. A 10.0-g. sample of X was converted to the acid chloride with an excess of purified[33] thionyl chloride. The crude acid chloride was then treated at 0° over a period of 25 minutes with 300 ml. of ether containing diazomethane from 31 g. of nitrosomethylurea. After the reaction mixture had stood at 0° for an additional hour, the volatile materials were removed under vacuum, and the residue was dissolved in methanol and decomposed by the method of Newman and Beal,[34] 95% of the theoretical amount of nitrogen being evolved. The resulting methyl ester was saponified by 2.5 hr. of refluxing with 50 ml. of 45% aqueous potassium hydroxide and 50 ml. of ethanol and yielded 9.3 g. (88%) of a solid with m.p. 56–78°. Two recrystallizations from petroleum ether (b.p. 63–69°) gave 7.5 g. (71%) of colorless, short, thick needles, m.p. 101–102°.

Anal. Calcd. for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 78.05; H, 8.98.

4-Cyclohexyl-3,4-dihydronaphthalenone (XII) was obtained in 85% yield by cyclization of XI with anhydrous hydrogen fluoride; b.p. 128–130° (0.06 mm.). For analysis, a portion of this material was redistilled and a center cut taken; n^{25}D 1.5640, $\bar{\nu}_{max}^{liquid}$ 1684 cm.$^{-1}$ (benzoyl).

Anal. Calcd. for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 83.60; H, 8.79.

A 2,4-dinitrophenylhydrazone of XII was obtained as fine, deep red needles after two recrystallizations from ethyl acetate; m.p. 234–234.5° dec.

Anal. Calcd. for $C_{22}H_{24}N_4O_4$: C, 64.69; H, 5.92. Found: C, 64.80; H, 5.77.

An 8.64-g. sample of XII was dissolved in 170 ml. of ethyl acetate, treated with 3 g. of 10% palladium-on-charcoal and 12 drops of 70% perchloric acid[35] and subjected to hydrogenation at two atmospheres pressure. After 30 minutes the theoretical amount of hydrogen for complete reduction of the carbonyl group had been absorbed. The product, **1-cyclohexyltetralin (V)**, consisted of 7.4 g. (91%) of a colorless oil with b.p. 101–102° (0.1 mm.). A middle fraction taken for analysis had n^{25}_{D} 1.5464; λ_{max}^{EtOH} mμ (ε); 212.5 (8305), 266.5 (488), 274 (479); $\bar{\nu}_{max}^{liquid}$ in cm.$^{-1}$ *736*, *753*, *761*, *802*, 841, 851, 867, *891*, *942*, 967, 1035, 1118, 1130, 1156, 1215, *1240*, *1265*, *1280*, *1325*, *1347*, *1451*, *1492*, 1585, *1608*, 1690, *2860*, *2920*, *3035*.[36]

Anal. Calcd. for $C_{16}H_{22}$: C, 89.65; H, 10.35. Found: C, 89.94; H, 10.19.

(B) **Attempted Synthesis from Hexahydrobenzophenone *via* Stobbe Method.**—An 18.8-g. (0.1 mole) sample of hexahydrobenzophenone was condensed with 73 g. (0.5 mole) of dimethyl succinate in the presence of 400 ml. of *t*-butyl alcohol containing 16.8 g. (0.43 g. atom) of dissolved potassium according to the method described for the Stobbe condensation with benzophenone.[37] The crude product consisted of 31 g. (102%) of a solid with m.p. 104–111°. After a number of recrystallizations of a portion of this material from petroleum ether (b.p. 63–69°)–benzene, a sample of feathery needles was obtained, m.p. 120–121°, which is presumed to be **β-carbomethoxy-γ-phenyl-γ-cyclohexylvinylacetic acid** or a bond isomer thereof.

Anal. Calcd. for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.18; H, 7.29.

Attempted decarboxylation of the half-ester by refluxing with acetic acid–48% hydrobromic acid–water[38] gave a mixture from which no pure compound could be isolated. However, when the crude material was subjected to treatment with phosphorus and hydrogen iodide, a solid could be separated which has an analysis and a spectrum in accord with **γ-phenyl-γ-cyclohexylparaconic acid**. After recrystallization from aqueous methanol, this material was obtained as prismatic needles, m.p. 182–182.5°; $\bar{\nu}_{max}^{CHCl_3}$ in cm.$^{-1}$ 1718 (carboxyl), 1766 (γ-lactone).

Anal. Calcd. for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99. Found: C, 70.91; H, 6.98.

Saponification of the Stobbe half-ester gave **β-carboxy-γ-phenyl-γ-cyclohexylvinylacetic acid**, m.p. 152–153°, in 94% yield. An analytical sample was prepared by further recrystallization from petroleum ether (b.p. 63–69°)–ethyl acetate and was obtained in the form of small pellets, m.p. 153–154°.

Anal. Calcd. for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99. Found: C, 70.81; H, 7.28.

Attempted decarboxylation of the dibasic acid by heating for 1 hr. at 160–180° over potassium bisulfate yielded 73% of a compound which, on the basis of the analysis and infrared spectrum, is presumed to be **α-(β-phenyl-β-cyclohexyl)-methylenesuccinic anhydride**, m.p. 123–126°. Further purification by recrystallization from methanol yielded diamond-shaped plates, m.p. 130–130.5°, $\bar{\nu}_{max}^{CHCl}$ 1780 and 1840 cm.$^{-1}$ (anhydride).

Anal. Calcd. for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.58; H, 7.30.

(C) **Isolation from Cyclization Product of IVa.**—Fraction 8 from the fractional distillation of the cyclization product from IVa (*cf.* above), b.p. 108° (0.7 mm.), n^{25}D 1.5495, possessed an infrared spectrum identical in every detail with that given above for authentic 1-cyclohexyltetralin except for an additional weak band at 696 cm.$^{-1}$. This band, which is strong in the earlier fractions of the distillation, is probably due to slight contamination from these materials. Similarly, fraction 13 from the chromatographic separation of the cyclization product from IVa (*cf.* above) possessed an infrared spectrum identical with that of authentic 1-cyclohexyltetralin.

Anal. Calcd. for $C_{16}H_{22}$: C, 89.65; H, 10.35. Found: Fraction 8 from distillation: C, 89.94; H, 10.19. Fraction 13 from chromatography: C, 89.55; H, 10.05.

(D) **Synthesis from 2-(γ-Phenylpropyl)-cycloheptanol (XXI).**—The reduction of the ketone IVa to the alcohol XXI was accomplished in 89% yield with lithium aluminum hydride in ether solution. The **2-(γ-phenylpropyl)-cycloheptanol** was obtained as a colorless oil, b.p. 132–134° (0.3 mm.), n^{25}D 1.5272.

Anal. Calcd. for $C_{16}H_{24}O$: C, 82.70; H, 10.41. Found: C, 83.14; H, 10.61.

A solution of 2.71 g. (0.012 mole) of XXI in 20 ml. of carbon disulfide was cooled to 10° and treated with 2.00 g. (0.015 mole) of anhydrous aluminum chloride. The reaction mixture was allowed to warm to room temperature whereupon hydrogen chloride was evolved. After the evolution of gas had ceased, the mixture was gently boiled for a few minutes and then poured onto ice and sulfuric acid. The product, isolated in the usual manner, consisted of 1.91 g. (76%) of a colorless liquid, b.p. 109–110° (0.4 mm.), n^{25}D 1.5460; λ_{max}^{EtOH} mμ (ε): 210 (8700), 266 (850), 274 (725); $\bar{\nu}_{max}^{liquid}$ in cm.$^{-1}$: *696*, *737*, *753*, *762*, *802*, 842, 851, 867, *891*, *942*, *971*, *989*, 1020–1040 (broad), 1118, 1127, 1158, 1218, *1238*, *1266*, *1280*, *1324*, *1347*, *1450*, *1491*, 1581, *1605*, 1690, 1702, 1800, 1910, 1940, 2650, *2840*, *2900*, *3010* and *3020*.[36]

Anal. Calcd. for $C_{16}H_{22}$: C, 89.65; H, 10.35. Found: C, 89.44; H, 10.39.

That the product resulting from the cyclization of XXI contains 1-cyclohexyltetralin is indicated by the infrared

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(33) L. F. Fieser, "Experiments in Organic Chemistry," 2nd Ed., D. C. Heath and Co., Boston, Mass., 1941, p. 381.

(34) M. S. Newman and P. F. Beal, This Journal, **72**, 5163 (1950).

(35) K. W. Rosenmund and E. Karg, *Ber.*, **75**, 1850 (1942).

(36) The absorption bands which are italicized are strong and/or well-defined.

(37) W. S. Johnson and G. H. Daub, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 1.

(38) W. S. Johnson, J. W. Petersen and W. P. Schneider, This Journal, **69**, 74 (1947).

spectrum and, more conclusively, by the formation of solid derivatives identical with those from authentic V (*cf.* below). Other compounds must also be present, however, as suggested by certain bands (*e.g.*, 696, 971 and 989 cm.$^{-1}$) in the infrared spectrum which are not present in the spectrum of pure V.

(E) **Acetyl Derivatives of 1-Cyclohexyltetralin.**—Acetylation of a sample of authentic 1-cyclohexyltetralin with acetyl chloride and aluminum chloride in carbon disulfide yielded 100% of a pale yellow oil. This was treated with 2,4-dinitrophenylhydrazine to yield a solid which could be separated, by fractional crystallization from ethanol-ethyl acetate, into two compounds: (a) yellow, microcrystalline material with m.p. 239–240°; *Anal.* Calcd. for $C_{24}H_{28}N_4O_4$: C, 66.03; H, 6.47. Found: C, 66.04; H, 6.16. (b) An orange-red micro-crystalline material with m.p. 177–178°. *Anal.* Calcd. for $C_{24}H_{28}N_4O_4$: C, 66.03; H, 6.47. Found: C, 65.99; H, 6.29.

In similar fashion, fraction 8 from distillation and fraction 13 from chromatography (from the cyclization product of IVa) were acetylated and converted to a 2,4-dinitrophenylhydrazone mixture from which in each case two compounds, identical with those described above, were isolated.

Also, the product resulting from the cyclization of 2-(γ-phenylpropyl)-cycloheptanol (XXI) yielded the same two 2,4-dinitrophenylhydrazone derivatives, although in somewhat lower yield, when subjected to this treatment.

2-Cyclohexyltetralin. (A) Synthesis from Cyclohexylsuccinic Anhydride.—β-Carbethoxy-β-cyclohexenylpropionic acid was prepared from cyclohexanone and diethyl succinate according to the method of Johnson, *et al.*[39] The half-ester was hydrogenated in the presence of 10% palladium-on-charcoal catalyst, saponified to cyclohexylsuccinic acid and converted, with acetic anhydride, to cyclohexylsuccinic anhydride, m.p. 35–36°. To a stirred solution of 8.84 g. (0.048 mole) of the anhydride in 35 ml. of dry, thiophene-free benzene cooled to 5–10°, 13.08 g. (0.098 mole) of anhydrous aluminum chloride was added slowly. The reaction mixture was allowed to stand for 16 hr. at room temperature, then heated for 2 hr. at 60–70° and finally worked up in the usual fashion to yield 12 g. (95%) of crude product, m.p. 110–120°. Two recrystallizations from benzene–hexane yielded 9.20 g. (73%) of colorless, fine needles, m.p. 125–126°, presumed to be **α-cyclohexyl-β-benzoylpropionic acid (XV)**.

Anal. Calcd. for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 74.26; H, 7.81.

Concentration of the mother liquors from the recrystallizations followed by two further recrystallizations from benzene–hexane yielded 1.61 g. (13%) of colorless needles, m.p. 99–100°, presumed to be **β-cyclohexyl-β-benzoylpropionic acid (XIV)**.

Anal. Calcd. for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.92; H, 7.67.

A 5.0-g. sample of the higher-melting keto acid was reduced by the Huang-Minlon modification of the Wolff–Kishner method[40] to give 3.2 g. (68%) of **α-cyclohexyl-γ-phenylbutyric acid (XIX)**, with b.p. 174–175° (0.15 mm.), m.p. 59–60°.

Anal. Calcd. for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.88; H, 9.01.

2-Cyclohexyl-3,4-dihydronaphthalenone (XVIII) was obtained when a 4.5-g. sample of XIX was treated with 150 ml. of anhydrous hydrogen fluoride, allowed to stand for 6 hr. and worked up in the usual fashion to yield 3.44 g. (83%) of pale yellow liquid with b.p. 140° (0.13 mm.), $n^{25}\mathrm{D}$ 1.5547, $\bar{\nu}_{\max}^{\mathrm{liquid}}$ 1685 cm.$^{-1}$ (benzoyl).

Anal. Calcd. for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.10; H, 8.84.

The 2,4-dinitrophenylhydrazone of XVIII was obtained, after two recrystallizations from ethanol–ethyl acetate, as orange-red needles, m.p. 231–231.5°.

Anal. Calcd. for $C_{22}H_{24}N_4O_4$: C, 64.69; H, 5.92. Found: C, 64.71; H, 5.96.

The 2,4-dinitrophenylhydrazone of 3-cyclohexyl-3,4-dihydronaphthalenone (XVII) was obtained by reducing the lower-melting keto acid XIV to β-cyclohexyl-γ-phenylbutyric acid (XVI) followed by cyclization to the ketone XVII and derivatization with 2,4-dinitrophenylhydrazine. The pure material was obtained as bright orange, very small needles after two recrystallizations from ethanol–ethyl acetate; m.p. 235–236° dec.

Anal. Calcd. for $C_{22}H_{24}N_4O_4$: C, 64.69; H, 5.92. Found: C, 65.06; H, 6.16.

2-Cyclohexyltetralin (VI) was obtained in 80% yield by hydrogenolysis of XVIII in the presence of 10% palladium-on-charcoal in an ethyl acetate solution containing perchloric acid. It consisted of a colorless, mobile liquid with b.p. 132–134° (0.6 mm.), $n^{25}\mathrm{D}$ 1.5413; $\lambda_{\max}^{\mathrm{EtOH}}$ mμ (ϵ): 210 (8280), 266.5 (613), 273.5 (710); $\bar{\nu}_{\max}^{\mathrm{liquid}}$ in cm.$^{-1}$: *739*, 810, 840, 886, 910, *942*, 968, 1034, 1096, 1185, 1249, *1346*, 1370, *1432*, *1448*, *1494*, *1583*, 1678, *2850* and *2912*.[36]

Anal. Calcd. for $C_{16}H_{22}$: C, 89.65; H, 10.35. Found: C, 89.39; H, 10.13.

(B) **Isolation from Cyclization Product from IVa.**—Fraction 20 from the chromatographic separation of the cyclization product from IVa (*cf.* above) showed an infrared spectrum almost identical with that of authentic 2-cyclohexyltetralin. The infrared spectrum of 1-cyclohexyltetralin contains more bands than that of 2-cyclohexyltetralin and includes all of those present in the former compound. Only two of these show any noticeable shift (736 and 891 cm.$^{-1}$ in 1-cyclohexyltetralin, 739 and 886 cm.$^{-1}$ in 2-cyclohexyltetralin). Concurrent spectral determinations charted on the same graph, however, show quite clearly the difference between V and VI and support the identity of fraction 20 with VI.

(C) **Acetyl Derivatives of 2-Cyclohexyltetralin.**—Acetylation of a sample of authentic 2-cyclohexyltetralin with acetyl chloride and aluminum chloride in carbon disulfide yielded a liquid which was then treated with 2,4-dinitrophenylhydrazine. The resulting solid was recrystallized from ethanol–ethyl acetate and yielded two compounds: (a) dark yellow, microcrystalline material with m.p. 247–248°. *Anal.* Calcd. for $C_{24}H_{28}N_4O_4$: C, 66.03; H, 6.47. Found: C, 66.03; H, 6.18. (b) yellow, micro-crystalline material with m.p. 187–188°.

Anal. Calcd. for $C_{24}H_{28}N_4O_4$: C, 66.03; H, 6.47. Found: C, 66.02; H, 6.53. Mixed m.p.'s of these derivatives with the corresponding ones from 1-cyclohexyltetralin showed marked depressions. Insufficient VI was available from fraction 20 of the chromatographic separation to allow identification through the acetyl derivative.

1-Cyclohexylnaphthalene (VII). (A) Synthesis from 1-Cyclohexyltetralin.—A 1.0-g. sample of 1-cyclohexyltetralin was heated for 5 hr. at 235–258° with 0.7 g. of 5% palladium-on-charcoal. The crude product was chromatographed on 40 g. of alumina using petroleum ether (b.p. 63–69°) as the elutrient, and 0.25 g. of VII was obtained, $n^{25}\mathrm{D}$ 1.6005; $\lambda_{\max}^{\mathrm{EtOH}}$ mμ (ϵ): 225 (80,050), 273 (6170), 283 (7285), 294 (5120), 313.5 (387) [reported[41] $\lambda_{\max}$ mμ (ϵ): 225 (31,500), 274 (4000), 283 (4800), 294 (3300), 314 (320)]; $\bar{\nu}_{\max}^{\mathrm{liquid}}$ in cm.$^{-1}$: 699, *729*, 741, *775*, *788*, *795*, *842*, *856*, *887*, *898*, 947 965, *989*, 1015, *1028*, *1090*, 1130, 1142, *1168*, *1232*, *1263*, 1300, 1325, *1350*, *1400*, *1453*, *1516*, *1606*, *2867*, *2930* and *3080*.[36]

Anal. Calcd. for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.34; H, 8.68.

A picrate of VII with m.p. 126–127° (reported[42] 122–123.5°) and a trinitrobenzene complex with m.p. 118–119° (reported[42] 116.5–117.5°) could be prepared.

(B) **Isolation from Cyclization Product of IVa.**—Inspection of the infrared spectra of distillation fractions 18–22 indicated that 1-cyclohexylnaphthalene was present (based particularly on the bands at 775, 795, 887, 947, 1263 and 1400 cm.$^{-1}$ which are prominent in VII but weak or absent in VIII) although contaminated with other materials. When a 2.25-g. sample comparable to fraction 18 of the distillation, b.p. 115–117° (0.7 mm.), $n^{25}\mathrm{D}$ 1.5870, was treated with an alcoholic solution of picric acid, 1.47 g. of an orange picrate, m.p. 112–115°, precipitated. Several recrystallizations of this material from methanol saturated with picric acid yielded 0.37 g. of orange needles, m.p. 124–125°, which

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(39) W. S. Johnson, C. E. Davis, R. H. Hunt and G. Stork, THIS JOURNAL, **70**, 3021 (1948).

(40) Huang-Minlon, *ibid.*, **68**, 2487 (1946).

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

(42) J. W. Cook and C. A. Lawrence, *J. Chem. Soc.*, 1431 (1936).

showed no depression in m.p. when admixed with the picrate of authentic VII. The picrate was decomposed by dissolving in benzene and passing through a column of alumina. The resulting product was an oil ($\lambda_{\max}^{\text{EtOH}}$ mμ (ϵ): 225 (78,000), 273 (5800), 283 (6800) 294 (4550), 313.5 (398)) which was converted to a trinitrobenzene complex, m.p. 118–119°, which showed no depression in m.p. when admixed with the same derivative of authentic VII.

2-Cyclohexylnaphthalene (**VIII**). (**A**) **Synthesis from 2-Naphthylmagnesium Bromide.**—A stirred mixture of 6.79 g. (0.033 mole) of 2-bromonaphthalene, 1.59 g. (0.066 g. atom) of magnesium and 50 ml. of dry ether was treated over a period of 30 minutes with a solution of 3.58 g. (0.033 mole) of ethyl bromide in 15 ml. of ether. After an additional 3 hr. of stirring, the reaction mixture was cooled and treated with a solution of 6.44 g. (0.066 mole) of cyclohexanone in 25 ml. of ether. After refluxing the reaction mixture for 3.5 hr. and allowing it to stand at room temperature overnight, the product was isolated in the usual fashion. The crude material was slowly distilled from 3 g. of fused potassium bisulfate in a Claisen flask to yield 4.0 g. (59%) of 2-cyclohexenylnaphthalene, b.p. 135° (0.06 mm.), m.p. 55–57°. One recrystallization from methanol yielded colorless needles, m.p. 60–60.5° (reported[14] 61–62°). Reduction of the olefin with hydrogen in the presence of 10% palladium-on-charcoal yielded 89% of 2-cyclohexylnaphthalene as a colorless, mobile liquid, b.p. 150–152° (0.65 mm.), n^{25}D 1.5955; $\lambda_{\max}^{\text{EtOH}}$ mμ (ϵ): 225 (114,000), 268 (4700), 275 (5050), 285 (3400), 304 (475), 310 (280) 319 (430); $\bar{\nu}_{\max}^{\text{liquid}}$ in cm.$^{-1}$: *745*, 768, 786, *815*, *852*, *883*, 920, *954*, *1018*, *1127*, 1142, 1155, 1203, *1270*, *1352*, 1380, *1451*, *1510*, *1610*, *1640*, *2867*, *2934*, and *3067*.[36]

Anal. Calcd. for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.48; H, 8.87.

A trinitrobenzene complex of VIII was obtained as feathery, yellow needles after several recrystallizations from methanol; m.p. 122–123°.

Anal. Calcd. for $C_{22}H_{21}N_3O_6$: C, 62.40; H, 5.00. Found: C, 62.55; H, 4.86.

A picrate with m.p. 98–103° which could not be further purified could be prepared from VIII.

(**B**) **Isolation from Cyclization Product of IVa.**—Fraction 24 from the distillation (*cf.* above) and fractions 27–45 from the chromatographic separation (*cf.* above) had infrared spectra very close to that of authentic 2-cyclohexylnaphthalene.

Anal. Calcd. for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: Fraction 24 from distillation: C, 91.28; H, 8.90. Fraction 27–45 from chromatography: C, 91.31; H, 8.44.

When a 0.35-g. sample of distillation fraction 24 was treated with an alcoholic solution of trinitrobenzene, 0.26 g. of bright yellow needles, m.p. 116–120°, precipitated. Several recrystallizations from methanol produced feathery yellow needles, m.p. 122–123°, which showed no depression in m.p. when admixed with the trinitrobenzene complex of authentic VIII.

Unidentified Product.—A 1.70-g. sample of fraction 25 from the distillation of the cyclization product of IVa, b.p. 127–128° (0.3 mm.), was treated with an alcoholic solution of trinitrobenzene. The precipitate, consisting of 1.61 g. of bright orange needles with m.p. 100–114°, was recrystallized from methanol to give 1.0 g. of dull orange needles, m.p. 115–119°. This material was dissolved in petroleum ether (b.p. 63–69°), passed through a column of alumina and 0.46 g. of an oil collected, n^{32}D 1.6255. Upon standing, the oil partially solidified and was thereupon pressed on a porous plate to yield 0.21 g. of material with m.p. 78–84°. Recrystallization from methanol yielded glistening plates, m.p. 91–92°; $\lambda_{\max}^{\text{EtOH}}$ (ϵ): 230 (55,000), 235 (79,000), 285 (6300), 295 (6600), 314 (3800), 328 (3800).

Anal. Calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.01; H, 7.66.

Dehydrogenation Experiments. (**A**) **Dehydrogenation of 1-Cyclohexyltetralin** (**V**).—The low temperature dehydrogenation of V to give cyclohexylnaphthalene is described above. A more strenuous dehydrogenation was carried out by mixing 1.0 g. of V with 0.3 g. of 10% palladium-on-charcoal catalyst and heating at 235–310° for 10.5 hr. The product consisted of 0.6 g. of a colorless liquid with a slight bluish fluorescence, b.p. 140–143° (0.4 mm.), n^{25}D 1.6598; $\lambda_{\max}^{\text{EtOH}}$ mμ (ϵ): 225 (55,600), 240 (6530), 282.5 (8230), 287.5 (9515), 341.5 (186) [reported[43] $\lambda_{\max}^{\text{EtOH}}$ mμ (ϵ): 226 (62,000), 282 (11,000), 288 (11,000)].

(**B**) **Dehydrogenation of 2-Cyclohexyltetralin** (**VI**).—A mixture of 0.5 g. of 2-cyclohexyltetralin and 0.2 g. of 10% palladium-on-charcoal was heated for 3 hr. at 260–330°. The product consisted of 0.3 g. of solid, m.p. 95–99°, from which pure 2-phenylnaphthalene could be obtained after two recrystallizations from ethanol; m.p. 102–103° (reported[43] 102–103°); $\lambda_{\max}^{\text{EtOH}}$ mμ (ϵ): 212 (36,000), 250 (63,000), 285 (11,000) [reported[43] $\lambda_{\max}^{\text{EtOH}}$ mμ (ϵ): 251 (63,000), 269 (12,500), 288 12,500)].

(**C**) **Dehydrogenation of Cyclization Product of IVa.**—A 2.67-g. sample of cyclization product, b.p. 109–126° (0.4 mm.), was treated with 1.0 g. of 5% palladium-on-charcoal catalyst and heated for 2.5 hr. at 390°. The product consisted of 2.00 g. of a red oil from which 1.30 g. of 1-cyclohexylnaphthalene and 0.50 g. of 2-phenylnaphthalene could be separated by chromatography on alumina.

(**D**) **Dehydrogenation of Chromatographic Fractions from Cyclization Product of IVa.**—A 0.5-g. sample of chromatographic fractions 8–18 (*cf.* above) dehydrogenated in the presence of 0.35 g. of 5% palladium-on-charcoal at 245–300° for 22 hr. yielded a mixture of 1-cyclohexylnaphthalene and 1-phenylnaphthalene and 4% of 2-phenylnaphthalene, separated by chromatography on alumina. Although the 2-phenylnaphthalene may have arisen by rearrangement during the dehydrogenation, it is thought more probable that it was formed from the small amount of 2-cyclohexyltetralin probably present in chromatographic fractions 8–18. A 0.2-g. sample of chromatographic fractions 27–45 (*cf.* above) dehydrogenated in the presence of 0.1 g. of 10% palladium-on-charcoal at 300–350° for 3.5 hr. yielded 60% of 2-phenylnaphthalene.

(**E**) **Dehydrogenation of Distillation Fractions from Cyclization Product of IVa.**—A 0.83-g. sample of distillation fraction 9, b.p. 107–108° (0.7 mm.) (*cf.* above), was dehydrogenated in the presence of 0.2 g. of 5% palladium-on-charcoal at 290° for 2.5 hr. and yielded 2-cyclohexylnaphthalene, isolated as the picrate in 27% yield. A 0.96-g. sample of distillation fraction 24, b.p. 125–126° (0.8 mm.), (*cf.* above) was dehydrogenated in the presence of 0.2 g. of 5% palladium-on-charcoal at 360° for 3 hr. and yielded 90% of 2-phenylnaphthalene.

(**F**) **Dehydrogenation of Cyclization Product of XXI.**—A 0.44-g. sample of the cyclization product of XXI was treated with 0.20 g. of 5% palladium-on-charcoal and heated for 3 hr. at 390°. The product consisted of 0.38 g. of a greenish-yellow oil with $\lambda_{\max}^{\text{EaOH}}$ mμ (ϵ): 225 (55,000), 285 (8100) and $\lambda_{\min}^{\text{EtOH}}$ 250 mμ. This is very similar to the ultraviolet spectrum of 1-phenylnaphthalene and different from that of 2-phenylnaphthalene which has a maximum at 250 mμ (63,000).

(**G**) **Dehydrogenation of Unidentified Product.**—A 40-mg. sample of the unidentified product obtained from the cyclization of IVa (*cf.* above) was treated with 20 mg. of 10% palladium-on-charcoal and heated for 3 hr. at 260–300°. The solid product was recrystallized from ethanol to give colorless plates: m.p. 107–108°; $\lambda_{\max}^{\text{EtOH}}$ mμ (ϵ): 212 (26,000), 224 (16,000), 250 (47,000), 257 (58,000), 280 (10,400), 291 (10,500), 303 (13,700), 321 (890), 336 (1600).

Anal. Calcd. for $C_{16}H_{12}$: C, 94.08, H, 5.92. For $C_{16}H_{10}$: C, 95.02, H, 4.98. Found: C, 94.74; H, 6.24.

A trinitrobenzene complex of the dehydrogenation product was obtained after recrystallization from ethanol, as yellow feathery needles, m.p. 168–169°.

Anal. Calcd. for $C_{22}H_{15}N_3O_6$: C, 63.31; H, 3.62. For $C_{22}H_{13}N_3O_6$: C, 63.61; H, 3.15. Found: C, 63.81; H, 3.48.

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[43] L. F. Fieser and E. B. Hershberg, THIS JOURNAL, **60**, 940 (1938).