Summary

1. The synthesis of 3,3′-, 4,4′-, and 5,5′-dimethyl-2,2′-bipyridyls is described.
2. 2,2′-Bipyridyl-4,4′- and 5,5′-dicarboxylic acids and their methyl esters have been prepared.
3. The synthesis of 5,5′-dinitro, dichloro and dibromo-2,2′-bipyridyls is described.
4. The ferroin reaction is given by the compounds mentioned in (1), by the acids in (2), but not by the compounds in (3).

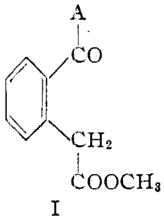
PHILADELPHIA, PENNA. RECEIVED SEPTEMBER 6, 1946

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

1,2,5,6-Dibenzcycloöctatetraene[1]

BY LOUIS F. FIESER AND MAURICE M. PECHET

In a previous investigation[2] directed toward the further elucidation of the character of the cyclooctatetraene ring a nine-step process was worked out for the preparation of benzcycloöctanol-3, a possible intermediate for the synthesis of the as yet unknown benzcycloöctatetraene. In this continuation of the research an attempt was first made to dehydrate the alcohol by cleavage of the tosylate, but with discouraging results. Various condensation reactions that might afford benzo derivatives of cycloöctatetraene were then explored. Homophthalic acid was prepared by a very convenient process consisting in the chromic acid oxidation of indene (60% yield) and converted into the known half ester I (A = OH) with the idea that the corresponding ester-aldehyde (I, A = H) might be obtained and condensed to dicarbethoxydibenzcyclooctatetraene. However, all attempts to prepare the acid chloride preliminary to Rosenmund reduction led merely to the production of the known 3-chloroisocoumarin, II. The next trial was based upon the work of Thiele and Schneider,[3] who condensed phthalaldehyde with acetonedicarboxylic ester and obtained benzcycloheptadienone dicarboxylic ester in good yield. We investigated the condensation of homophthalaldehyde with acetone dicarboxylic ester but isolated only known products of the self-condensation of each component.



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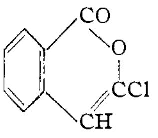

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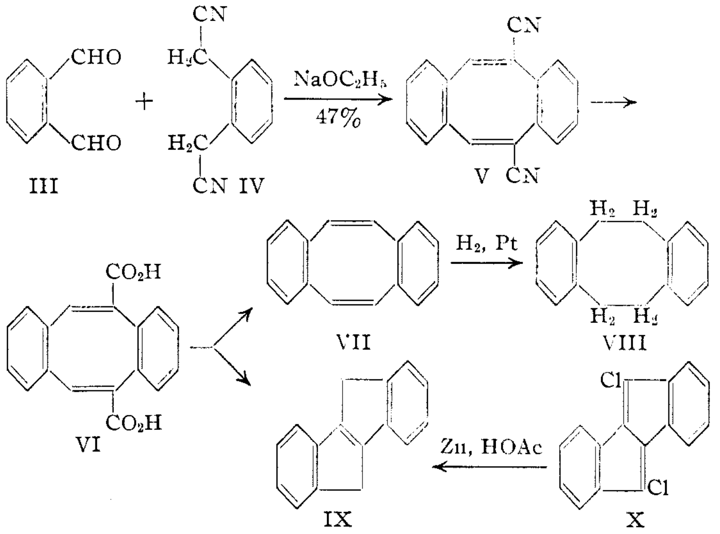

A successful synthesis was finally found in the condensation of *o*-phthaldehyde (III) with *o*-phenylenediacetonitrile (IV) in the presence of sodium ethoxide. A white substance having the composition of the expected 3,8-dicyano-1,2,5,6-dibenzcycloöctatetraene (V) was isolated in moderate yield along with a bright red by-product. The white substance on hydrolysis with 50% sulfuric acid yielded a half amide of the dibasic acid and on alcoholysis gave chiefly the diester, along with a little monoester. The diacid (VI) was obtained readily from the diester, but the decarboxylation step went poorly under the best of several conditions tried. In most experiments two isomeric hydrocarbons were formed, neither of which could be converted into the other. The higher melting, less soluble isomer corresponded in properties to the known diphenylsuccindene-10 (IX) and proved to be identical with a sample prepared by reduction of 9,10-dichlorodiphenylsuccindadiene[4] (X). The other hydrocarbon, a colorless substance of the formula $C_{16}H_{16}$ and melting at 107–108°, decolorized permanganate and bromine solutions in the cold, and in the presence of catalyst absorbed two moles of hydrogen and gave a hydrocarbon that did not depress the

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[1] The results of this investigation were described in the doctoral dissertation of Maurice M. Pechet, February 1, 1944; a preliminary report of the work was presented at the Detroit meeting of the American Chemical Society.

[2] Fry and Fieser, THIS JOURNAL, **62**, 3489 (1940).

[3] Thiele and Schneider, *Ann.*, **369**, 294 (1909).

[4] Brand and Müller, *Ber.*, **55**, 601 (1922).

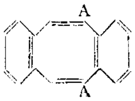
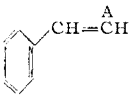
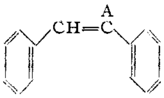
melting point of a sample of *s*-dibenzcycloöctadiene[5] (VIII, synthesized from *o*-xylylene bromide), for which we are indebted to Dr. Wilson Baker. The unsaturated hydrocarbon is thus assigned the structure of 1,2,5,6-dibenzcycloöctatetraene, VII.

The red by-product of the condensation was obtained in only very small amounts and is sparingly soluble in the usual solvents and hence not easily characterized. The composition is the same as that of the dicyanodibenzcycloöctatetraene V, and the results of a Rast determination suggest that the red substance probably has double the molecular weight. The by-product thus may be formed from the condensation of two moles of each component and may have a sixteen-membered conjugated ring system, but the evidence is as yet undecisive.

The chemical reactivity of the *s*-dibenz derivative of cycloöctatetraene is such as to indicate that the eight-membered conjugated ring system does not have the aromatic quality characteristic of benzene. A spectrographic comparison of the dicyano and dicarboxy derivatives of the hydrocarbon and of the hydrocarbon itself with corresponding derivatives of ethylene, styrene and stilbene is recorded in Table I. The dicarboxy derivative is most nearly comparable in spectrum to the ethylene model, and the similarity decreases with the introduction of one and then two benzene rings conjugated with the ethylenic linkage; this would indicate that the benzene rings of *s*-dibenzcycloöctatetraene are not in conjugation with the bridging double bonds, and hence that the molecule is non-planar. The dicyano derivative, however, is intermediate in absorption characteristics between acrylonitrile and the aromatic models. *s*-Dibenzcycloöctatetraene itself shows an ill-defined shoulder at 330 mμ (log *E* 2.6) close to the peak for stilbene in wave length but of optical exaltation more comparable to the maximum for ethylene or to that of an isolated benzene ring (*o*-xylene, log *E* 2.24, max. 260 mμ). The comparisons as a whole show that full conjugation, with resulting strong stabilization by resonance comparable with a fully aromatic system, assuredly does not exist but that the eight-membered ring is perhaps in partial conjugation with at least one of the benz rings.

TABLE I

ULTRAVIOLET ABSORPTION SPECTRA IN ABSOLUTE ALCOHOL; WAVE LENGTHS (mμ) AND LOG *E* VALUES OF ABSORPTION MAXIMA

Substituent A		$\overset{A}{CH_2{=}CH}$		
CN	257, 4.45	(200, 4.2)[a]	304, 4.5	312, 4.4
COOH	228, 4.42	225, 4.5[b]	273, 4.5	285, 4.3
H	(330, 2.6)	(190, 2–4)[c]	240, 4.0	295, 4.44

[a] Compare Bruylants and Castille, *Bull. soc. chim. Belg.*, **34**, 261 (1925). [b] Compare Lüthy, *Z. physik. Chem.*, **107**, 285 (1923). [c] Snow and Allsopp, *Trans. Faraday Soc.*, **30**, 93 (1934).

The results of this investigation thus agree with observations concerning the tri- and tetrabenz derivatives of cycloöctatetraene.[6] A full characterization of cycloöctatetraene (Reppe[7]) has not as yet come to our attention.

Experimental[8]

Preliminary Trials

Benzocycloöctanol-3 Tosylate.—Benzocycloöctanol-3 was prepared by the method of Fry and Fieser[2] except that the terminal step was conducted by reduction with aluminum isopropoxide (74% yield of crystallized product, m. p. 62–64°). A solution of 1.44 g. of the alcohol in 8 g. of pyridine was treated slowly with 3 g. of powdered *p*-toluenesulfonyl chloride and after six hours the mixture (containing a white precipitate) was poured into 36 cc. of 10% sulfuric acid. The ester separated in a crystalline condition and melted at 98.5–101°; yield 2.36 g. (87%). Crystallization from alcohol gave material melting at 100–101.8°.

Anal. Calcd. for $C_{19}H_{22}O_3S$: C, 69.06; H, 6.71; S, 9.70. Found: C, 68.92; H, 7.02; S, 9.97.

Attempts to prepare benzocycloöctene by cleavage of the tosylate with sodium bicarbonate in methanol according to Hückel[9] were unsuccessful, although in a model experiment cyclohexene was obtained readily after a period of refluxing of one hour. Benzocycloöctanol-3 tosylate was recovered unchanged after being refluxed with bicarbonate in methanol or ethanol for as long as twelve hours and even after heating in a sealed tube at 100–110° for twenty-four hours.

Homophthalic Acid.[10]—A 3-liter flask equipped with a condenser, dropping funnel and Hershberg stirrer was charged with 34.8 g. of freshly distilled indene, 104 g. of chromic oxide and 400 cc. of water. The mixture was stirred vigorously, with ice cooling, and 256 cc. of concentrated sulfuric acid was added in the course of one and one-half hours. The solution was then refluxed for two hours, filtered hot by suction and cooled, when colorless crystals of homophthalic acid separated. The yield of product melting at 174–178° was 32 g. (60%). One crystallization from water raised the m. p. to 177–178.5°.

The half ester, *o*-carboxyphenylacetic methyl ester (m. p. 96–97°), was obtained in 71% yield by Fischer esterification at room temperature, but attempts to convert this substance into the acid chloride by interaction with phosphorus pentachloride, alone or in benzene solution, or with thionyl chloride in ether led only to the production of 3-chloroisocoumarin (II). Thus the product resulting from interaction with phosphorus pentachloride was obtained by distillation and crystallization from carbon tetrachloride in 81% yield in the form of colorless needles melting at 98–98.5°.

Anal. Calcd. for $C_9H_5O_2Cl$: C, 59.88; H, 2.79; Cl, 19.63. Found: C, 59.72; H, 2.83; Cl, 19.55.

The substance was identified by saponification to homo-

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(5) Baker, Banks, Ryan and Mann, *J. Chem. Soc.*, 27 (1945).

(6) Rapson, Shuttleworth and van Niekerk, *ibid.*, 326 (1943); Shuttleworth, Rapson and Stewart, *ibid.*, 71 (1944); Karle and Brockway, THIS JOURNAL, **66**, 1974 (1944); see review by Baker, *J. Chem. Soc.*, 258 (1945).

(7) *Modern Plastics*, **23**, No. 6, 169 (1946).

(8) All melting points are corrected.

(9) Hückel, Danneel, Schwartz and Gercke, *Ann.*, **474**, 121 (1929).

(10) Compare the procedure of Meyer and Vittenet, *Ann. Chim.*, [10] **17**, 272 (1932); *Compt. rend.*, **194**, 1250 (1932).

phthalic acid (m. p. 176–177°) and by comparison with a sample prepared from the free acid.[11]

Attempted Condensation of Homophthalaldehyde with Dicarbethoxy Acetone.—The reaction mixture resulting from the treatment of equivalent amounts of the components with sodium ethoxide in ethanol afforded on fractional crystallization two products that were identified as arising from the self condensation of each component. One, m. p. 126.2–127.1°, proved to be 2-phenylnaphthalenedialdehyde-5,2′[12] (mixed m. p. determination).

Anal. Calcd. for $C_{18}H_{12}O_2$: C, 83.06; H, 4.65. Found: C, 82.95; C, 4.82.

The second substance, m. p. 97.5–99°, was found to be orcinoltricarboxylic ethyl ester, derived from dicarbethoxyacetone[13] (mixed m. p.).

Anal. Calcd. for $C_{16}H_{20}O_8$: C, 56.46; H, 5.92. Found: C, 56.23; H, 6.03.

Synthesis of 1,2,5,6-Dibenzcycloöctatetraene

Starting Materials.—The photobromination of 100 g. of *o*-xylene at 145°[14] afforded 240 g. (61%) of once crystallized ω,ω,ω′,ω′-tetrabromo-*o*-xylene, m. p. 115–116°. Hydrolysis of 150 g. of the tetrabromide with potassium oxalate[14] gave 25 g. (52%) of distilled and crystallized *o*-phthalaldehyde, m. p. 56–57°. ω,ω′-Dibromo-*o*-xylene, prepared[15] in 60% yield (m. p. 94.5–96°), was converted into *o*-phenylenediacetonitrile according to Moore and Thorpe[16] except that an increase in the proportion of water seemed advantageous: 40 g. of dibromide, 27 g. of potassium cyanide in 100 cc. of water, 200 cc. of alcohol; the yield of crystalline material, m. p. 59–60°, was 14.5 g. (20%).

3,8-Dicyano-1,2,5,6-dibenzcycloöctatetraene.—A solution of 3 g. of *o*-phenylenediacetonitrile and 3 g. of *o*-phthalaldehyde in 40 cc. of absolute alcohol was stirred under reflux and 6 cc. of 10% sodium ethoxide in ethanol was run in slowly. The mixture warmed somewhat and darkened, and a solid soon began to separate. After two hours at room temperature, the mixture was cooled in ice and the solid was collected and washed with cold alcohol. The yield of white product, m. p. 210–212°, was 2.6 g. (49%). The isolation of a red by-product from the filtrate is described in the next section. One crystallization of the white product from alcohol gave 2.5 g. (47%) of satisfactory material, m. p. 217.5–218.6°. A crystallographic characterization is as follows[17]: the substance forms elongated crystals showing three pinacoids and having parallel extinction, probably orthorhombic; they are biaxial negative, with $\alpha = 1.625$, β about 1.735, and γ about 1.77.

Anal. Calcd. for $C_{18}H_{10}N_2$: C, 85.02; H, 3.97; N, 11.02; mol. wt., 254.28. Found: C, 84.68; H, 4.03; N, 10.95; mol. wt. (Rast), 270.

The dinitrile is moderately soluble in alcohol, dioxane, or benzene. A solution in purified dioxane and water decolorizes permanganate very readily. No decolorization of bromine in carbon tetrachloride was noted even under illumination with a photoflood bulb, but α,β-diphenylacrylonitrile also failed to react under the same conditions.

Red By-product.—The filtrate from the above reaction mixture on evaporation gave a tarry sirup, and when this was leached with hot alcohol a beautiful crystalline bright red substance was left undissolved and in a state of purity satisfactory for analysis (long slender needles).

Anal. Calcd. for $(C_{18}H_{10}N_2)_n$: C, 85.02; H, 3.97; N, 11.02; mol. wt., $(254.28)_n$. Found: C, 85.56; H, 4.31; N, 11.31; mol. wt. (Rast), 400.

The red substance has very little solubility in the common solvents; 10 cc. of alcohol dissolves about 1 mg. of material at room temperature. A solution in purified dioxane and water decolorized permanganate readily. The spectrum in ethanol is characterized by the following maxima (in mμ; log *E* values in parentheses): 293 (4.83), 307 (4.89), 335 (4.94).

Alcoholysis of the Dinitrile.—A solution of 1 g. of 3,8-dicyano-1,2,5,6-dibenzcycloöctatetraene in 50 cc. of absolute alcohol was treated with hydrogen chloride gas until hot and refluxed for five hours. The solution was filtered from ammonium chloride and evaporated in vacuum, and the residue was taken up in ether and the solution washed with water and then extracted with 10% sodium carbonate solution. The neutral fraction recovered from the ether layer was a colorless, crystalline solid consisting of **3,8-dicarbethoxy-1,2,5,6-dibenzcycloöctatetraene**. After two crystallizations from alcohol the material weighed 1.0 g. (73%) and melted at 118–119° (small diagonal prisms). The substance decolorizes permanganate in dioxane–water.

Anal. Calcd. for $C_{22}H_{20}O_4$: C, 75.85; H, 5.79. Found: C, 76.01; H, 6.00.

The sodium carbonate extract on acidification gave a white solid, and crystallization of this material from alcohol afforded 35 mg. (2.9%) of prisms of **3-carboxy-8-carbethoxy-1,2,5,6-dibenzcycloöctatetraene**, m. p. 228.7–229.8°.

Anal. Calcd. for $C_{20}H_{16}O_4$: C, 74.95; H, 5.04; mol. wt., 320.33. Found: C, 74.92; H, 5.07; neut. equiv., 308.

3-Carboxy-8-carbamido-1,2,5,6-dibenzcycloöctatetraene.—A mixture of 100 mg. of the dinitrile with 15 cc. of 50% sulfuric acid was heated in an oil-bath at 135° for five hours and the solution poured onto ice. A greyish solid was obtained and on crystallization from alcohol yielded 85 mg. of colorless, pointed plates melting at 281–283°.

Anal. Calcd. for $C_{18}H_{13}O_3N$: C, 74.21; H, 4.49; N, 4.86. Found: C, 73.87; H, 4.23; N, 5.02.

1,2,5,6-Dibenzcycloöctatetraene-3,8-dicarboxylic Acid.—A solution of 3.0 g. of the diethyl ester in 25 cc. of alcohol was treated with 40 cc. of 20% sodium hydroxide and refluxed for four and one-half hours. The mixture was diluted, extracted with ether to remove any unchanged ester, and the alkaline solution was run slowly into hydrochloric acid and ice. A solid separated, and on crystallization from aqueous alcohol afforded 2.3 g. of pure diacid as thin plates, m. p. 279–280°. The substance decolorizes permanganate in aqueous dioxane or acetone.

Anal. Calcd. for $C_{18}H_{12}O_4$: C, 73.96; H, 4.11; neut. equiv., 146.14. Found: C, 74.17; H, 4.23; neut. equiv., 142.

Hydrolysis of the monoethyl ester (100 mg.) also afforded the diacid (65 mg., m. p. 279–280.6°).

Decarboxylation to Diphenylsuccindene-10 and 1,2,5,6-Dibenzcycloöctatetraene.—An intimate mixture of 500 mg. of the above 3,8-dicarboxylic acid with 4 g. of copper powder (Baker) that had been washed with benzene and ether and freshly reduced by hydrogen was placed in a sublimation apparatus and covered with a layer of reduced copper. When the mixture was gradually heated, gas evolution commenced at a bath temperature of 260° and continued as the temperature was slowly increased to 295° in the course of forty-five minutes and then stopped, with the production of gas corresponding to 53% of the theoretical amount of carbon dioxide. A yellowish, crystalline deposit on the condenser when crystallized once from alcohol (charcoal) afforded 115 mg. of material m. p. 96–147°. The copper residue when leached with hot alcohol and benzene afforded 20 mg. of unchanged diacid. After repeated crystallization from alcohol, the sublimed material was separated into two fractions. The less soluble fraction afforded pale yellow crystals, m. p. 205.1–206.4°, and sublimation of this product *in vacuo* yielded 35 mg. of **diphenylsuccindene-10**, m. p. 206.5–207.8°.

Anal. Calcd. for $C_{16}H_{12}$: C, 94.07; H, 5.92; mol.

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(11) Davies and Poole, *J. Chem. Soc.*, 1616 (1928).

(12) Baumgarten, *Ber.*, **68**, 1316 (1935).

(13) Cornelius and von Pechmann, *ibid.*, **19**, 1446 (1886).

(14) Thiele and Günther, *Ann.*, **347**, 106 (1906).

(15) Perkin, *J. Chem. Soc.*, **53**, 5 (1888); Perkin and Titley, *ibid.*, **121**, 1565 (1922).

(16) Moore and Thorpe, *ibid.*, **93**, 175 (1908).

(17) Kindly conducted by Miss E. J. Weichel, through the courtesy of Dr. C. D. West of the Polaroid Corporation.

wt., 204.26. Found: C, 94.05; H, 5.95; mol. wt. (Rast), 215.

The product did not depress the melting point of a sample of diphenylsuccindene-10, m. p. 205.4–207.8°, prepared essentially according to Brand and Müller[4]; the final reduction of 9,12-dichlorodiphenylsuccindadiene-9,12 was conducted with zinc dust in refluxing acetic acid solution (37% yield of crystallized product; found: C, 94.02; H, 6.00; absorption spectrum in ethanol: max. 310 mμ, log *E* 4.56).

From the more soluble fraction there was obtained 60 mg. of **1,2,5,6-dibenzcycloöctatetraene** in the form of colorless crystals, m. p. 106.8–108.1°. A crystallographic examination[20] indicated acicular crystals showing parallel and 45° extinction and probably monoclinic; they are biaxial positive with α near $\beta = 1.678$, $\gamma > 1.76$, moderate 2 v.

Anal. Calcd. for $C_{16}H_{12}$: C, 94.07; H, 5.92; mol. wt., 204.26. Found: C, 94.05; H, 5.90; mol. wt. (Rast), 212.

The hydrocarbon gave distinct melting point depressions when mixed with diphenylsuccindane and with dihydroanthracene. The substance readily decolorizes permanganate solution and a solution of bromine in carbon tetrachloride. Solutions in benzene are fluorescent. The hydrocarbon apparently does not form a picrate.

Other Decarboxylation Experiments.—Several further trials were made in an endeavor to improve the yield of the desired product and to determine how the by-product arises. In an experiment conducted as just described but with rigid control of the temperature to 260–265°, dibenzcycloöctatetraene was the sole product but the yield was no better. Decarboxylation of 200 mg. of diacid with freshly reduced copper powder in quinoline solution at 225–245° (forty-five minutes) afforded 26 mg. (19%) of dibenzcycloöctatetraene, m. p. 106–108°; the hydrocarbon was obtained in about the same yield when the reaction was conducted in a sealed tube at 285°, and no diphenylsuccindene was detected in either instance. Decarboxylation in quinaldine at 240–250° gave similar results (16% yield of material melting at 100–103°). Trials in a subliming apparatus with reduced copper or with basic copper carbonate as catalyst resulted in the formation of both isomers in low yields.

The best results were obtained with copper chromite catalyst as follows. A mixture of 1 g. of the diacid with 2 g. of copper chromite catalyst 39KAF, layered with 1 g. of catalyst, was placed in a 25-cc. flask connected by a ground-glass joint and a right-angle tube to a receiving flask cooled in a dry ice-bath. Moderate suction was applied to the system and the temperature of the reaction mixture was raised to 260–300° for one hour. A crystalline product that collected in the receiver was crystallized from alcohol and afforded 150 mg. (22%) of colorless needles of 1,2,5,6-dibenzcycloöctatetraene, m. p. 107.2–108.8°. Decidedly less satisfactory results were obtained with the same catalyst and a solution of the diacid in 2,6-dimethylquinoline or in 1,6-dimethylnaphthalene.

1,2,5,6-Dibenzcycloöctadiene-1,5.—Dibenzcycloöctatetraene (76 mg.) was hydrogenated in absolute alcohol (30 cc.) in the presence of Adams catalyst (100 mg.) at a pressure of 2300 lb. (five hours). When the filtered solution was concentrated and diluted with a few drops of water the product separated in colorless, rectangular crystals, m. p. 106–109°; yield 50 mg. (65%). Recrystallization from ligroin (30–60°) raised the melting point to 108.5–110°. Mixtures with the starting material and with diphenylsuccindane showed definite depressions in melting point. A mixture with a sample of the known *s*-dibenzcycloöctadiene[6] that became available after the completion of this work melted at 108.5–110°.

Anal. Calcd. for $C_{16}H_{16}$: C, 92.24; H, 7.75; mol. wt., 208.29. Found: C, 91.88; H, 8.00; mol. wt. (Rast), 197.

Diphenylsuccindane.[18]—This hydrocarbon was prepared for purposes of comparison, both by the hydrogenation of diphenylsuccindene-10, as reported by Brand and Müller,[4] and by the Clemmensen–Martin reduction of diphenylsuccindanedione-9,12; the yield from 3.8 g. of diketone was 2.7 g. (80%); m. p. 102.8–104°.

Summary

1,2,5,6-Dibenzcycloöctatetraene has been synthesized from *o*-phthalaldehyde and *o*-phenylenediacetonitrile and found to be chemically reactive. The spectra of the hydrocarbon and two of its derivatives show evidence of at most only partial conjugation between the benzene rings and the free double bonds, and it is concluded that the eight-membered ring is non-planar and hence incapable of full resonance stabilization.

[18] Roser, *Ann.*, **247**, 153 (1888).

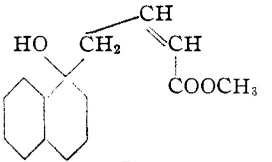
CAMBRIDGE, MASSACHUSETTS RECEIVED JULY 31, 1946

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

Synthesis of 1-Keto-$\Delta^{4a,10a}$-dodecahydrophenanthrene, *cis*-9-Methyl-1-decalone, and other Cyclic Ketones

BY W. E. BACHMANN AND N. L. WENDLER[1]

The unsaturated hydroxy ester I was prepared from 1-decalone, zinc and methyl γ-bromocrotonate.[2] In order to avoid the formation of a dienic ester,[3] the Reformatsky reaction was carried out in a mixture of equal volumes of ether and benzene at about 60°. The unsaturated hydroxy ester was reduced catalytically over Raney nickel in methanol, and the product was dehydrated and hydrolyzed to what is probably γ-($\Delta^{1,2}$-octahydro-1-naphthyl)-butyric acid (II). A sample of this acid was readily dehydrogenated to the known



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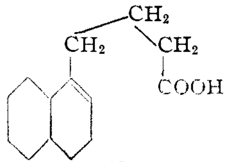

II

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[1] From the Ph.D. dissertation of N. L. Wendler, 1944.

[2] Ziegler, *et al.* [*Ann.*, **551**, 80, 120 (1942)] describe an elegant method of preparing methyl γ-bromocrotonate and its application in the Reformatsky reaction. See also Schmid and Karrer, *Helv. Chim. Acta*, **29**, 573 (1946).

[3] Fuson and his co-workers [Fuson, Arnold and Cooke, THIS JOURNAL, **60**, 2272 (1938); Fuson and Southwick, *ibid.*, **66**, 679 (1944)], who made the important discovery that methyl γ-iodocrotonate can be used in the Reformatsky reaction, prepared the dienic ester rather than the hydroxy ester from the reaction with cyclohexanone in boiling benzene. See also Cook and Schoental, *J. Chem. Soc.*, 289 (1945).