Attempted Reaction of 1-Butene with 3,5-Dinitrobenzoic Acid.—A slow stream of 1-butene was passed through a saturated solution of the acid in toluene for six hours. The mixture was poured into water, the mixture extracted with ether, the ether washed with aq. sodium hydroxide (5%) and the ether dried and evaporated. The infrared spectrum of the trace of residue was devoid of bands in the carbonyl region.

Ester Interchange Experiments.—One gram of isobutyl 3,5-dinitrobenzoate was dissolved in 15 ml. of glacial acetic acid at 25°. After three days, the solution was poured into water, the esters extracted with ether, the ether solution washed with aqueous sodium carbonate (5%), the ether dried and evaporated, and the residue held at 100° and 0.01 mm. for one hr. (to remove the volatile acetate). The residue weighed 0.97 g. (97%) and the infrared spectrum was identical with that of pure isobutyl 3,5-dinitrobenzoate. In a similar experiment (with acetic acid as solvent (115° for one hour)), 94% of the isobutyl 3,5-dinitrobenzoate was recovered.

The nitrosoamides apparently do not undergo acyl interchange, since N-nitroso-3,5-dinitrobenzamides can be prepared in 95% yield from the corresponding amides and nitrogen tetroxide[40] in acetic acid.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE McPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

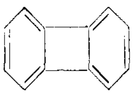
Condensed Cyclobutane Aromatic Systems. I. The Synthesis of 1,2-Benzobiphenylene and 1,2-Binaphthylene[1]

BY M. P. CAVA AND J. F. STUCKER

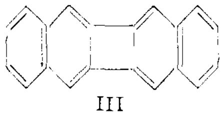
RECEIVED MAY 17, 1955

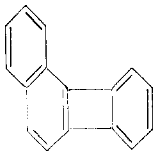
Two new benzo derivatives of biphenylene, 1,2-benzobiphenylene (IV) and 1,2-binaphthylene (V), have been synthesized using 1-(2-aminophenyl)-2-naphthylamine (VI) and 2,2′-diamino-1,1′-binaphthyl (XVI), respectively, as starting materials. Some chemical and physical properties of these hydrocarbons are described.

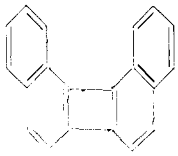
The hydrocarbon biphenylene (I) is a substance of considerable theoretical interest since it may be considered as the dibenzo derivative of the unknown and elusive cyclobutadiene (II). Biphenylene has been prepared by three different methods: (1) pyrolysis of 2,2′-dibromobiphenyl or, better, of biphenyleneiodonium iodide with cuprous oxide,[2] (2) treatment of the Grignard reagent of 2,2′-dibromobiphenyl with cupric chloride[3] and (3) pyrolysis of biphenylyl mercury with silver powder.[4] Although several substitution products of biphenylene are known,[5] only one other polynuclear aromatic system has been reported which contains a cyclobutadiene nucleus, that is, 2,3,6,7-dibenzobiphenylene or 2,3-binaphthylene (III).[6] As a part of a general program to prepare other such systems, we have now synthesized 1,2-benzobiphenylene (IV) and 1,2,7,8-dibenzobiphenylene or 1,2-binaphthylene (V).


I


II


III


IV


V

The starting material for the preparation of IV was 1-(2-aminophenyl)-2-naphthylamine (VI), which is obtained as a by-product in the preparation of 1,2-benzocarbazole from 2-naphthol and phenylhydrazine in the presence of sulfur dioxide.[7] In spite of its indirect mode of formation, the structure of this diamine is known with certainty because of its conversion to 1,2-benzocarbazole by sulfurous acid, and by its deamination to[7] 1-phenylnaphthalene (VII). Tetrazotization of VI in the usual manner gave a solution which reacted with sodium iodide to produce a 12% yield of crude 1,2-benzobiphenyleneiodonium iodide (VIII) as well as a 17% yield of 1-(2-iodophenyl)-2-iodonaphthalene (IX). When the iodonium iodide was pyrolyzed with cuprous oxide under the general conditions used to prepare biphenylene itself[5b] IV could be isolated in 6% yield as its black, sparingly soluble 2,4,7-trinitrofluorenone complex X. Pyrolysis of the diiodide IX in the same manner gave a product from which the same complex X was prepared in 63% yield, a remarkably high yield for the formation of a biphenylene type system. The exact nature of the cuprous oxide used was found to be a critical factor in the reaction. High yields were obtained only with one particular lot of Baker C.P. reagent, and with a sample prepared by the hydrazine reduction of cupric acetate.[8]

The diiodide IX reacted readily with lithium to give a solution of the dilithium derivative XI. The addition of mercuric chloride to this solution gave, in 65% yield, 3,4-benzobiphenylylmercury (XII). When XII was heated to 360° with silver powder a sublimate was produced from which, after treatment with 2,4,7-trinitrofluorenone, the black X was obtained in 17% yield.

Regeneration of the free hydrocarbon from X by chromatography on alumina gave an essentially quantitative recovery of pure IV as bright yellow

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[1] From the M.S. thesis of J. F. Stucker, The Ohio State University, 1955. A preliminary note concerning 1,2-binaphthylene has appeared in *Chem. and Ind.*, 446 (1955). The remainder of this work was presented before the Division of Organic Chemistry at Cincinnati, Ohio, March, 1955.

(2) W. C. Lothrop, THIS JOURNAL, **63**, 1187 (1941).

(3) W. S. Rapson and R. G. Shuttleworth, *J. Chem. Soc.*, 326 (1943).

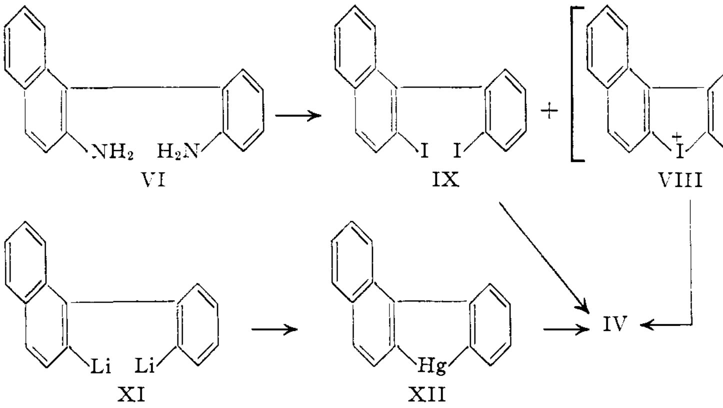
(4) G. Wittig and W. Hertig, *Ber.*, **87**, 1511 (1954).

(5) (a) W. C. Lothrop, THIS JOURNAL, **64**, 1698 (1942); (b) W. Baker, M. P. V. Boarland and J. F. W. Mc Omie, *J. Chem. Soc.*, 1476 (1954).

(6) R. F. Curtis and G. Viswanath, *Chem. and Ind.*, 1174 (1954).

(7) W. Fuchs and F. Niszel, *Ber.*, **60**, 209 (1927).

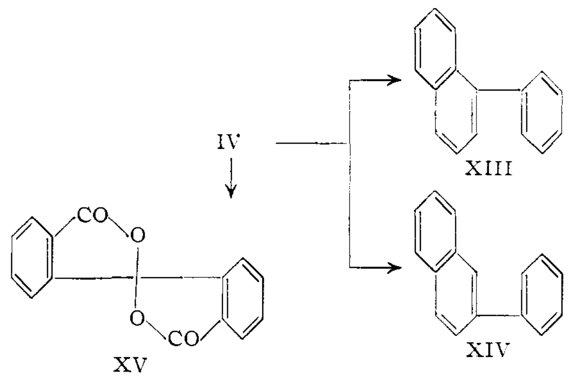
(8) G. Brauer, "Handbuch der Preparativen Anorganischen Chemie," Ferdinand Enke Verlag, Stuttgart, 1954, p. 755.



needles, m.p. 72.0–72.8°, which possess a faint but persistent rose-like odor. The new compound is very soluble in the common organic solvents and sublimes unchanged under vacuum at temperatures of 100° or over. Samples of IV have been kept for many months in the dark at room temperature in air-filled containers with no signs of decomposition. The compound is, however, slowly destroyed by light. A dilute ethanolic solution was completely bleached of its original yellow color after a number of hours of irradiation with an ultraviolet lamp. The nature of the product formed has not yet been determined.

The ultraviolet absorption spectrum of IV (Fig. 1) is rather complex, seven maxima of considerable intensity being observed. The general shape of the curve strongly resembles that of biphenylene.[5b] In addition, all of the maxima except those at 278 and 291 mμ actually correspond to maxima in the biphenylene spectrum, although the entire spectrum of IV is shifted to longer wave lengths.

Since the Raney nickel reduction of biphenylene[5b] produces biphenyl, and a similar reduction of 2,3-binaphthylene[6] gives 2,2′-binaphthyl, it would be expected that the analogous cleavage of 1,2-benzobiphenylene would produce 1-phenylnaphthalene (XIII), 2-phenylnaphthalene (XIV) or a mixture of XIII and XIV. Actually a mixture of the two isomers was formed. This was separated readily into its components by taking advantage of the fact that XIV forms a 2,4,7-trinitrofluorenone complex whereas XIII forms none.[9] The isolation of these reduction products confirms the structure of IV.



Also in accordance with the assigned structure was the result of a chromic acid oxidation of IV. The only product isolated was the dilactone of benzophenone 2,2′-dicarboxylic acid (XV).

The most logical starting material for the synthesis of 1,2-binaphthylene (V) appeared to be 2,2′-diamino-1,1′-binaphthyl (XVI), a compound which can be prepared readily from 2-naphthylamine.[10] The conversion of XVI *via* its tetrazonium chloride to 2,2′-diiodo-1,1′-binaphthyl (XVII) has been described previously,[11] no yield being reported: by modifying the isolation technique, XVII was obtained in 18% yield. The pyrolysis of XVII with cuprous oxide gave an orange solid from which a deep purple 2,4,7-trinitrofluorenone complex (XVIII) was prepared. The average yield in a series of seventy experiments was 5.65%, but the yields in individual runs were very variable, even when the most active samples of cuprous oxide available were employed.

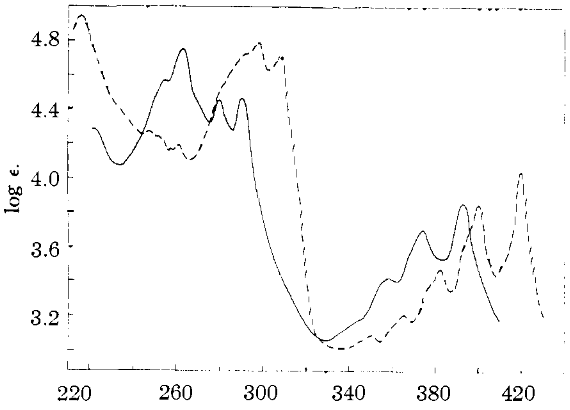


Fig. 1.———, 1,2-benzobiphenylene; – – –, 1,2-binaphthylene (solvent 95% EtOH).

When a solution of the analytically pure complex XVIII in benzene was chromatographed on alumina and the deep orange-red eluate evaporated under reduced pressure on a steam-bath, V crystallized out, but contaminated by a small amount of an amorphous decomposition product. Pure V was obtained by washing out the impurity with a little benzene, but the recovery from the complex was then only 31%. The new hydrocarbon V formed deep red needles, m.p. 136.8–138.9°. It was odorless, and dissolved readily in benzene or chloroform, but only to a small extent in methanol or petroleum ether. Its ultraviolet absorption spectrum (Fig. 1) exhibits eleven maxima. The general shape of the curve resembles that of IV, but as expected, the curve of V is shifted to longer wave lengths.

The general properties of V are those of a highly unsaturated system. Whereas the pale yellow isomer III sublimes at 275° with only slight decom-

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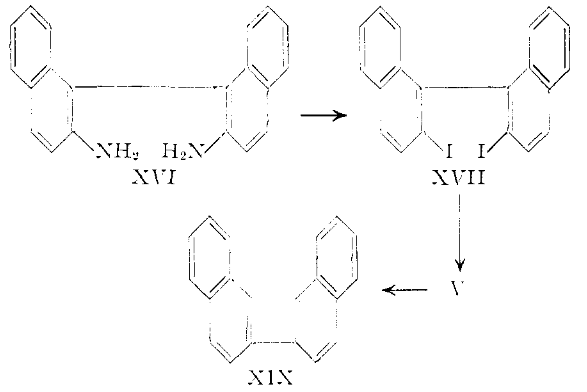
(9) R. Huisgen and G. Sorge, *Ann.*, **566**, 162 (1950).

(10) J. W. Cook, C. L. Hewett, E. L. Kennaway and N. M. Kennaway, *Am. J. Cancer*, **40**, 62 (1940).

(11) L. Mascarelli and G. Brusa, *Atti. Acad. Lincei* **22**, 494 (1913).

position,[6] an attempt to sublime V under vacuum at 160° led to complete conversion to a dark brown polymeric gum. Although dilute solutions of V were quite stable to air at room temperature in the dark,[12] boiling an ethanolic solution in darkness for one hour caused extensive decomposition. Solutions of V were much more sensitive to light than those of IV, being completely bleached by 20 minutes exposure to an ultraviolet lamp.

The Raney nickel reduction of V gave a product from which only 2,2′-binaphthyl (XIX) could be isolated. The formation of this one compound, however, confirms the structure of V, which was prepared from known derivatives of the isomeric 1,1′-binaphthyl.



Experimental[13]

1-(2-Aminophenyl)-2-naphthylamine (VI).—This amine was prepared by the method of Fuchs and Niszel[7] the following modification of which gave higher yields of diamine than previously obtained.

Sulfur dioxide was passed through a mixture of 70 ml. of phenylhydrazine and 500 ml. of water until the precipitate which first separated dissolved completely. After adding 70 g. of 2-naphthol the mixture was heated under reflux for 24 hours on a steam-bath. The solution was then cooled in an ice-bath and the precipitate was filtered off and washed with water. The solid was extracted three times with cold dilute hydrochloric acid, and the cold filtered extracts were made basic with aqueous ammonia. The curdy white precipitate was filtered off and recrystallized from aqueous ethanol to give the diamine as colorless needles, m.p. 155° (reported[7] 154°): yield 16.8 g. (15%, based on the 2-naphthol used). In some runs, carried out under apparently similar conditions, the yield was only 7%.

1-(2-Iodophenyl)-2-iodonaphthalene (IX) and 1,2-Benzobiphenyleneiodonium Iodide (VIII).—To an ice-cold solution of 1.94 g. of VI in 20 ml. of water and 9 ml. of concd. hydrochloric acid was added slowly and with stirring a solution of 1.2 g. of sodium nitrite in 5 ml. of water. After 15 minutes in the cold there was added an ice-cold solution of 10 g. of sodium iodide in 100 ml. of water. The solution was held in an ice-bath for one hour and then allowed to warm up to room temperature. Sodium bisulfite was added and the suspension warmed gently on the steam-bath to reduce any iodine present. The yellow brown precipitate was filtered off, washed with water and dried under vacuum. The dry powder was extracted for 2.5 hr. in a Soxhlet apparatus with Skellysolve F. Further extraction of the residue with ether left 0.420 g. (12.4%) of crude VIII as an amorphous brown powder, m.p. 129–134°.

Anal. Calcd. for $C_{16}H_{10}I_2$: I, 55.70. Found: I, 56.95.

The Skellysolve F extract contained 1.2 g. of a red oil, which was dissolved in cyclohexane and adsorbed on a column of alumina. Elution of the column with a large volume of cyclohexane gave, after evaporation of the eluate, a white solid residue of IX. After three crystallizations from cyclohexane–Skellysolve F it formed colorless needles, m.p. 99–101°: yield 0.650 g. (17%).

Anal. Calcd. for $C_{16}H_{10}I_2$: C, 42.10; H, 2.20; I, 55.70. Found: C, 42.36; H, 2.33; I, 55.50.

On larger scale preparations, a slightly less pure material (m.p. 89–92°) was obtained more conveniently by continuous elution of the alumina in a Soxhlet apparatus with Skellysolve F.

3,4-Benzobiphenylenemercury (XII).—To a solution of 1.5 g. of 1-(2-iodophenyl)-2-iodonaphthalene in 20 ml. of diethyl ether was added 0.21 g. of lithium. The solution turned dark red almost immediately. After heating for 40 minutes, 0.71 g. of mercuric chloride dissolved in 35 ml. of ether was added. The gray precipitate which was formed immediately was filtered off and washed with ether. The yield of gray powder was 0.871 g. (65.9%), m.p. 288–290°. Recrystallization from a methylene chloride–methanol mixture gave a white powder, m.p. 282–285°. Analysis indicated that the compound was not completely pure.

Anal. Calcd. for $C_{16}H_{10}Hg$: C, 49.75; H, 2.48. Found: C, 48.35; H, 2.70.

1,2-Benzobiphenylene–2,4,7-Trinitrofluorenone Complex (X). A. **From Diiodide IX.**—A mixture of IX (0.410 g.) and cuprous oxide (7.5 g.) was ground together thoroughly in a mortar and placed in a side-arm test-tube provided with a cold finger condenser. The air in the tube was replaced by nitrogen and the system was evacuated to 3.5 mm. pressure. The tube was placed in a salt-bath preheated to 330°. The heating was continued for 35 minutes, during which time the temperature of the bath was raised to 365°. The tube was cooled and the yellow solid which had collected on the cold finger was washed off with benzene, the washings being added to a concentrated solution of 2,4,7-trinitrofluorenone in benzene. The solution became deep brown and a dark crystalline precipitate separated. After three crystallizations from benzene–methanol X formed a voluminous charcoal-black mass of tiny needles, m.p. 201.5–202.5°; yield 0.296 g. (63%).

Anal. Calcd. for $C_{29}H_{25}O_7N_3$: N, 8.12. Found: N, 7.83.

B. **From Iodonium Iodide (VIII).**—When VIII (0.420 g.) was pyrolyzed with cuprous oxide in the manner described for IX, the yield of black complex X was only 0.025 g. (6.4%). After recrystallization from benzene–methanol it melted at 200–202°; the melting point was not depressed by a sample of X prepared from IX.

C. **From Mercury Compound XII.**—A well-ground mixture of XII (0.150 g.) and silver powder[14] (1.5 g.) was placed in a side-arm test-tube provided with a cold finger. The mixture was covered with silver powder (1.0 g.), and the test-tube was flushed with nitrogen, then evacuated to 3.5 mm. pressure and placed in a bath preheated to 340°. A yellow color formed on the cold finger almost immediately. After 30 minutes, when the temperature had risen to 360°, the cold finger was washed with benzene and the filtered solution added to a concentrated solution of 2,4,7-trinitrofluorenone in benzene. The yield of complex X, m.p. 200–203°, was 0.032 g. (16.8%). The melting point was not depressed by a sample of X prepared from IX.

1,2-Benzobiphenylene (IV).—The complex X was decomposed into its constituents by passing its solution in benzene through a column of alumina. The clear yellow filtrate was blown down with a stream of nitrogen on a steam-bath and the residue was sublimed in a cold finger sublimer on a steam-bath at 3 mm. pressure. 1,2-Benzobiphenylene collected on the cold finger as bright yellow feathery needles, m.p. 72.0–72.8°, which possess a pleasant rose-like odor; the yield from the complex was almost quantitative.

Anal. Calcd. for $C_{16}H_{10}$: C, 95.05; H, 4.95. Found: C, 94.74; H, 5.09.

The infrared spectrum was determined in carbon bisulfide solution and exhibited medium or low intensity bands at 3.24, 3.43, 3.64, 7.12, 7.37, 7.76, 8.02, 8.33, 8.55, 8.76, 8.98, 9.18, 9.96, 10.28, 10.57, 11.07, 11.44 and 11.74 μ. In addition, three bands of rather high intensity were observed at 12.38, 13.41 and 13.64 μ.

The ultraviolet spectrum was determined in 95% ethanol and the following maxima were found.

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(12) Determined by the constancy of the ultraviolet spectrum.

(13) All melting points are corrected. Analyses were carried out by Galbraith Laboratories, Knoxville, Tennessee.

(14) Prepared by the alkaline formaldehyde reduction of silver nitrate.

λmax (mμ)	log E	λmax (mμ)	log E
254	4.58	359	3.41
262	4.77	375	3.71
279	4.47	393	3.87
291	4.48		

Reduction of 1,2-Benzobiphenylene.—To a solution of 0.076 g. of pure IV in 15 ml. of methanol was added 2 ml. of a suspension of freshly prepared Raney nickel catalyst[15] in methanol. The solution was refluxed for 15 minutes and then filtered. The colorless filtrate was concentrated to a small volume and treated with an excess of 2,4,7-trinitrofluorenone in ethanol to give 0.040 g. (21%) of the yellow-orange crystalline trinitrofluorenone complex of 2-phenylnaphthalene (XIV). After several recrystallizations from alcohol it melted at 169.5–170.5°. A sample of the complex prepared from an authentic sample of 2-phenylnaphthalene[16] melted at 169.8–170.4° (reported[9] 168–169°) and the melting point of a mixture of both samples of complex was 169.5–170.5°. The complex derived from the reduction mixture was dissolved in benzene, passed through a column of alumina, and the filtrate evaporated to yield, after crystallization from aqueous methanol, 2-phenylnaphthalene, m.p. 100–102°. A sample of this product, when mixed with authentic 2-phenylnaphthalene (m.p. 102.4–103.2°) melted at 100–103°. In addition, the ultraviolet absorption spectra of both samples of hydrocarbon were identical.

The mother liquors from the Raney nickel reduction, after removal of all of the 2-phenylnaphthalene as trinitrofluorenone complex, were evaporated and the residue was dissolved in benzene and chromatographed on alumina to yield 0.038 g. (50%) of 1-phenylnaphthalene as a viscous, colorless oil. The ultraviolet spectrum of this material was in good agreement with that previously reported for 1-phenylnaphthalene.[17]

TABLE I

ULTRAVIOLET ABSORPTION MAXIMA OF 1-PHENYLNAPHTHALENE

Material from Raney nickel reduction (95% ethanol)		1-Phenylnaphthalene (cyclohexane)[17]	
$\lambda_{\max}$ (mμ)	log E	$\lambda_{\max}$ (mμ)	log E
226	4.60	226	4.80
287	3.79	288	4.03

Oxidation of 1,2-Benzobiphenylene.—To a solution of IV (0.100 g.) in 10 ml. of glacial acetic acid was added chromic oxide (0.390 g.) in 20 ml. of acetic acid. After refluxing for one hour, the acetic acid was distilled off leaving a dark green gum. Concentrated hydrochloric acid (25 ml.) was then added and the solution was boiled for a few minutes. After cooling and adding 5 ml. of water to the solution, a white precipitate was formed. The white precipitate was filtered off and sublimed at a bath temperature of 215° under a pressure of 3 mm. of mercury. The light yellow solid which formed on the cold finger was scraped off and recrystallized from hot absolute ethanol. The white needles (0.007 g., 5.6%) melted at 208–210°. The mixed melting point with an authentic sample of the dilactone of benzophenone-2,2′-dicarboxylic acid (XV), made by oxidizing 2,2′-dimethylbenzophenone, was also 208–210°. In addition the infrared spectra in chloroform of the two samples were identical.

2,2′-Diiodo-1,1′-binaphthyl (XVII).—To an ice-cold solution of 14 g. of XVI[10] in 53 ml. of concentrated hydrochloric acid and 120 ml. of water was added slowly a solution of 7 g. of sodium nitrite in 25 ml. of ice-water. After standing in an ice-bath for 15 minutes, a solution of 58 g. of sodium iodide in 580 ml. of ice-water was added rapidly. The solution was held at ice-bath temperature for 30 minutes and then allowed to warm to room temperature. Excess sodium bisulfite was then added to destroy any iodine present and the suspension was heated on a steam-bath to 70°. The yellow brown powder was filtered off, washed with water, and dried in a vacuum desiccator. The powder was then extracted in a Soxhlet apparatus with Skellysolve F for 8 hours giving 8.4 g. of a red solid. The solid was then dissolved in cyclohexane and adsorbed on a column of alumina. The alumina was extracted for 18 hours with Skellysolve F in a Soxhlet apparatus, giving 4.5 g. (18.1%) of orange colored crystals of diiodide, m.p. 213–216° (reported[11] 224–225°). A sample which was sublimed and crystallized from benzene–methanol melted at 222–225°.

1,2-Binaphthylene.—A well-ground mixture of XVII (0.200 g.) and cuprous oxide (7.5 g.) was covered with additional cuprous oxide (7.5 g.) after being placed in a side-arm test-tube provided with a cold finger condenser. The air in the tube was replaced with nitrogen and the system was evacuated to 3.5 mm. pressure. The tube was then placed in a salt-bath preheated to 230°. The heating was continued for 30 minutes during which time the temperature of the bath was raised to 330°. After cooling, the red solid on the cold finger was washed off with benzene and added to a concentrated solution of 2,4,7-trinitrofluorenone in benzene. On addition of methanol, a dark purple crystalline precipitate formed. The above procedure was repeated 70 times, giving an average yield of 5.65% of twice recrystallized complex XVIII, m.p. 205.0–206.0°.

Anal. Calcd. for $C_{33}H_{17}O_7N_3$: C, 69.84; H, 3.00; N, 7.41. Found: C, 69.97; H, 2.84; N, 7.42.

The trinitrofluorenone complex was decomposed into its constituents by passing its solution in benzene through a column of alumina. The dark red eluant was evaporated to a small volume on a steam-bath under a water pump vacuum. On adding Skellysolve F, dark red needle crystals with an amorphous brown coating were formed. Moistening this solid with benzene on a filter paper and sucking dry left the deep red needles of 1,2-binaphthylene. The yield of pure hydrocarbon from 0.150 g. of complex was 0.021 g. (31.3%), m.p. 136.8–138.9°.

Anal. Calcd. for $C_{20}H_{12}$: C, 95.24; H, 4.76. Found: C, 95.06; H, 4.75.

A Nujol mull infrared spectrum showed low or medium intensity bands at 5.93, 6.28, 6.38, 7.35, 7.84, 8.11, 8.25, 8.36, 8.48, 8.66, 8.72, 9.15, 9.98, 10.60, 10.80, 11.80, 12.19, 12.35 and 14.98. There were also three high intensity bands at 12.50, 13.22 and 13.78 μ.

The ultraviolet spectrum was determined in 95% ethanol and the following maxima were obtained.

λmax (mμ)	log E	λmax (mμ)	log E
216	4.94	350	3.08
247	4.26	365	3.20
257	4.17	382	3.47
261	4.20	400	3.86
298	4.79	420	3.05
308	4.72		

Reduction of 1,2-Binaphthylene.—To a solution of V (0.076 g.) in 15 ml. of methanol was added 2 ml. of an ethanolic Raney nickel suspension.[15] The red color was destroyed almost immediately leaving a yellow solution the color of which was not destroyed by refluxing for 15 minutes. The yellow filtrate was evaporated to dryness, dissolved in benzene, and added to a concentrated solution of 2,4,7-trinitrofluorenone in benzene. A red complex (0.022 g.) formed which, after recrystallization from a benzene–methanol mixture, melted at 168–170°. A sample of complex prepared from authentic 2,2′-binaphthyl[16] had a melting point of 168–170° (reported[18] 170.6–171.0°), and did not depress the melting point of the sample prepared from the reduction mixture. In addition, this latter complex was separated into its constituents by passing through a column of alumina in benzene, evaporating the eluate to dryness, and recrystallizing from a benzene–methanol mixture. White crystals of 2,2′-binaphthyl (0.004 g.) were obtained, m.p. 185–187°. The mixed melting point with authentic 2,2′-binaphthyl (m.p. 186.6–188.5°) was 185–187°.

The mother liquors from the reduction, after removal of 2,2′-binaphthyl as the complex, were chromatographed through a column of alumina in benzene to remove the excess trinitrofluorenone. The eluant was light yellow colored and all attempts to crystallize it failed. An authentic

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[15] R. Mozingo, *Org. Syntheses*, **21**, 15 (1941).

[16] We should like to thank Prof. M. S. Newman of this department for kindly supplying us with this sample.

[17] R. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 290.

[18] M. Orchin and E. O. Woolfolk, THIS JOURNAL, **68**, 1727 (1946).

sample of 1,1'-binaphthyl[19] was recovered unchanged when subjected to the conditions used to reduce 1,2-binaphthylene.

COLUMBUS 10, OHIO

[19] Kindly supplied by Mr. Daniel Lednicer.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE FLORIDA STATE UNIVERSITY]

Cyclopropanes: The Cyclopropyl Carbanion[1,2]

BY H. M. WALBORSKY AND F. M. HORNYAK

RECEIVED MAY 6, 1955

2,2-Diphenylcyclopropanecarboxylic acid was prepared by the condensation of 1,1-diphenylethylene with ethyl diazoacetate and by the condensation of methyl acrylate with diphenyldiazomethane. The acid was resolved into its enantiomorphs and converted to optically active 2,2-diphenylcyclopropyl cyanide. The optically active cyanide derivative underwent facile racemization when treated with lithium diisopropylamide. The cyclopropyl carbanion was unable to retain its geometric configuration.

Introduction

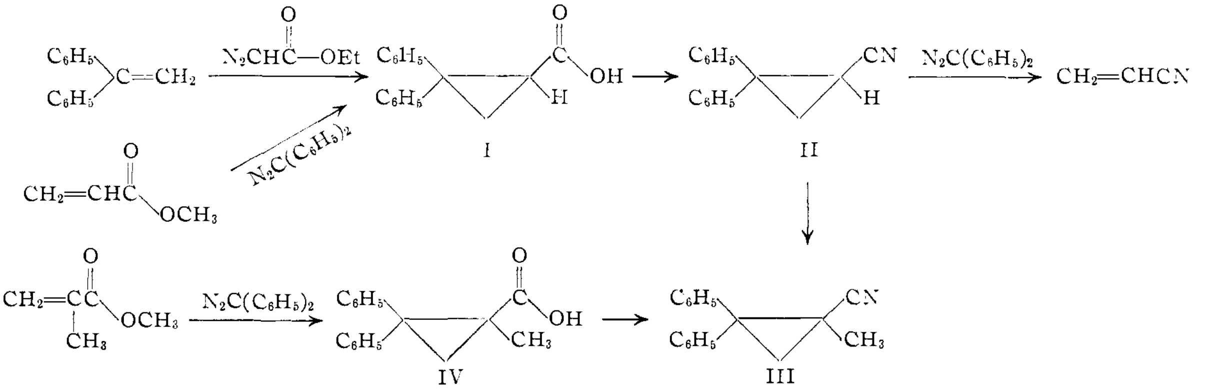
Many claims for the existence of optically stable carbanions have appeared in the literature. In nearly all cases, subsequent work has shown these reports to be in error. It had been reported that 2-nitrobutane[3] and 2-nitroöctane[4] gave, on treatment with base, optically active salts. Kornblum[5] and Theilacker[6] demonstrated that the activity was due to an alkyl nitrate contaminant and that nitro compounds formed inactive salts.

Wallis and Adams[7] reported that optically active 12-phenyl-12-B-benzoxanthenethioglycolic acid on treatment with sodium and liquid ammonia yielded optically active 12-phenyl-B-benzoxanthene. It was believed that the desulfurization reaction involved a carbanion intermediate which retained its asymmetry. Wittig and co-workers[8] repeated the work but could not duplicate the results.

The only case of an optically active carbanion which has not been refuted is found in a communication by Letsinger[9] who described the production of an optically active acid from the reaction of optically active 2-iodoöctane with *sec*-butyllithium and subsequent carbonation of the lithium exchange product.

Many other experiments have demonstrated that carbanions which can resonate with an adjacent group cannot retain optical activity such as the racemization of 2-dimethylamine-9-methylfluorene by lithium,[10] methylethylacetonitrile by lithium diethylamide,[11] and the facile racemization of ethyl ethylmethylacetate by sodium ethylate.[12]

In all of the above cases there are no obvious barriers to the planarity and, therefore, to the racemization of the intermediate carbanion. Thus it became of interest to prepare a molecule whose carbanion would possess a barrier to planarity and to determine whether or not this carbanion could retain its configuration. To this end the synthesis of optically active 2,2-diphenylcyclopropylcyanide (II) was undertaken.



2,2-Diphenylcyclopropyl Cyanide.—A successful synthesis of 2,2-diphenylcyclopropanecarboxylic acid (I) from ethyl diazoacetate and 1,1-diphenylethylene was accomplished in 46% yield using a procedure similar to that of Drake and Sweeney.[13] Previous syntheses of this acid gave yields of 5–7%.[14] It was found that purity of the product was enhanced by using freshly prepared ethyl diazoacetate and controlling the saponification time of the ester.

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[1] This paper is based on a portion of the thesis submitted by F. M. Hornyak in 1955 to the Florida State University in partial fulfillment of the requirements for the Ph.D. degree in Chemistry.

[2] Presented in part at the 126th Meeting of the American Chemical Society, New York, N. Y., September, 1954.

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