product boiled at 112–114° (0.1 mm.); yield 5.6 g. (72%); m.p. 22–24° after recrystallization from aqueous ethanol.

From 6-Dimethylaminomethylguaiacol (Ib).—A solution of 18.1 g. (0.1 mole) of Ib in 50 ml. of acetic anhydride was refluxed for six hours and then poured into 300 ml. of water. The product, isolated as described above, boiled at 110–112° (0.05 mm.) and weighed 20.7 g. (87%). When recrystallized from aqueous ethanol and redistilled for analysis it melted at 23–25° and did not depress the melting point of the authentic specimen described above.

Anal. Calcd. for $C_{12}H_{14}O_5$: C, 60.49; H, 5.92; sapn. equiv., 119. Found: C, 60.33; H, 6.10; sapn. equiv., 120.

From 6-Piperidinomethylguaiacol (Ia).—When 6.6 g. of Ia and 15 ml. of acetic anhydride were refluxed for four hours and the reaction mixture was worked up as described before, 4.1 g. (58%) of material melting at 22–24° was obtained. The mixed melting point of this material with *o*-vanillyl diacetate (above) was not depressed.

Catalytic Reduction of 6-Dimethylaminomethylguaiacol (Ib).—Nine grams of Ib, dissolved in 50 ml. of dioxane, was reduced at 150–175° and an initial pressure of 2600 p.s.i. in the presence of 5 g. of copper chromite.[2b,12] The catalyst was removed by filtration and the solution concentrated *in vacuo*. The residue was steam distilled and the oil in the distillate was extracted with two 100-ml. portions of ether. The solution was dried over sodium sulfate, concentrated and the residue distilled at 11 mm. The *o*-creosol, collected at 93–94°, weighed 4.2 g. (61%) and melted at 41–42° (lit.[7] 41–42°). The compound gave a reddish-brown color with ferric chloride as reported.[7]

2-Hydroxy-3-methoxyphenylacetic Acid (VII).—A solution of 18.1 g. (0.1 mole) of 6-dimethylaminomethylguaiacol (Ib) and 12.5 g. of sodium cyanide in 125 ml. of ethylene glycol and 12.5 ml. of water was refluxed for two hours in an atmosphere of nitrogen. The mixture was then diluted with 400 ml. of water and solid carbon dioxide was added until the aqueous solution was faintly acidic. An amorphous precipitate formed and was removed by filtration. The filtrate was acidified with hydrochloric acid, extracted twice with 200 ml. of ether, the extracts washed twice with water, combined, dried over sodium sulfate and concentrated. When the viscous brown sirup was subjected to distillation at 0.5 mm. pressure, a small amount of distillate was collected at 130–155°. The distillate crystallized in part and on recrystallization from benzene-petroleum ether (b.p. 30–60°) yielded 0.71 g. (3.9%) of waxy solid. After a second recrystallization this material (0.23 g.) melted at 119.5–122.5° and gave a green color with ferric chloride in ethanol. The melting point was not changed by recrystallization from ethyl acetate-petroleum ether. Mosimann and Tambor[13] report a melting point of 124° for 2-hydroxy-3-methoxyphenylacetic acid and also mention that this material gives a green ferric chloride test.

Anal. Calcd.: neut. equiv., 182. Found: neut. equiv., 188.

The lactone[13] melted at 78–79° after recrystallization from petroleum ether (lit.[13] 80°).

Reaction of 6-Dimethylaminomethylguaiacol Ib with Ethyl Cyanoacetate.—A solution of 9 g. of Ib in 25 ml. of ethyl cyanoacetate was heated at 190° under nitrogen for three hours. Upon fractionation, 4.6 g. of distillate, b.p. 103–128° (0.2 mm.), was collected. It crystallized in the receiver to a waxy solid. After several recrystallizations from benzene, the material melted at 65–66° and the mixed melting point with an authentic sample of N,N-dimethylcyanoacetamide (prepared from ethyl cyanoacetate and dimethylamine in aqueous solution) was not depressed.

Anal. Calcd. for $C_5H_8N_2O$: C, 53.56; H, 7.18; N, 24.99. Found: C, 53.70; H, 7.07; N, 24.25.

Hydrolysis of the product with 10% aqueous sodium hydroxide yielded basic gases and malonic acid (m.p. 132.5–134° dec., not depressed by admixture of an authentic sample; neut. equiv. calcd., 52.0; found, 52.6).

Summary

1. The reaction of guaiacol with formaldehyde and dimethylamine or piperidine results in substitution ortho to the phenol function.
2. 6 - Dimethylaminomethylguaiacol alkylates sodium cyanide in very low yield; it does not alkylate ethyl cyanoacetate.
3. Convenient syntheses of *o*-vanillyl alcohol and its diacetate are described.

NOTRE DAME, INDIANA RECEIVED JULY 13, 1950

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[12] (a) Caldwell and Thompson, THIS JOURNAL, **61**, 765 (1939); (b) Bruson and Covert, U. S. Patent 2,194,215 (1940); *C. A.*, **34**, 4742 (1940); (c) Reeve and Sadle, THIS JOURNAL, **72**, 3252 (1950).

[13] Mosimann and Tambor, *Ber.*, **49**, 1258 (1916).

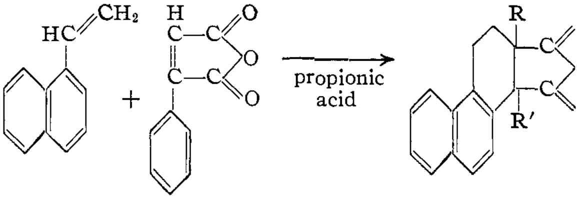
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Phenylmaleic Anhydride as a Diene in the Diels-Alder Reaction[1]

BY LEONARD E. MILLER AND D. J. MANN[2]

It has been reported[3] that phenylmaleic anhydride participates in the Diels–Alder reaction as a dienophile when such dienes as 1,3-butadiene, 2-methyl-1,3-butadiene, 2-ethyl-1,3-butadiene, 2-isopropyl-1,3-butadiene, 2,3-dimethyl-1,3-butadiene, cyclopentadiene and anthracene are employed.

Since 1-vinylnaphthalene behaves as a diene on reaction with maleic anhydride or citraconic anhydride[4] in boiling propionic acid to give derivatives of tetrahydrophenanthrene, it was thought that a similar reaction might occur with phenylmaleic anhydride as



Ia, R = H, R' = C_6H_5
Ib, R = C_6H_5, R' = H

Contrary to this expected result, when freshly prepared 1-vinylnaphthalene was treated with phenylmaleic anhydride and trace of *p-t*-butylcatechol in boiling propionic acid for 48 hours, the chief product isolated (II) proved to be a derivative of 1,1'-binaphthyl. *The formation of II can most reasonably be explained if one considers that phenylmaleic anhydride has participated as a*

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[1] Presented before the Division of Organic Chemistry of the American Chemical Society, Philadelphia, April 10, 1950.

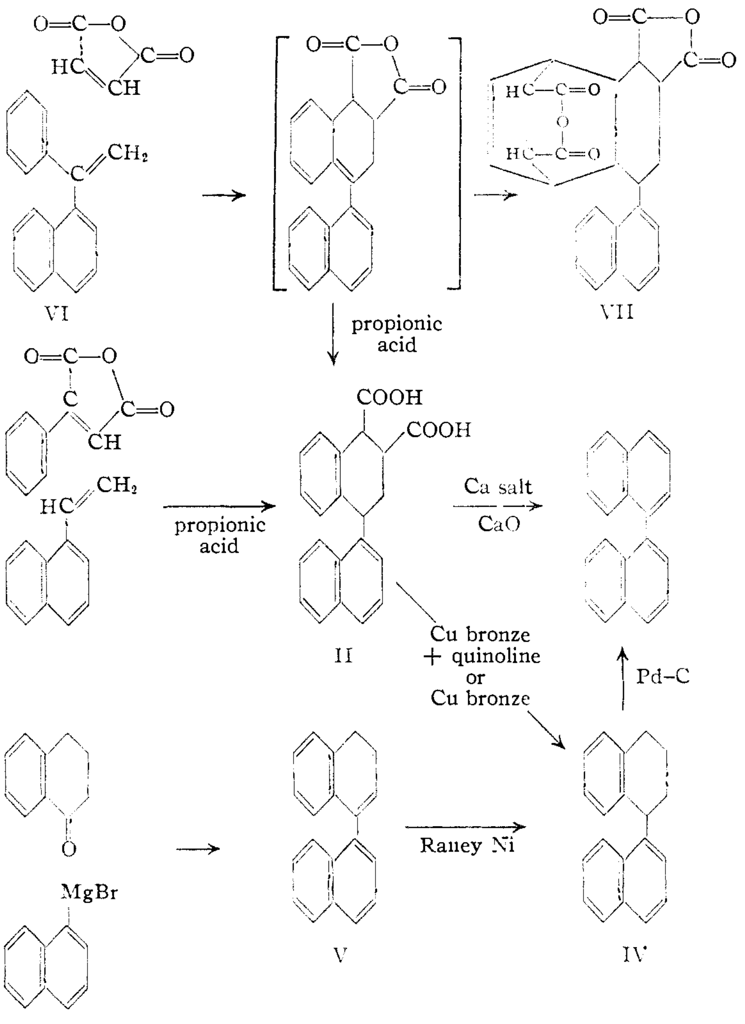
[2] Atlantic Research Corporation, 812 N. Fairfax Street, Alexandria, Virginia.

[3] L. E. Miller and D. J. Mann, THIS JOURNAL, **72**, 1484 (1950).

[4] W. E. Bachmann and L. B. Scott, *ibid.*, **70**, 1462 (1948).

diene and that 1-vinylnaphthalene has acted as a dienophile in a Diels–Alder reaction.[5]

Since neither cinnamic acid nor other derivatives of styrene, possessing negative substituents on the side chain, have been reported to have diene activity, it would appear that the reactivity of phenylmaleic anhydride as a diene is unique in type. However, several examples have been reported in which a double bond of a benzene nucleus in conjugation with extranuclear unsaturation has furnished a diene system sufficiently active to undergo a Diels–Alder reaction. Thus, isosafrole,[6,7] isoeugenol methyl ether,[6,7] anethole,[6,7] diphenylethylene[8] and hydrindene[9] react with maleic anhydride in a Diels–Alder reaction.



Of the two compounds isolated from this reaction mixture, the first (II) was obtained in 36.6% yield, was soluble in 5% aqueous sodium bicarbonate, had an elementary composition corresponding to the empirical formula $C_{20}H_{18}O_4$ and a neutralization equivalent in agreement with the value for a dibasic acid; the second compound (III) was isolated in a 2% yield, was insoluble in 5% aqueous sodium bicarbonate and had an elementary composition corresponding to the empirical formula $C_{20}H_{16}O_3$. Compound III dissolved slowly in hot concentrated aqueous potassium hydroxide, and upon acidification of the resulting clear solution was regenerated. Since this stable anhydride was obtained in only very small amounts, its constitution has not been investigated further.

When II was converted to its calcium salt and heated with calcium oxide at 450°, the material which sublimed from the mixture was identified as 1,1′-binaphthyl by its melting point, lack of melting point depression when mixed with an authentic sample[10] and similarity of its ultraviolet absorption spectrum with that of the authentic material.[11]

Since rearrangements might conceivably occur at the high temperature which was employed to form the 1,1′-binaphthyl, further study of the adduct II was undertaken. Treatment of II with copper bronze in boiling quinoline or with copper bronze alone at 250° gave rise to IV whose elementary analysis corresponded to that calculated for a tetrahydrobinaphthyl.

3,4-Dihydro-1,1′-binaphthyl V was prepared from 1-naphthylmagnesium bromide and 1-tetralone; the procedure employed was similar to that used by Hooker and Fieser[12] for 1,2′-binaphthyl. When this compound was treated with Raney nickel and ethanol,[13] 1,2,3,4-tetrahydro-1,1′-binaphthyl and 1,1′-binaphthyl were formed. The tetrahydrobinaphthyl prepared in this manner gave no melting point depression when mixed with the decarboxylated adduct IV; in addition, the ultraviolet absorption spectra of the two compounds were similar.

Heating IV, prepared by either of the above methods, with 5% palladium-on-carbon at 310–350° resulted in the formation of 1,1′-binaphthyl.

The final step in the structure proof of II consisted of the synthesis of this compound via an independent route. Szmuszkowicz and Bergmann[14] have shown that maleic anhydride forms a bis adduct VII with 1-phenyl-1-(1′-naphthyl)-ethylene VI in

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[5] When a solution of phenylmaleic anhydride and a trace of *p-t*-butylcatechol in propionic acid was heated under reflux for 48 hours no reaction occurred; upon removing the propionic acid by distillation under diminished pressure, pure phenylmaleic anhydride crystallized. This experiment was performed by Mr. C. J. Strickler.

[6] V. Bruckner, *Ber.*, **75**, 2034 (1942).

[7] B. J. F. Hudson and R. Robinson, *J. Chem. Soc.*, 715 (1941).

[8] Wagner-Jauregg, *Ann.*, **491**, 1 (1931).

[9] K. Alder, *Ber.*, **75**, 1501 (1942).

[10] F. Lossen, *Ann.*, **144**, 78 (1867).

[11] The ultraviolet absorption spectra of these two samples of 1,1′-binaphthyl were the same as that reported by V. L. Frampton, J. D. Edwards, Jr., and H. R. Henze, THIS JOURNAL, **70**, 2284 (1948). The sublimate did give a significant melting point depression when mixed with an authentic sample of 2-phenylphenanthrene kindly furnished by Dr. M. S. Newman; in addition the ultraviolet absorption spectra of the two compounds were significantly dissimilar.

[12] S. C. Hooker and L. F. Fieser, THIS JOURNAL, **58**, 1216 (1936).

[13] M. Orchin, *ibid.*, **66**, 535 (1944); M. Orchin and L. Reggel, *ibid.*, **69**, 505 (1947).

[14] J. Szmuszkowicz and F. Bergmann, *ibid.*, **69**, 1779 (1947).

the absence of a solvent. When these reagents were dissolved in propionic acid and heated under reflux for 17 hours, an adduct was isolated in low yield which proved to be identical with II as shown by an undepressed mixed melting point and the same ultraviolet absorption spectra. Presumably, this product was formed by the aromatization of the mono adduct by the propionic acid.

In Fig. 1, the ultraviolet absorption spectrum for the adduct II is presented; in Fig. 2 the ultraviolet absorption spectra of 2-phenylphenanthrene, 3,4-dihydro-1,1′-binaphthyl and 1,2,3,4-tetrahydro-1,1′-binaphthyl are given. These spectra were determined with a Cary automatic recording spectrophotometer using 95% ethanol as the solvent.

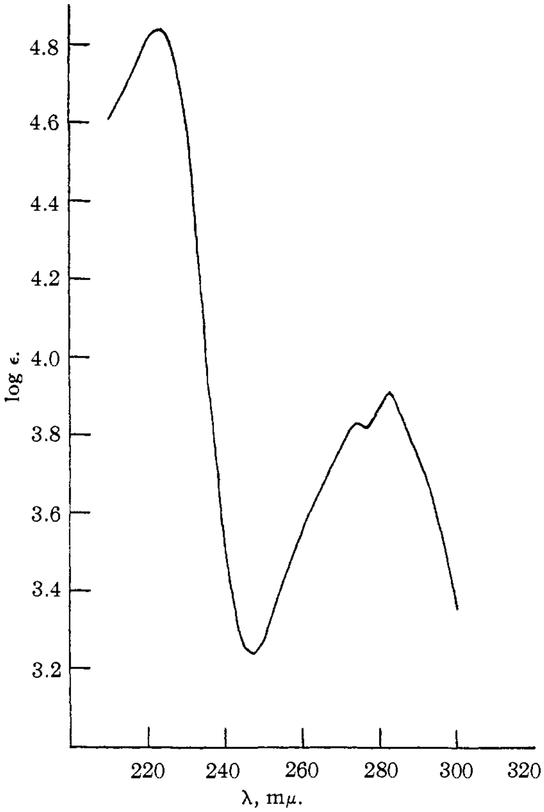

Fig. 1.—Ultraviolet absorption spectrum of 1,2,3,4-tetrahydro-1,1′-binaphthyl-3,4-dicarboxylic acid II.

Experimental[15]

1-Vinylnaphthalene was prepared by the method of Cohen and Warren[16]; the method of Wilds[17] was used for the preparation of the intermediate β-(1-naphthyl)-ethyl alcohol.

The Reaction of Phenylmaleic Anhydride with 1-Vinylnaphthalene.—A solution of 6.1 g. (0.040 mole) of freshly prepared 1-vinylnaphthalene, 9.05 g. (0.052 mole) of phenylmaleic anhydride[18] and a crystal of *p*-*t*-butylcatechol in 50 ml. of redistilled propionic acid was heated under reflux in an atmosphere of nitrogen for 48 hours. After removing the propionic acid by distillation *in vacuo* (water-pump) the yellow residue was treated with 32 ml. of 45% aqueous potassium hydroxide and then 200 ml. of hot water. The resulting cloudy solution was cooled and then washed with six 100-ml. portions or ether to give a clear yellow aqueous solution. This solution was heated to the boiling point, treated with Norite, filtered through Filtercel and then added with stirring to 90 ml. of concd. hydrochloric acid (sp. gr. 1.19). A light yellow semi-solid substance separated and after standing in a refrigerator for 12 hours solidified completely. This solid material was collected on a filter, washed well with water, dried in air and recrystallized from 95% ethanol. The first crop of crystals consisted of 4.5 g. of light yellow material, m. p. 216–219°, which on recrystallization gave 3.76 g. of colorless prisms II, m. p. 230–232° (with the evolution of gas). Upon concentrating the filtrate from the first crop, a second crop of almost colorless crystals formed which, after three further recrystallizations, gave 1.31 g. of colorless prisms II, m. p. 230–232°. The precipitate which formed from the combined and concentrated filtrates was recrystallized twice to give 0.27 g. (2%) of colorless prisms III which were insoluble in 5% aqueous sodium bicarbonate; m. p. 182–184°. The total yield of adduct melting at 230–232° was 5.07 g. (36.6%).

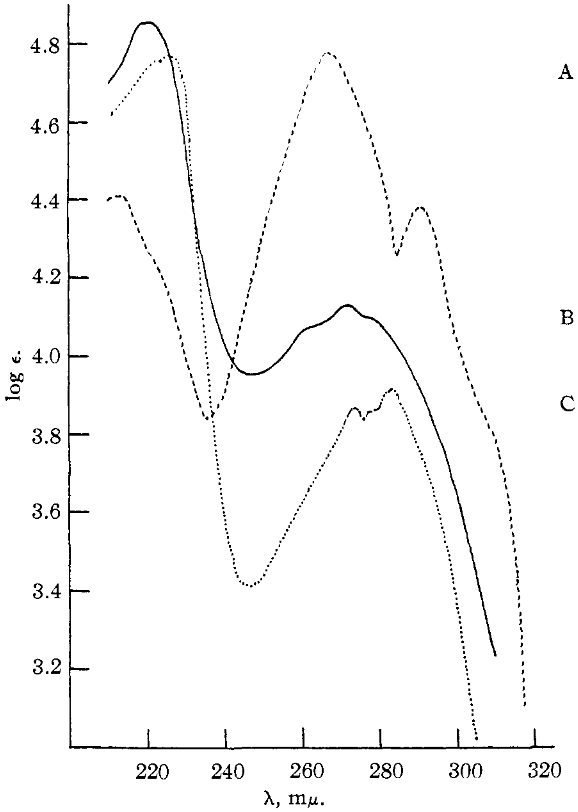

Fig. 2.—Ultraviolet absorption spectra for: A, 2-phenylphenanthrene; B, 3,4-dihydro-1,1′-binaphthyl; C, 1,2,3,4-tetrahydro-1,1′-binaphthyl.

Anal. Calcd. for $C_{22}H_{18}O_4$: C, 76.28; H, 5.24; neut. equiv., 173. Found (II): C, 76.18; H, 5.38; neut. equiv., 171. *Anal.* Calcd. for $C_{22}H_{16}O_3$: C, 80.46; H, 4.91. Found (III): C, 80.54; H, 5.14.

Decarboxylation and Dehydrogenation of the 1-Vinylnaphthalene Adduct Diacid II. Method A.[19]—To 0.5 g. of the adduct II dissolved in 20 ml. of warm water containing 0.15 g. of sodium hydroxide was added 0.22 g. of powdered calcium oxide. After evaporating the mixture to dryness, the residue was mixed intimately with 1.3 g. of calcium oxide. The mixture was placed in a test-tube having a knife-edge indentation 5 cm. from the closed end and was heated in an electrically-controlled heating jacket at 450° (atm. pressure). The red oil, which distilled, solidified at the open end of the tube and was dissolved in benzene and treated with Norite. After removing the solvent, the residue was distilled at 180–200° (0.2 mm.). The yellow distillate solidified in the tube and was recrystallized twice from benzene to give colorless leaflets; m. p. 150–152°; yield 0.12 g. (34%). When mixed with an authentic

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[15] All melting points and boiling points are uncorrected.

[16] A. Cohen and F. L. Warren, *J. Chem. Soc.*, 1318 (1937).

[17] A. L. Wilds, THIS JOURNAL, **64**, 1421 (1942).

[18] L. E. Miller, H. B. Staley and D. J. Mann, *ibid.*, **71**, 374 (1949).

[19] W. E. Bachmann and M. Kloetzel, *ibid.*, **60**, 2204 (1938).

sample of 1,1′-binaphthyl (m. p., 154–156°), the melting point was 152–154°. The ultraviolet absorption spectra of the degradation products and of the authentic sample were the same.

Method B (Stepwise Procedure).[20]—A mixture of 1.0 g. of the adduct diacid II, 2 ml. of redistilled quinoline and 100 mg. of copper bronze was heated under reflux for 15 minutes, cooled, dissolved in 50 ml. of ether and filtered. The clear ether solution was washed with three 20-ml. portions of 2 *N* HCl, three 20-ml. portions of water and then dried over magnesium sulfate. After removing the ether, the residue was distilled (250–260° at 3.0 mm.) to give a yellow solid on cooling. This intermediate (0.1 g.) was mixed with 30 mg. of 10% palladium-on-carbon in a test-tube and heated at 310–350° for one hour in an atmosphere of nitrogen. During the heating period a colorless liquid distilled and solidified along the wall of the tube; m. p., 149–154° (without recrystallization). When mixed with an authentic sample of 1,1′-binaphthyl the melting point was 150–154°.

When a mixture of 1.5 g. of the diacid adduct II and 300 mg. of copper bronze was heated at 240–250° (0.2 mm.) a colorless liquid distilled and solidified on cooling. After dissolving this distillate in ether, it was extracted with two 10-ml. portions of 10% aqueous potassium hydroxide. Upon evaporation of the ether layer, there was no residue; however, acidification of the alkaline layer with concd. hydrochloric acid produced a precipitate. A mixture of 0.40 g. of this precipitate and 100 mg. of copper bronze was heated under reduced pressure as before. The colorless distillate which solidified on cooling was dissolved in ether and washed with 10% aqueous sodium hydroxide. Acidification of the aqueous layer at this point produced only a slight turbidity. The ether solution was dried over magnesium sulfate and upon evaporation of the solvent, the colorless solid residue was recrystallized from 95% ethanol to give 30 mg. of colorless prisms IV, m. p. 103–106°. When mixed with an authentic sample of 1,2,3,4-tetrahydro-1,1′-binaphthyl (m. p. 105–106°), there was no depression of the melting point.

3,4-Dihydro-1,1′-binaphthyl (V).—γ-Phenylbutyric acid was prepared by the catalytic reduction of β-benzoylpropionic acid in 67% yield using the method of Horning and Reisner.[21]

This acid was cyclized to α-tetralone in 78% yield using the procedure reported by Bachmann and Thomas.[22]

To an ethereal solution of α-naphthylmagnesium bromide, prepared from 1.5 g. of magnesium turnings, 12.5 g. of α-bromonaphthalene, a crystal of iodine and 50 ml. of ether, was added with stirring 7.5 g. of α-tetralone dissolved in 50 ml. of ether at such a rate as to cause gentle boiling. The resulting clear solution was heated under reflux for one hour and then allowed to stand overnight at room temperature. After cooling the reaction mixture in an ice-bath, 50 ml. of cold 25% sulfuric acid was added dropwise with stirring and then 50 ml. of water. The red liquid residue was fractionally distilled at 0.5 mm. At 88–90° several grams of naphthalene distilled; at 123–180° several grams of α-bromonaphthalene were collected. (This forerun was discarded.) A yellow viscous oil, which solidified on standing, was collected at 204–206°. It was recrystallized from petroleum ether (high boiling) to give 3.3 g. (25.3%) of colorless prisms, m. p. 117–118.5°.

Anal. Calcd. for $C_{20}H_{16}$: C, 93.71; H, 6.29. Found: C, 93.84; H, 6.24.

1,2,3,4-Tetrahydro-1,1′-binaphthyl (IV).—A mixture of 1.0 g. of V, 4.0 g. of Raney nickel and 25 ml. of absolute ethanol was heated under reflux for six hours. The mixture was filtered and concentrated. On cooling, a colorless material crystallized and was collected on a filter. This solid material was extracted with 10 ml. of hot 95% ethanol. Upon concentration and cooling of this ethanol solution, 0.1 g. of material crystallized; m. p. 114–127°. The filtrate from this material was further concentrated and cooled to give an additional crop of crystals which, after one recrystallization from 95% ethanol formed 30 mg. of colorless prisms IV, m. p. 105–106°.

Anal. Calcd. for $C_{20}H_{18}$: C, 92.97; H, 7.02. Found: C, 92.91; H, 6.87.

The solid residue from the hot alcohol extraction was recrystallized three times from 95% ethanol to give 0.15 g. of colorless leaflets; m. p. 151–153°. When mixed with an authentic sample of 1,1′-binaphthyl, the melting point was 151–154°.

The Reaction of Maleic Anhydride and 1-Phenyl-1-(α-naphthyl)-ethylene VI.—1-Phenyl-1-(α-naphthyl)-ethylene was prepared by the method of Stoermer and Simon.[23]

A solution of 0.98 g. (0.01 mole) of maleic anhydride, 2.99 g. (0.013 mole) of 1-phenyl-1-(α-naphthyl)-ethylene and a crystal of *p*-*t*-butylcatechol in 25 ml. of propionic acid was heated under reflux in an atmosphere of nitrogen for 17 hours. The reaction mixture was treated in the same manner as that employed with the 1-vinylnaphthalene adduct II. Upon acidification of the alkaline filtrate with concd. hydrochloric acid a colorless solid separated after the mixture was permitted to stand in a refrigerator overnight. When this material was collected on a filter and washed with water it became soft but hardened upon drying in air. When treated with 50 ml. of 5% aqueous sodium bicarbonate a slightly turbid solution was formed. This solution was heated, treated with Norite and filtered to give a clear colorless filtrate. Upon acidification of the filtrate with concd. hydrochloric acid, a colorless solid separated but remained in suspension; a small amount of brown solid material settled to the bottom. The suspension was decanted from the brown solid, centrifuged and was separated on a filter. After two recrystallizations from 95% ethanol, 0.16 g. (4.6%) of colorless prisms was isolated; m. p. 229–231. When mixed with a sample of the 1-vinylnaphthalene adduct diacid (m. p. 230–232°), the melting point was 229–231°.

Summary

1. Phenylmaleic anhydride and 1-vinylnaphthalene react to form the adduct 1,2,3,4-tetrahydro-1,1′-binaphthyl-3,4-dicarboxylic acid. This adduct formation is explained on the basis that phenylmaleic anhydride has acted as a diene.

2. The same adduct is formed when a solution of 1-phenyl-1-(α-naphthyl)-ethylene and maleic anhydride in propionic acid is heated under reflux.

URBANA, ILLINOIS RECEIVED JUNE 19, 1950

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[20] A. F. Shepard, N. R. Winslow and J. R. Johnson, THIS JOURNAL, **52**, 2083 (1930).

[21] E. C. Horning and D. B. Reisner, *ibid.*, **71**, 1036 (1949).

[22] W. E. Bachmann and D. G. Thomas, *ibid.*, **64**, 95 (1942).

[23] R. Stoermer and M. Simon, *Ber.*, **37**, 4163 (1904).