dure described above. Attempts to reduce[28] 4-benzo(f)-thiachromanone in both acid and basic media gave very low yields of benzo(f)thiachroman. Benzo(f)thiachroman was recrystallized from methanol, m.p. 91–92°.

Anal. Calcd. for $C_{13}H_{12}S$: C, 77.95; H, 6.04. Found: C, 78.24; H, 5.92.

Oxidation of benzo(f)thiachroman in glacial acetic acid with 30% hydrogen peroxide gave the sulfone, benzo(f)-thiachroman-1-dioxide. Recrystallization from methanol gave white needles, m.p. 155–156°.

Anal. Calcd. for $C_{13}H_{12}O_2S$: C, 67.21; H, 5.21. Found: C, 66.98; H, 5.22.

Independent Synthesis of Benzo(g)homothiachroman-1-dioxide.—4-(β-Naphthylmercapto)-butanenitrile was prepared from 34 g. (0.23 mole) of 4-bromobutanenitrile[29] and 36 g. (0.23 mole) of 2-naphthalenethiol (74%) by the method employed for the preparation of the analogous phenyl compound[7]; b.p. 184–186° (1 mm.), 227–230° (6–7 mm.). This nitrile, 38 g. (0.167 mole), was hydrolyzed[7] to give 39 g. (94%) of 4-(β-naphthylmercapto)-butanoic acid. Recrystallization from 90–100° petroleum ether gave white needles, m.p. 86–87°.

Anal. Calcd. for $C_{14}H_{14}O_2S$: C, 68.26; H, 5.73. Found: C, 68.61; H, 5.42.

4-(β-Naphthylmercapto)-butanoyl chloride (amide, m.p. 150–151°) was prepared from 10 g. (0.04 mole) of the corresponding acid by treatment with phosphorus pentachloride in benzene (1 hour at room temperature, then 10 minutes on a steam-cone). The reaction mixture was chilled on an ice-bath and a solution of 22 g. (0.08 mole) of stannic chloride and 15 ml. of dry benzene was added. The resulting mixture was agitated occasionally, allowed to stand for 16 hours, and then it was hydrolyzed with ice-water and hydrochloric acid. The resulting yellow organic layer was evaporated and the residual material was recrystallized from methanol to give 6 g. (65%) of 5-benzo-(g)homothiachromanone, white plates, m.p. 78–79°.

Anal. Calcd. for $C_{14}H_{12}OS$: C, 73.64; H, 5.30. Found: C, 73.85; H, 5.20.

Several attempts to cyclize 4-(β-naphthylmercapto)-butanoyl chloride, obtained by treatment of the corresponding acid with thionyl chloride, with either anhydrous aluminum chloride or ferric chloride in carbon disulfide were unsuccessful.

5-Benzo(g)homothiachromanone was oxidized with 30% hydrogen peroxide in glacial acetic acid to give 5-benzo(g)-homothiachromanone-1-dioxide. Recrystallization of the crude product from ethanol gave white needles, m.p. 176–177°.

Anal. Calcd. for $C_{14}H_{12}O_3S$: C, 64.59; H, 4.69. Found: C, 64.37; H, 4.67.

Reduction of 5-benzo(g)homothiachromanone-1-dioxide by the modified Wolff–Kishner procedure described above gave the sulfone, benzo(g)homothiachroman-1-dioxide. Recrystallization from methanol gave white needles, m.p. 134–135°.

Anal. Calcd. for $C_{14}H_{14}O_2S$: C, 68.26; H, 5.73. Found: C, 68.21; H, 5.86.

LAFAYETTE, INDIANA

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(28) E. L. Martin, *ibid.*, **58**, 1438 (1936).

(29) A. A. Goldberg and W. Kelly, *J. Chem. Soc.*, 1369 (1947).

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

p-Nitrophenylmaleic Anhydride in the Diels–Alder Reaction[1]

BY LEONARD E. MILLER AND CHARLES J. STRICKLER[2]

RECEIVED SEPTEMBER 14, 1953

p-Nitrophenylmaleic anhydride has been prepared by the reaction of *p*-nitrophenylsuccinic anhydride with N-bromosuccinimide in the presence of cumene hydroperoxide. That this compound does participate in the Diels–Alder reaction as a dienophile has been demonstrated by its adduct formation with 1,3-butadiene, 2,3-dimethyl-1,3-butadiene, isoprene, 2-ethyl-1,3-butadiene, 2-isopropyl-1,3-butadiene, cyclopentadiene and anthracene. A single product was obtained in each case. The adducts with the unsymmetrical dienes have been shown to be 1-*p*-nitrophenyl-4-alkyl-4-cyclohexene-1,2-dicarboxylic acids. This compound plays the role of a diene in its reaction with 1-vinylnaphthalene to give a derivative of 1,1′-binaphthyl.

Since it has been demonstrated that phenylmaleic anhydride can participate in the Diels–Alder reaction as either dienophile[3a] or diene,[3b] *p*-nitrophenylmaleic anhydride has been prepared in order to observe the influence of a strongly polar group, which is sterically removed from the reactive centers, upon the course of this reaction.

p-Nitrophenylmaleic anhydride was synthesized by modifications of the method used for the preparation of phenylmaleic anhydride.[4] The starting material, *p*-nitrophenylsuccinic acid, was prepared by the nitration[5] of phenylsuccinic acid.[6] The *p*-nitro acid was, in turn, converted to the corresponding anhydride by treatment with acetyl chloride.[7] The resulting oil was used directly in the dehydrogenation with N-bromosuccinimide to give *p*-nitrophenylmaleic anhydride. During the first attempts to carry out this dehydrogenation, it was observed that the red color of bromine which developed in solution would disappear as the reaction proceeded. However, under these conditions, only an uncrystallizable oil which gave a positive test for a vicinal dihalide[8] could be isolated. To avoid this difficulty the bromine was distilled from the reaction mixture in an azeotrope with carbon tetrachloride as the reaction proceeded.

It was found, further, that cumene hydroperoxide was superior to benzoyl peroxide as a catalyst, although under the best conditions found the yield was but 34% of the theoretical amount.

When an attempt was made to prepare *p*-nitro-

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(1) Presented before the Division of Organic Chemistry at the 121st Meeting of the American Chemical Society, Milwaukee, Wisconsin, March 31 to April 2, 1952.

(2) From portions of a thesis submitted by Charles J. Strickler to the Graduate College of the University of Illinois, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) (a) L. E. Miller and D. J. Mann, THIS JOURNAL, **72**, 1484 (1950); (b) **73**, 45 (1951).

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

(5) Fr. Fischter and O. Walter, *Ber.*, **42** [4], 4312 (1909).

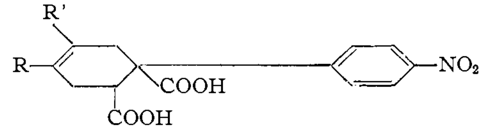
(6) *Org. Syntheses*, **30**, 83 (1950).

(7) M. A. Wali, A. K. Khalil, R. L. Bhatia and S. S. Ahmad, *Proc. Indian Acad. Sci.*, **14A**, 139 (1941), have reported this preparation and the isolation of the anhydride by crystallization from "ether." All of our efforts to duplicate their crystallization from all available solvents were unsuccessful.

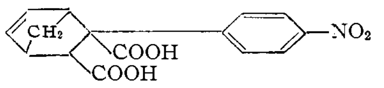
(8) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, New York, N. Y., 1948, p. 141.

phenylmaleic anhydride by the direct nitration of phenylmaleic anhydride, the only product isolated was *o*-nitrophenylmaleic anhydride. When this compound was oxidized with potassium permanganate, the known *o*-nitrobenzoic acid was formed. On the other hand, *p*-nitrophenylmaleic anhydride, prepared from *p*-nitrophenylsuccinic acid, gave *p*-nitrobenzoic acid on oxidation.

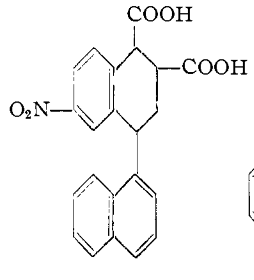
In a manner similar to phenylmaleic anhydride, *p*-nitrophenylmaleic anhydride formed 1:1 adducts with 1,3-butadiene (I), 2,3-dimethyl-1,3-butadiene (II), cyclopentadiene (VI), anthracene (VIII), isoprene (III), 2-ethyl-1,3-butadiene (IV), 2-isopropyl-1,3-butadiene (V) and 1-vinylnaphthalene (VII). With the latter, *p*-nitrophenylmaleic anhydride acted as a diene; with the others it was the dienophile.



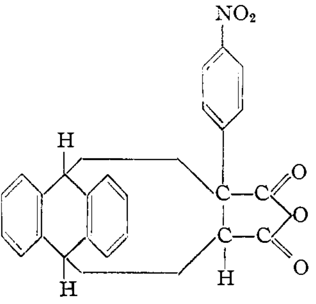
I, R = H, R′ = H
II, R = CH_3, R′ = CH_3
III, R = CH_3, R′ = H
IV, R = CH_3CH_2–, R′ = H
V, R = $(CH_3)_2CH$–, R′ = H



VI



VII



VIII

A single adduct was isolated from the reaction of *p*-nitrophenylmaleic anhydride with all of the structurally symmetrical reagents. This conforms with the results obtained with phenylmaleic anhydride. As in the latter cases all of the adducts but anthracene were isolated as the dicarboxylic acids.

In contrast to the results obtained with phenylmaleic anhydride, its *p*-nitro derivative formed a *single* adduct with each of the three unsymmetrically substituted butadienes used. Two structurally isomeric adducts had been obtained from each of the unsymmetrical dienes with the parent compound.

The proof of the structures of the adducts formed with the unsymmetrical dienes and *p*-nitrophenylmaleic anhydride depends upon establishing the relative positions of the alkyl groups and the *p*-nitrophenyl group on the cyclohexene ring. Since the corresponding 1-phenyl-4-alkyl-4-cyclohexene-1,2-dicarboxylic acids are known,[3a] this relationship was established by removal of the nitro group from the new adducts. The removal was accomplished by the reduction of the nitro compounds to amines, diazotization of the amines and reduction of the diazonium salts with hypophosphorous acid to the reference compounds. Fortunately the carboxyl groups had the same stereochemical relationship to each other as the known 1-phenyl-4-alkyl-4-cyclohexene-1,2-dicarboxylic acids so that further degradation was not necessary. These final products of degradation were shown to be the 4-alkyl substituted derivatives by melting points of mixtures with the reference compounds and by comparison of the infrared spectra. This degradation was not attempted with the 2-isopropyl-1,3-butadiene adduct since the structure of the known 1-phenyl-4-isopropylcyclohexene-1,2-dicarboxylic acid had been inferred by analogy.

The structures of the adducts formed with *p*-nitrophenylmaleic anhydride and the unsymmetrical dienes taken individually or in comparison with the adducts produced with phenylmaleic anhydride are in agreement with what would be predicted on the basis of an ionic mechanism for the reactions.

In the reaction with 1-vinylnaphthalene only one isomer VII was isolated and a large amount of polymer was formed even in the presence of an inhibitor. Preliminary experiments using aqueous potassium hydroxide to isolate the product were unsuccessful. When sodium bicarbonate was used for this purpose the adduct was isolated in a yield of 38% of the theoretical amount.

The determination of the structure of this adduct by the same procedure used for the other unsymmetrical adducts of *p*-nitrophenylmaleic anhydride might be considered inconclusive because of the low yield obtained. However, the ultraviolet spectrum of the adduct before degradation indicated that it contained the 1,2,3,4-tetrahydro-1,1′-binaphthyl nucleus.[3b]

Although the nitro group of the adduct underwent smooth reduction to the amine, diazotization and deamination of the amino compound were accompanied by tar formation. The deaminated product could only be separated from the tar by distillation under reduced pressure as the corresponding anhydride. The anhydride was then reconverted to the diacid. The elementary analysis and ultraviolet spectrum of the acid isolated in this manner were identical with those of 1,2,3,4-tetrahydro-1,1′-binaphthyl-3,4-dicarboxylic acid,[3b] but the melting points were not the same. However, decarboxylation and dehydrogenation of the calcium salt of the deaminated adduct gave 1,1′-binaphthyl.

The discrepancy in the melting points was readily demonstrated as a consequence of a difference in stereochemical configuration of the two carboxyl groups. A sample of the known 1,2,3,4-tetrahydro-1,1′-binaphthyl-3,4-dicarboxylic acid was distilled *in vacuo* as the anhydride and was reconverted to the diacid by dissolving in cold aqueous 10% potassium hydroxide and reprecipitating with glacial acetic acid. This product proved to be identical with the product of degradation of VII. It is reasonable to assume that the reference compound had been isomerized originally since its isolation involved a treatment with hot aqueous 40% potassium hydroxide.

Experimental[9]

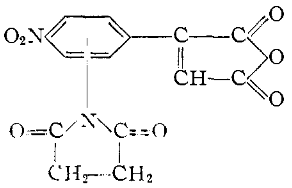
p-Nitrophenylmaleic Anhydride.—In a 2-l., three-necked flask 32 g. (0.134 mole) of p-nitrophenylsuccinic acid[5] and 140 ml. of acetyl chloride were heated under reflux for six hours. The excess acetyl chloride was removed by distillation at atmospheric pressure and then two 100-ml. portions of dry benzene were distilled from the residual oil *in vacuo* to aid in the removal of the acetic acid. The flask was then equipped with a Claisen head joined to a downward distillation condenser, a mechanical Hershberg stirrer made of Nichrome wire[10] and a dropping funnel, and 54 g. (0.303 mole) of N-bromosuccinimide, 0.4 g. (0.0026 mole) of cumene hydroperoxide and 1750 ml. of carbon tetrachloride were added. During the reaction period, the bromine–carbon tetrachloride azeotrope was distilled and additional carbon tetrachloride was added to maintain a constant volume. At the end of 2.5 hours, when the distillate was only faintly colored the reaction mixture was cooled to room temperature and separated on a suction filter.

The solid material was extracted with three 100-ml. portions of benzene by heating to boiling and cooling in an ice-bath before separation on a filter. The solid material remaining on the filter was succinimide. To the combined filtrates was added 600 ml. of petroleum ether (high boiling). The yellow-colored precipitate which had formed at the end of three hours gave, after three recrystallizations from ethyl acetate, 9.23–9.96 g. (31.5–34% of the theoretical amount) of yellow needles, m.p. 128–129°.

Anal. Calcd. for $C_{10}H_5NO_5$: C, 54.80; H, 2.30; N, 6.39. Found: C, 54.61; H, 2.28; N, 6.42.

When a greater excess of either cumene hydroperoxide or N-bromosuccinimide was used the only product isolated was a colorless solid, m.p. 222–224°, after recrystallization from acetone. This material was insoluble in 5% aqueous sodium bicarbonate and was readily oxidized by potassium permanganate in acetone. Its infrared absorption spectrum indicated a compound which has a nitro, a phenyl and an anhydride group. The typical amide, secondary amine and hydroxyl absorption frequencies were absent. There was absorption at 1730 cm.$^{-1}$ which could be attributed to an imide linkage; the other band was obscured by the anhydride absorption. The known reaction in which N-bromosuccinimide in the presence of a peroxide attacked benzene to give N-phenylsuccinimide in 15% yield[11] leads us to suspect that this material has the generalized structure given by IX.

Anal. Calcd. for $C_{14}H_8N_2O_7$: C, 53.17; H, 2.55; N, 8.86. Found: C, 53.28, 53.20; H, 2.75, 2.42; N, 8.63, 8.85.



o-Nitrophenylmaleic Anhydride.—Into a 200-ml., three-necked flask equipped with a mechanical stirrer was placed 50 ml. of fuming nitric acid (sp. gr. 1.52). After cooling the nitric acid to 0° in an ice–salt-bath, 10 g. (0.57 mole) of phenylmaleic anhydride[4] was added portionwise at a rate which maintained the temperature below 5°. After the additions were completed, the mixture was stirred for six hours and then poured into 50 g. of ice. The oil which separated solidified on standing. This material was collected on a filter, washed thoroughly with water, dried in air and extracted with two 25-ml. portions of hot carbon tetrachloride. Upon cooling the combined extracts gave 1.43 g. of colorless platelets, m.p. 141–142°. When this product was recrystallized from carbon tetrachloride the yield was 1.35 g. or 11% of the theoretical amount, m.p. 141–142°.

Anal. Calcd. for $C_{10}H_5NO_5$: C, 54.80; H, 2.30; N, 6.39. Found: C, 54.92; H, 2.47; N, 6.57.

When this material (0.5 g.) was oxidized by heating with aqueous potassium permanganate a product was formed which, after two recrystallizations from benzene gave 0.1 g. of a tan crystalline substance, m.p. 147–148°. Mixtures of this compound with o-nitrobenzoic acid, m.p. 147.5°, showed no melting point depression.

Upon the oxidation of p-nitrophenylmaleic anhydride under the same conditions a yellow crystalline material was obtained, m.p. 242.5–243.5°. When mixed with an authentic sample of p-nitrobenzoic acid (m.p. 240–242°), no melting point depression was observed. The methyl ester (m.p. 95–96°) of this acid was prepared by reaction with methanol and sulfuric acid. No melting point depression was observed when it was mixed with an authentic sample of methyl p-nitrobenzoate, m.p. 95–96°.

1-p-Nitrophenyl-4-cyclohexene-1,2-dicarboxylic Acid (I).—Into a screw-capped polymerization bottle was placed 2.19 g. (0.01 mole) of p-nitrophenylmaleic anhydride, 5 g. (0.09 mole) of 1,3-butadiene, 30 ml. of dry benzene and a crystal of hydroquinone. After enough of the butadiene had vaporized to sweep air from the bottle, it was capped tightly and rotated in a water-bath at 50° for 24 hours. The bottle was cooled, opened and the butadiene was permitted to distil spontaneously. The benzene was then removed by distillation *in vacuo*. The large residue, containing much polymer, was treated with 30 ml. of hot 5% aqueous sodium bicarbonate and separated on a filter. On acidification of the filtrate with dilute (1:1) hydrochloric acid a precipitate formed. It was collected on a filter, washed thoroughly with water, dried in air and recrystallized twice from dioxane–petroleum ether (high boiling). The yield was 1.52 g.

The dimethyl esters of all the adducts were prepared in the usual manner using an ethereal solution of diazomethane and were recrystallized from methanol.

1-p-Nitrophenyl-4,5-dimethyl-4-cyclohexene-1,2-dicarboxylic Acid (II).—In a 10-ml. flask 2.0 g. (0.0091 mole) of p-nitrophenylmaleic anhydride and 2.9 g. (0.035 mole) of 2,3-dimethyl-1,3-butadiene were heated under reflux for 18 hours. After removal of the excess diene by distillation, the solid residue was treated with 10 ml. of 45% aqueous potassium hy-

TABLE I

Diene	Yield, %	M.p., °C. diacid adduct	Anal. diacid adduct[a] Carbon Calcd.	Found	Hydrogen Calcd.	Found	Nitrogen Calcd.	Found	M.p., °C. dimethyl ester	Anal. dimethyl ester Carbon Calcd.	Found	Hydrogen Calcd.	Found	Nitrogen Calcd.	Found
1,3-Butadiene (I)	52	200 dec.	57.73	57.49	4.49	4.71	4.84	4.78	118–119	60.19	60.49	5.37	5.60	4.39	4.51
2,3-Dimethyl-1,3-butadiene (II)	67	206–208[b]	60.18	60.06	5.37	5.23	4.39	4.48	127.5–128.5	62.24	62.48	6.09	5.99	4.03	4.02
2-Methyl-1,3-butadiene (III)	87.5	182–184[b]	59.01	59.02	4.95	5.15	4.59	4.52	132–133	61.26	61.36	5.75	5.95	4.20	4.33
2-Ethyl-1,3-butadiene (IV)	88.5	173–175[b]	60.18	60.00	5.37	5.54	4.39	4.67	102–103	62.24	62.38	6.09	6.05	4.03	4.28
2-Isopropyl-1,3-butadiene (V)	70	179.5–181[b]	61.25	61.38	5.75	5.72	4.20	4.27	88–89	63.15	63.08	6.41	6.55	3.88	3.94
Cyclopentadiene (VI)	61	167.5–169.5[b]	59.40	59.64	4.32	4.37	4.62	4.63	132–133	61.63	61.87	5.17	5.35	4.23	4.29

[a] All elementary analyses were accomplished by Miss Emily Davis, Mr. J. Nemeth, Mrs. Katherine Pih and Mrs. Esther Fett. [b] Melted with bubbling.

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(9) All melting points and boiling points are uncorrected.

(10) When an all-glass stirrer was used, the only product isolated contained bromine.

(11) E. R. Buchman and D. R. Howton, THIS JOURNAL, **70**, 2517 (1948).

droxide followed by 65 ml. of water. The solution was heated to boiling, cooled, washed with three 50-ml. portions of diethyl ether, boiled to remove the dissolved ether, treated with Darco and filtered through Filtercel. To the cool, clear, yellow filtrate 20 ml. of concd. hydro-chloric acid (sp. gr. 1.19) was added with stirring. The pale yellow precipitate which formed was collected on a filter, washed thoroughly with water, dried in air and recrystallized from 95% ethanol. The yield of pale yellow prisms was 1.94 g.

cis-**9,10-Dihydroanthracene-9,10-endo-α-(*p*-nitrophenyl)-α,β-succinic Anhydride (VIII).**—A mixture of 2.19 g. (0.01 mole) of *p*-nitrophenylmaleic anhydride, 3.56 g. (0.02 mole) of anthracene and 30 ml. of glacial acetic acid was heated under reflux for six days. The product was isolated using the procedure described immediately above except that the crude product was dissolved in a minimum volume of hot ethyl acetate and petroleum ether (high boiling). Upon cooling a brown, sticky solid separated. The supernatant liquid was decanted and mixed with an equal volume of petroleum ether. The yellow solid which separated was recrystallized twice from ethyl acetate–petroleum ether to give 0.69 g. (17.4% of the theoretical amount) of yellow prisms, m.p. 190–192° (bubbling). This material was insoluble in 5% sodium bicarbonate and gave an elementary analysis in agreement with an anhydride formulation.

Anal. Calcd. for $C_{24}H_{15}NO_5$: C, 72.54; H, 3.81; N, 3.53. Found: C, 72.29; H, 4.19; N, 3.63.

When this reaction was carried out under similar conditions using benzene as the solvent, the yield of adduct was 5% of the theoretical amount.

1-*p*-Nitrophenyl-3,6-endomethylene-4-cyclohexene-1,2-dicarboxylic Acid (VI).—The same molar quantities of cyclopentadiene, *p*-nitrophenylmaleic anhydride and glacial acetic acid were used as in the preparation of the anthracene adduct. This procedure differed in that a crystal of hydroquinone was added and the reaction mixture was heated for 24 hours at 60–70°. The product was isolated and recrystallized, as in the case of the anthracene adduct, to give 1.90 g. of colorless prisms.

When the benzene was used as a solvent, under similar conditions, the yield was but 18% of the theoretical amount.

Adducts with 2-Methyl-, 2-Ethyl- and 2-Isopropyl-1,3-butadienes (III, IV, V).—In each case 0.02–0.03 mole of diene was dissolved in 30 ml. of benzene containing 0.01 mole of *p*-nitrophenylmaleic anhydride and a crystal of hydroquinone. The solution was heated under reflux for 24 hours in an atmosphere of nitrogen. All three adducts were isolated as above and recrystallized from ethyl acetate–petroleum ether (high boiling). The neutralization equivalents determined in 95% ethanol or in benzene solution and infrared spectra indicated, however, that a partial lactonization of one of the carboxyl groups had occurred across the alicyclic double bond, perhaps during recrystallization. When the neutralization equivalent was determined by dissolving a sample of the adduct in an aliquot of 0.1 *N* sodium hydroxide, and then back-titrating with a standardized aqueous hydrochloric acid solution, the values obtained were in agreement with the calculated values for the respective acids.

TABLE II

Adduct	Neut. equiv. Calcd.	Neut. equiv. Found[a]	Neut. equiv. Found[b]	Dimethyl ester Crystalline form[c]	Dimethyl ester Yield, %	Diacid esterified, g.
I	145.6		147.7	Needles	81.5	0.291
II	159.7		160.2	Needles	63.3	.638
III	152.6	148.7	173.7	Plates	54.2	.305
IV	159.7	159.3	174.6	Plates	54.6	.658
V	166.6	167.1	192.7	Plates	47.6	.300
VI	151.6		150.7	Plates	54.5	.303

[a] Back titration with hydrochloric acid. [b] Direct titration with aqueous sodium hydroxide. [c] The diesters were all colorless.

Proof of Structure of the Isoprene (III) and 2-Ethyl-1,3-butadiene (IV) Adducts. A.—The reduction of the nitro group of the isoprene adduct by catalytic hydrogenation with Raney nickel and by iron and hydrochloric acid was unsuccessful. The following procedure, however, proved satisfactory: A solution of 1.53 g. (0.005 mole) of the isoprene adduct (III) in 30 ml. of aq. ammonia (6 *N*) was saturated with hydrogen sulfide and was heated for one hour on a steam-bath. It was then diluted with 10 ml. of aq. ammonia (6 *N*), and the sulfur which precipitated was collected on a filter. The *p*H of the filtrate was adjusted to 4 with acetic acid and the solution was permitted to stand for six hours. The colorless, finely divided solid which precipitated was collected on a filter and suspended in 20 ml. of 10% aq. potassium hydroxide. This cloudy solution was then filtered and the amine was reprecipitated as before. The yield of impure material was 1.08 g. (77%), m.p. 245–247°.

A solution of this impure amine in 10 ml. of water and 3 ml. of concd. hydrochloric acid was cooled to 0° and was diazotized by the dropwise addition of a solution of 0.275 g. of sodium nitrite in 5 ml. of water.

Eleven milliliters of a precooled 30% aq. hypophosphorous acid solution was added dropwise and the resulting solution was placed in a refrigerator for four days. At this time the mixture was allowed to warm to room temperature and the precipitate which had formed was separated on a filter, washed thoroughly with water and dried. This solid material was dissolved in a minimum volume of hot ethyl acetate. Petroleum ether (high boiling) was added until the solution was faintly cloudy. A red-brown oil separated. The supernatant liquid was decanted and was treated in a similar manner two additional times. The resulting clear solution was evaporated to dryness and the reddish solid thus obtained was recrystallized twice from ethyl acetate. The yield was 0.33 g. (33%) of slightly colored needles, m.p. 173–175°. There was no depression of the melting point when this material was mixed with an authentic sample of 1-phenyl-4-methyl-4-cyclohexene-1,2-dicarboxylic acid (m.p. 173–175°).[3a] The infrared absorption spectra of the two samples were identical.

B.—The same molar quantities of reagents were used for the degradation of the 2-ethyl-1,3-butadiene adduct. The yield of crude amine was 0.821 g. (57%), m.p. 223–225°. The yield of the deaminated adduct was 0.155 g. (20%), m.p. 161–163°. This compound proved to be identical with an authentic sample of 1-phenyl-4-ethyl-4-cyclohexene-1,2-dicarboxylic acid (m.p. 161–163°)[3a] by use of the criteria shown above.

1,2,3,4-Tetrahydro-7-nitro-1,1′-binaphthyl-3,4-dicarboxylic Acid (VII).—A solution of 8.76 g. (0.04 mole) of *p*-nitrophenylmaleic anhydride, 12.4 g. (0.08 mole) of 1-vinylnaphthalene[12] and a crystal of *p*-*t*-butylcatechol in 60 ml. of glacial acetic acid was heated at 80–90° for 36 hours under an atmosphere of nitrogen. After distillation of the solvent *in vacuo* (water pump), the yellow residue was extracted with two 100-ml. portions of hot 5% aq. sodium bicarbonate. The combined extracts were washed with two 100-ml. portions of benzene and one 100-ml. portion of diethyl ether, boiled to remove the dissolved organic solvents, treated with Darco and filtered through Filter-cel. The acid was then precipitated with 6 *N* hydrochloric acid, collected on a filter, washed thoroughly with water and dried. The yield of the crude product was 15.1 g., m.p. 215–218°. It was recrystallized from acetone–petroleum ether (high boiling) to give 5.92 g. (38% of the theoretical amount) of colorless needles, m.p. 223–225° dec.

Anal. Calcd. for $C_{22}H_{17}NO_6$: C, 67.51; H, 4.38; N, 3.58; neut. equiv., 195.7. Found: C, 67.85; H, 4.16; N, 3.67; neut. equiv., 200.9.

Proof of Structure of the 1-Vinylnaphthalene Adduct (VII).—Following the procedure used for establishing the structure of the isoprene adduct, 1.34 g. of the 1-vinylnaphthalene adduct was reduced with ammonium sulfide. The resulting amine was not dried but was immediately diazotized and treated with 30% aq. hypophosphorous acid as before. The brown tar which formed was collected on a filter, dried and evaporatively distilled at 200° (0.3 mm.). The yellow solid distillate which was obtained was dissolved in hot 10% aq. potassium hydroxide, filtered and reprecipitated with glacial acetic acid. It was collected with the aid of a centrifuge. After two recrystallizations from 95% ethanol, the yield was 60 mg. (1.8%) of a colorless finely-divided material, m.p. 214–216°. The weight of the remaining crude residues from the recrystallizations was 173 mg.

The ultraviolet spectrum was identical with that of 1,2,3,-

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[12] A. Cohen and F. L. Warren, *J. Chem. Soc.*, 1318 (1937). The method of A. L. Wilds, THIS JOURNAL, **64**, 1421 (1942), was used to prepare the intermediate β-(1-naphthyl)-ethyl alcohol.

4-tetrahydro-1,1'-binaphthyl-3,4-dicarboxylic acid, m.p. 227–229°.[3b]

Anal. Calcd. for $C_{22}H_{18}O_4$: C, 76.29; H, 5.24. Found: C, 75,88; H, 5.57.

A small sample (0.1 g.) of the reference compound, 1,2,3,4-tetrahydro-1,1'-binaphthyl-3,4-dicarboxylic acid, m.p. 227–229°, was sublimed at 200° (0.3 mm.). The sublimate, m.p. 97–98°, was insoluble in 5% aq. sodium bicarbonate. It was dissolved in 20 ml. of cold 10% aq. potassium hydroxide and reprecipitated with glacial acetic acid. The precipitate was collected with the aid of a centrifuge and was washed with water. The yield was 0.1 g., m.p. 213–215°. When mixed with a sample of the degradation product obtained above, no depression of the melting point was observed.

The 173 mg. of crude residue obtained from the degradation (see above) was decarboxylated and dehydrogenated by the procedure reported previously[3b] to give 18 mg. of a product, m.p. 153–155°. When samples of this material were mixed with an authentic sample of 1,1'-binaphthyl, m.p. 156–158°, there was no melting point depression.

Urbana, Ill.

[Contribution from the Noyes Chemical Laboratory, University of Illinois]

Quinone Imides. XXXII. Reactions of 1,4-Naphthoquinonedibenzenesulfonimide with Pyridine and its Derivatives

By Roger Adams and Seymour H. Pomerantz

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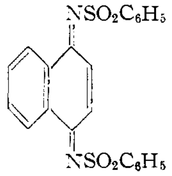
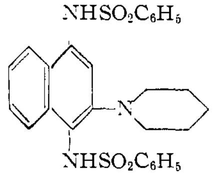
1,4-Naphthoquinonedibenzenesulfonamide in pyridine reacts with dilute hydrochloric acid to form 1,4-dibenzenesulfonamido-2-naphthylpyridinium chloride. This compound is hydrogenated in ethanol with platinum oxide to 2-(N-piperidino)-1,4-naphthalenedibenzenesulfonamide; in aqueous sodium carbonate to a 5-benzenesulfonamidotetrahydrobenzo[e]pyrido[a]benzimidazole; in ethanolic alkali with Raney nickel to 5-benzenesulfonamido-8,9;10,11;11a,12-hexahydrobenzo[e]pyrido[a]benzimidazole. This last product was also obtained by hydrogenation of the tetrahydro analog in ethanolic alkali with Raney nickel. The structure of the hexahydrobenzimidazole was proved by its identity with the reduction product of the compound formed by interaction of 1,4-naphthoquinonedibenzenesulfonimide with 2-aminopyridine; hydrolysis converts this 5-benzenesulfonamidobenzo[e]pyrido[a]benzimidazole to the known 5-aminobenzo[e]pyrido[a]benzimidazole. Moist silver oxide reacts with the naphthylpyridinium chloride to give 5-benzenesulfonamido-12-benzenesulfonyl-11a,12-dihydrobenzo[e]pyrido[a]benzimidazole. 1,4-Naphthoquinonedibenzenesulfonimide adds the sodium salt of 2-pyridone to form N-(1',4'-dibenzenesulfonamido-2'-naphthyl)-2-pyridone.

The reaction of 1,4-naphthoquinonedibenzenesulfonimide (I) with pyridine and an excess of aqueous hydrochloric acid resulted in the formation of a colorless product in essentially quantitative yield. It was hygroscopic and readily formed a hydrate containing one mole of water. The compound contained halogen, and its solution in ethanol gave an immediate precipitate with aqueous ethanolic silver nitrate. It was brilliantly fluorescent under ultraviolet light. It dissolved readily in aqueous sodium carbonate with the formation of an orange-red solution from which the original compound could be obtained by acidification.



I



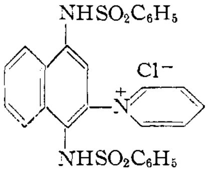
II

Analysis of a dry sample indicated that it was composed of one mole of diimide, one mole of pyridine and one mole of hydrogen chloride. The infrared spectrum in Nujol mull showed the $-SO_2$ band generally associated with sulfonamides at 1171 and 1335 cm.$^{-1}$. There were no bands characteristic of sulfonimides. No normal N–H band appeared in the spectrum of the non-hydrated material, but a broad medium band at about 2720 cm.$^{-1}$ indicated the probability of some sort of bonded N–H in the solid. The limited solubility in a suitable organic solvent prevented a study of the solution spectrum. This same absence of an N–H band also was observed in another sulfonamide described in this communication when the spectrum was determined in Nujol mull, but one appeared in the solution spectrum.

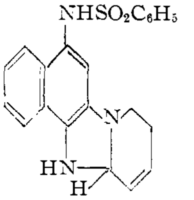
The compound was easily hydrogenated in ethanol solution in the presence of platinum oxide to form 2-(N-piperidino)-1,4-naphthalenedibenzenesulfonamide (II). The latter structure was established by its synthesis from I and piperidine.

From these data the most likely structure of the compound was deduced as the pyridine–hydrogen chloride adduct, 1,4-dibenzenesulfonamido-2-naphthylpyridinium chloride (III). The facile hydrogenation of III to II is in agreement with earlier work[1] on the catalytic hydrogenation of a number of pyridinium salts.

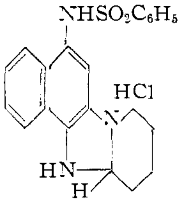
Hydrogenation of III in aqueous sodium carbonate over platinum oxide at ordinary pressure resulted in a compound formulated as IV. The position of the double bond in the pyridine residue was not determined.



III



IV



V

The infrared spectrum of IV in Nujol mull showed no N–H band. In chloroform solution, however, an N–H band at 3360 cm.$^{-1}$ was present and in pyridine solution a very broad N–H band occurred at about 3400 cm.$^{-1}$. A medium band at 1632 cm.$^{-1}$ occurred in both mull and solution spectra. The spectra also showed characteristic $-SO_2$ bands.

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[1] T. S. Hamilton and R. Adams, This Journal, **50**, 2260 (1928).