n 2 ml. of dry chloroform. The flask was stoppered immediately and shaken vigorously. After about twenty minutes, the adduct began to crystallize. The reaction mixture was permitted to stand at room temperature for 48 hours. The crystalline material present was collected by filtration and dried in the air; yield 1.25 g. (87%). This product was washed with two 7–8 ml. portions of boiling dry chloroform and was then recrystallized from hot dry chloroform to which sufficient dry ethyl acetate was added to effect complete solution. Further recrystallization from chloroform–ethyl acetate gave the analytically pure thiophenol adduct, m. p. 189–190.5°, with softening at 187°.

Anal. Calcd. for $C_{18}H_{15}NO_3S$: C, 60.48; H, 4.23; N, 3.92. Found: C, 60.74; H, 4.51; N, 3.78.

Attempted Addition of Morpholine to *p*-Quinone Monobenzenesulfonimide.—To a solution of 1 g. of the quinone imide in 10 ml. of dry chloroform was added a chloroform solution of 0.4 g. of morpholine. The resulting mixture became violet in color, then greenish-black. The reaction mixture was permitted to stand 48 hours and was then evaporated to dryness. The tarry residue was dissolved in 5% aqueous sodium hydroxide (Darco). Dilute hydrochloric acid was added dropwise with stirring to the alkaline solution, until a *p*H of approximately 7.5 was reached. A tar resulted, which resisted all attempts at crystallization.

Reduction of *p*-Quinone Monobenzenesulfonimide with Sodium Hydrosulfite.—To an absolute ethanolic solution of 0.5 g. of the quinone imide was added sufficient 10% aqueous sodium hydrosulfite to effect decolorization. Inorganic material was removed by filtration and the filtrate was evaporated to dryness. The residue was washed with water, filtered and dried in the air; yield 0.4 g. Recrystallization from ethyl acetate gave *p*-benzenesulfonamidophenol, m. p. 154–155°, not depressed upon admixture with authentic material.

Hydriodic Acid Reduction of *p*-Quinone Monobenzenesulfonimide.—To 5 ml. of concd. hydriodic acid (sp. gr. 1.50) was added 0.5 g. of solid *p*-quinone monobenzenesulfonimide. An instant liberation of iodine occurred. The reaction mixture was heated on the steam-bath for 30 minutes. The crude product was collected by filtration, washed with water, dried in the air and washed with chloroform; yield 0.3 g. Recrystallization from ethyl acetate gave pure *p*-benzenesulfonamidophenol, m. p. 155–156°, unchanged upon admixture with authentic material.

Hydrolysis of *p*-Quinone Monobenzenesulfonimide.—A suspension of 0.5 g. of the quinone imide in 20 ml. of water was heated under reflux over a low flame for 45 minutes. The reaction mixture was cooled and the crystalline material present was collected by filtration and dried in the air; yield 0.2 g. Recrystallization from dilute ethanol gave a virtually colorless compound, m. p. 151–152°, not depressed upon admixture with authentic benzenesulfonamide, m. p. 152–153°. A depression of 30° was obtained upon admixture with *p*-benzenesulfonamidophenol, m. p. 156°.

A small quantity of *p*-benzoquinone, m. p. 110–114°, collected in the lower part of the condenser tube. Further evidence for the presence of quinone was found in the detection of its characteristic odor in the reaction mixture and in the steam volatility of the reaction product remaining in the reaction mixture after removal of the benzenesulfonamide.

Hydrolysis of 3-Methyl-*p*-quinone 1-Benzenesulfonimide.—A suspension of 1.0 g. of the quinone imide in 40 ml. of water was heated under reflux for 15 minutes. A quantity of *p*-toluquinone, m. p. 67–68°, collected in the lower part of the condenser. Upon cooling, solid material separated from the reaction mixture. Recrystallization from benzene gave nicely crystalline material, m. p. 148–150°, not depressed upon admixture with authentic benzenesulfonamide.

URBANA, ILL. RECEIVED JULY 27, 1950

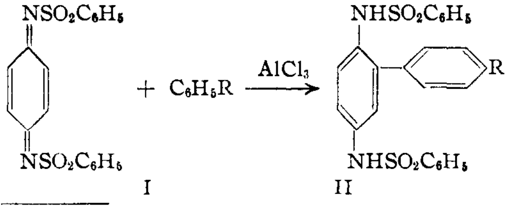
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Quinone Imides. V. Aluminum Chloride-catalyzed Arylations of *p*-Quinone Dibenzenesulfonimides

BY ROGER ADAMS AND KENDRICK R. EILAR

Aromatic hydrocarbons, phenols and phenolic ethers in the presence of aluminum chloride react with *p*-quinone dibenzenesulfonimides to give 2-aryl-*p*-phenylenedibenzenesulfonamides in yields of 26 to 67%. In the addition of hydrocarbons, it is essential that the quinone diimide be added to the aluminum chloride in the hydrocarbon; addition of the aluminum chloride to the hydrocarbon solution of the quinone diimide results in quantitative reduction of the quinone diimide to *p*-phenylenedibenzenesulfonamide. Boron trifluoride, as catalyst, is effective in the addition of phenolic compounds and phenol ethers but not of the hydrocarbons regardless of the order of addition of reactants. Attempted oxidation of the 2-aryl-*p*-phenylenedibenzenesulfonamides to the corresponding quinones was successful only in the case of 2-(β-hydroxy-α-naphthyl) compound; the other sulfonamides either resisted oxidation or were degraded to *p*-quinone dibenzenesulfonimide.

Pummerer and co-workers discovered that a variety of aromatic compounds in the presence of aluminum chloride will add, presumably by a 1,4 process, to *p*-benzoquinone to give 2,5-diarylhydroquinones.[1] This reaction has now been extended to *p*-quinone dibenzenesulfonimide (I).[2] The arylation of the quinone diimide terminates with the monosubstituted *p*-phenylenediamine derivative; thus, reaction of *p*-quinone dibenzenesulfonimide (I) with benzene gives 2-phenyl-*p*-phenylenedibenzenesulfonamide (II, R = H) in 67% yield, when the quinone diimide is added to a mixture of aluminum chloride in benzene. When the addition is reversed, the introduction of aluminum chloride to a solution of the quinone diimide in benzene, reduction takes place quantitatively with formation of the parent *p*-phenylenedibenzenesulfonamide. The oxidation product of the benzene in the latter reaction was presumably biphenyl, although it was not isolated and identified.



I II

The reaction of *m*-xylene with I, carried out by adding the quinone diimide to a mixture of aluminum chloride in *m*-xylene, gives a mixture of products. Three were isolated; one was the expected adduct (III), the second, *p*-phenylenedibenzenesulfonamide formed by reduction of the quinone di-

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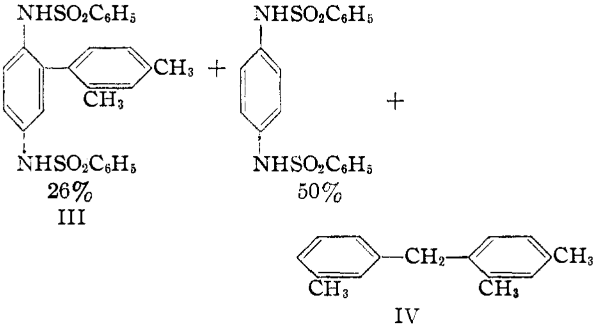
[1] R. Pummerer and E. Prell, *Ber.*, **55**, 3105 (1922); R. Pummerer and H. Fiedler, *ibid.*, **60**, 1439 (1927); R. Pummerer and G. Huppmann, *ibid.*, **60**, 1442 (1927); R. Pummerer, M. Dally and S. Reissinger, *ibid.*, **66**, 792 (1933).

[2] R. Adams and A. S. Nagarkatti, THIS JOURNAL, **72**, 4601 (1950); see also R. Adams and J. L. Anderson, *ibid.*, **72**, 5154 (1950); R. Adams and R. A. Wankel, *ibid.*, **73**, 131 (1951); R. Adams and J. H. Looker, *ibid.*, **73**, 1145 (1951).

imide, and the third, a hydrocarbon (IV) formed by the oxidation of the *m*-xylene.



26%
III

50%

IV

The oxidation product of the *m*-xylene was a liquid of empirical formula $C_{16}H_{18}$ whose physical properties did not correspond to those of 2,2′,4,4′-tetramethylbiphenyl.[3] It proved to be 2,3′,4-trimethyldiphenylmethane (IV). Compound IV was synthesized by an unequivocal method, the condensation of *m*-xylyl chloride with *m*-xylene in presence of aluminum amalgam and shown to be identical in physical properties and ultraviolet spectrum with the isolated by-product. It is thus probable that the quinone diimide in presence of aluminum chloride converted part of the *m*-xylene to the *m*-xylyl radical which reacted with the *m*-xylene used as solvent to form IV.

When boron trifluoride is substituted for aluminum chloride as catalyst, by bubbling the former into a solution of the quinone diimide in benzene or by introducing the boron trifluoride into the benzene and adding the quinone diimide, the *p*-quinone diimide is reduced quantitatively to *p*-phenylenedibenzenesulfonamide. Reduction of the quinone diimide also occurs exclusively when boron trifluoride is passed into a solution of quinone diimide in *m*-xylene.

Several phenols and phenol ethers were found to react with the quinone diimide in the presence of aluminum chloride or boron trifluoride to give compounds of the type shown in II in yields of 27 to 67%. The adduct, (II, R = OH), produced when phenol was used, contains a free hydroxy group as proved by conversion into the corresponding acetate. The position of the hydroxy group was not established, but by analogy with the products in the benzoquinone series[1] it is reasonable to expect that the hydrogen *para* to the hydroxy has taken part in the addition reaction. *o*- and *m*-cresol and β-naphthol react in a similar way to give products analogous to II; *p*-cresol, however, did not add to the quinone diimide but induced reduction of the quinone diimide to the *p*-phenylenediamine derivative. Neither the product of phenol and the quinone diimide nor those obtained from *o*- and *m*-cresol and β-naphthol give a color with ferric chloride; however, they all give a definite coloration in the phosphomolybdic acid test for hindered phenols.[4] The products from anisole, phenetole and veratrole, as well as the acetate of II (R = OH), give negative phosphomolybdic acid tests. The biphenyls derived from the addition of various phenols to the quinone diimide are thus unquestionably phenols, exemplified by II (R = OH), and not diaryl ethers. The crude products obtained from the phenolic ethers (anisole, phenetole and veratrole) and the quinone diimide contain merely traces of ether cleavage compounds as shown by the very faint color tests.

Oxidation of 2-phenyl-*p*-phenylenedibenzenesulfonamide took an unexpected course. It did not give the corresponding quinone diimide but resulted in a cleavage of the molecule with elimination of the phenyl ring and formation of *p*-quinone dibenzenesulfonimide. The analogous oxidation occurred, although in poorer yield, with 2-(*p*-hydroxyphenyl)-*p*-phenylenedibenzenesulfonamide. The product (II, R = OCH_3) from anisole resisted oxidation even over a long period of time. The acetate of II (R = OH) was also recovered after refluxing for 16 hours with lead tetraacetate in glacial acetic acid solution. Attempted oxidation of this compound with chromic acid was unsuccessful. The only 2-arylated *p*-phenylenedibenzenesulfonamide which was successfully oxidized to its quinone was 2-(β-hydroxy-α-naphthyl)-*p*-phenylenedibenzenesulfonamide, although it was never obtained completely pure.

The 2-methyl-*p*-quinone dibenzenesulfonimide reacted with *o*-cresol to give 2-methyl-5-(3-methyl-4-hydroxyphenyl)-*p*-phenylenedibenzenesulfonamide. The 2-chloro-*p*-quinone dibenzenesulfonimide, however, gave with anisole and *o*-cresol only intractable tars. All of the aluminum chloride- and boron trifluoride-catalyzed reactions were characterized by a certain amount of tar formation.

TABLE I

ADDITION PRODUCTS[a] OF *p*-QUINONE DIBENZENESULFONIMIDES IN PRESENCE OF $AlCl_3$

Adduct	*p*-Phenylenedibenzenesulfonamide	Yield, %	M. p., °C. (cor.)	Analyses, % Calcd.	Found
Benzene	2-Phenyl-	67	196	C, 62.05	61.92
				H, 4.34	4.55
m-Xylene	2-(2,4-Dimethylphenyl)-	26	196 sl. dec.	C, 63.39	63.28
				H, 4.91	5.09
Phenol	2-(*p*-Hydroxyphenyl)-	63	227–228 dec.	C, 60.00	59.83
				H, 4.20	4.42
o-Cresol	2-(3-Methyl-4-hydroxyphenyl)-	67	217–218 dec.	C, 60.70	60.54
				H, 4.48	4.66
m-Cresol	2-(2-Methyl-4-hydroxyphenyl)-[b]	27	175	C, 60.70	60.93
				H, 4.48	4.58
β-Naphthol	2-(β-Hydroxy-α-naphthyl)-	41	237–238 dec.	C, 63.38	63.03
				H, 4.18	4.06
Anisole	2-(*p*-Methoxyphenyl)-[c]	61.5	193–195 dec.	C, 60.70	60.72
				H, 4.48	4.52
Phenetole	2-(*p*-Ethoxyphenyl)-	50	188–189 dec.	C, 61.38	61.01
				H, 4.95	4.94
Veratrole	2-(3,4-Dimethoxyphenyl)-	25	197–198 dec.	C, 59.59	60.07
				H, 4.59	4.72

[a] These reactions were all carried out in essentially the same manner as that described in the Experimental section for the preparation of 2-phenyl-*p*-phenylenedibenzenesulfonamide. In cases where the aromatic reactant was a solid, carbon disulfide was used as solvent, and a four-mole excess of the aromatic compound was used. [b] This compound crystallized from ethanol with one molecule of ethanol of crystallization; in this form it melted at 114–115°, then upon further heating solidified and finally melted at 175°. *Anal.* Calcd. for $C_{25}H_{22}O_5N_2S_2 \cdot C_2H_5OH$: C, 60.00; H, 5.23. Found: C, 60.32; H, 5.35. A sample was heated *in vacuo* at 140° for 6 hours; wt. sample, 0.2252 g.; loss in weight, 0.0191 g.; calcd. loss in weight for one molecule of ethanol 0.0191 g. [c] By use of boron trifluoride in place of aluminum chloride, the same product was obtained in 52% yield.

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(3) F. Ullmann and G. M. Meyer, *Ann.*, **332**, 45 (1904).

(4) K. Brauer, *Chem. Ztg.*, **50**, 553 (1926).

The compounds prepared from I by aluminum chloride catalysis are summarized in Table I.

The authors are indebted to Miss Emily Davis and Miss Rachel Kopel for the microanalyses and to Miss Ella Richards for the determination of ultraviolet absorption spectra.

Experimental

***p*-Quinone Dibenzenesulfonimide.**—This product was prepared in earlier work by the oxidation of *p*-phenylenedibenzenesulfonamide in glacial acetic acid with lead tetraacetate. A somewhat cheaper and indeed more convenient procedure for preparing large quantities has now been found. It employs pure red lead in place of lead tetraacetate. Some grades of red lead are better than others and consequently that which proved best is indicated. The use of less suitable grades of red lead result in quinone diimide of lower purity which requires an additional crystallization or two before it is pure. This reaction was first performed by Dr. C. Robert Walter, Jr.

A suspension of 43 g. of *p*-phenylenedibenzenesulfonamide in 500 ml. of glacial acetic acid in an 800-ml. beaker was heated to and maintained at 65° with continuous stirring while 76.2 g. of red lead (Pb_3O_4, Baker Analyzed) was added in portions over a period of 45 minutes. The yellow suspension was then cooled in an ice-bath for an hour, after which it was filtered. The crude product weighed 41 g. (96%), m. p. 167–178°. To purify, 150 ml. of glacial acetic acid was heated to boiling, the crude quinone was added, and the solution stirred for 1 minute, filtered and quickly cooled. The product amounted to 36.3 g. (85%), m. p. 178–179° (cor.). One to four additional crystallizations raise the melting point to a maximum of 188° (cor.), the number necessary depending upon any particular preparation. Product, m. p. 178–179°, is entirely satisfactory for subsequent reactions.

The product, m. p. 188°, appears to be relatively stable at room temperature and the melting point is only slightly lower after two months. A less pure sample, however, deteriorates more rapidly and the melting point in a few months may be as low as 150–160°. These older samples are readily purified to the maximum melting point by crystallization from glacial acetic acid.

2-Phenyl-*p*-phenylenedibenzenesulfonamide.—To 100 ml. of dry benzene in a 400-ml. beaker cooled by an ice-bath was added with stirring 15 g. of anhydrous aluminum chloride. After 15 minutes of continued stirring, 10 g. of *p*-quinone dibenzenesulfonimide[1] was added in portions over a period of 15 minutes. The solution was then stirred for a period of 2 hours after which the ice-bath was removed. After a further hour of stirring with external cooling, the black solution was poured with stirring into 300 ml. of of water and a little hydrochloric acid containing enough ice to prevent warming beyond room temperature.

The yellow-brown solid was filtered, washed with water and air-dried. It was purified by crystallization from ethanol (Darco). The yield of once crystallized material was 8 g. (67%). When pure, the product formed white crystals, m. p. 196° (cor.) with slight sintering starting at 192°.

To a suspension of 2 g. of 2-phenyl-*p*-phenylenedibenzenesulfonamide in 5 ml. of glacial acetic acid was added 1.9 g. of lead tetraacetate. The mixture was heated to 50° with stirring for 10 minutes, then cooled in an ice-bath. The yellow crystals were filtered and washed with a little cold acetic acid and then with petroleum ether (b. p. 30-60°). The yield was 1.5 g. of *p*-quinone dibenzenesulfonimide. A further quantity of 0.1 g. of product was obtained by adding water to the filtrate, making a total of 1.6 g. (96%). Two recrystallizations from ethyl acetate gave material melting at 179° (cor.) with decomposition. Reduction with aqueous sodium hydrosulfite gave *p*-phenylenedibenzenesulfonamide, m. p. 247° (cor.). It did not depress the melting point of an authentic sample.

2-(2,4-Dimethylphenyl)-*p*-phenylenedibenzenesulfonamide.—With aluminum chloride: Substitution of *m*-xylene for benzene in the procedure described for the preparation of 2-phenyl-*p*-phenylenedibenzenesulfonamide gave, upon hydrolysis of the reaction mixture, 5 g. of *p*-phenylenedibenzenesulfonamide which was removed by filtration. The *m*-xylene layer of the filtrate was separated and distilled at reduced pressure on the water-bath. The dark colored residue was extracted with ether, leaving 3.3 g. (26%) of 2-(2,4-dimethylphenyl)-*p*-phenylenedibenzenesulfonamide. Recrystallization from ethanol gave pure white crystals, m. p. 196° (cor.) with slight decomposition.

When boron trifluoride was used only reduction occurred. A suspension of 6 g. of *p*-quinone dibenzenesulfonimide in 100 ml. of redistilled *m*-xylene in a 200 ml., 3-necked flask fitted with a stirrer, calcium chloride tube and a glass tube whose outlet dipped just below the surface of the solution, was cooled in an ice-bath. Boron trifluoride was admitted through the glass tube until fumes began emerging from the calcium chloride tube. The boron trifluoride was turned off and stirring was continued for one-half hour. The solution was filtered and the purple solid was washed with ethanol, and dried in an oven at 110°, yielding 6 g. (100%) of *p*-phenylenedibenzenesulfonamide, m. p. 247–249°. When mixed with an authentic sample[1] the melting point was not depressed.

2,3′,4-Trimethyldiphenylmethane.—(A) The ether extract described above in the aluminum chloride experiment was distilled at reduced pressure; the distillate weighing 1.4 g. was a clear, colorless oily liquid, b. p. 122–125° at 2 mm. (309° at 757 mm. by a micro determination); $n^{20}\text{D}$ 1.5630; $d^{25}{}_4$ 1.0523; it did not solidify when cooled to 0°.

Anal. Calcd. for $C_{16}H_{18}$: C, 91.43; H, 8.57. Found: C, 91.41; H, 8.57.

(B) *m*-Xylyl chloride[5] was condensed with *m*-xylene by the use of amalgamated aluminum according to the procedure given by Hartman and Phillips[6] for the preparation of diphenylmethane from benzyl chloride and benzene. It was not necessary to reflux the reactants, however; the reaction commenced immediately upon mixing at room temperature. The crude yield of 2,3′,4-trimethyldiphenylmethane was 84%; one distillation gave pure material in 60% yield, 123–125° at 2 mm., $n^{20}\text{D}$ 1.5641.

Anal. Calcd. for $C_{16}H_{18}$: C, 91.43; H, 8.57. Found: C, 91.02; H, 9.04.

The ultraviolet absorption spectrum of the synthetic material was identical with that of the hydrocarbon produced in the reaction of the *p*-quinone dibenzenesulfonimide with *m*-xylene in presence of aluminum chloride.

2-(*p*-Acetoxyphenyl)-*p*-phenylenedibenzenesulfonamide.—To a solution of 2 g. of 2-(*p*-hydroxyphenyl)-*p*-phenylenedibenzenesulfonamide in 10 ml. of pyridine, 25 ml. of acetic anhydride was added and the mixture allowed to stand at room temperature for 24 hours. It was then poured onto ice. After standing 24 hours, the white solid was collected by filtration and dried at 110°. The yield was 2.1 g. (97%). After purification by recrystallization from ethanol, it melted at 179–180° (cor.).

Anal. Calcd. for $C_{26}H_{22}N_2O_6S_2$: C, 59.77; H, 4.62. Found: C, 59.75; H, 4.71.

2-(β-Hydroxy-α-naphthyl)-*p*-quinone Dibenzenesulfonimide.—A suspension of 1 g. of 2-(β-hydroxy-α-naphthyl)-*p*-phenylenedibenzenesulfonamide and 1 g. of lead tetraacetate in 2 ml. of glacial acetic acid in a test-tube was shaken for 15 minutes. After addition of 5 ml. of water, the yellow precipitate was filtered, washed with water, and recrystallized from ethyl acetate. The yield was 0.3 g. (30%) of orange-yellow crystals, m. p. 208° (cor.) when placed in a preheated bath at 208° (in an ordinary melting point determination without a preheated bath, the compound slowly turned tan and finally charred at 241°). The product was not absolutely pure as shown by analysis.

Anal. Calcd. for $C_{28}H_{20}N_2O_5S_2$: C, 63.62; H, 3.82. Found: C, 64.40; H, 3.92.

***x*-Chloro-(β-hydroxy-α-naphthyl)-*p*-phenylenedibenzenesulfonamide.**—To a solution of 0.1 g. of 2-(β-hydroxy-α-naphthyl)-*p*-quinone dibenzenesulfonimide in 5 ml. of glacial acetic acid was added five drops of concd. hydrochloric acid. Complete decolorization of the solution occurred within 3 minutes. Water was then added dropwise until a faint turbidity appeared. After standing overnight, fluffy, white crystals had formed. These were filtered, washed with water and recrystallized from aqueous ethanol; m. p. 214° (cor.). The product was not entirely pure.

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[5] M. S. Kharasch and H. C. Brown, THIS JOURNAL, **61**, 2142 (1939).

[6] Phillips, "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., p. 232.

Anal. Calcd. for $C_{28}H_{21}ClN_2O_5S_2$: C, 59.52; H, 3.75. Found: C, 58.67; H, 3.46.

Attempted Preparation of 2-(*p*-Hydroxyphenyl)-*p*-quinone Dibenzenesulfonimide.—A mixture of 0.5 g. of 2-(*p*-hydroxyphenyl)-*p*-phenylenedibenzenesulfonamide and 0.5 g. of lead tetraacetate was shaken for 1 hour at room temperature in 20 ml. of dry chloroform. The solution was filtered, the filtrate was evaporated to dryness, and the residue was stirred with 1 ml. of ethyl acetate. The yellow solid was filtered, washed with one ml. of ethyl acetate and then recrystallized from 2 ml. of ethyl acetate. The yield was 0.1 g. (20%) of yellow crystals, m. p. 178–179° (dec.). Reduction with aqueous sodium hydrosulfite gave *p*-phenylenedibenzenesulfonamide; m. p. 247°. It did not depress the melting point of an authentic sample. 2-(3-Methyl-4-hydroxyphenyl)-*p*-phenylenedibenzenesulfonamide gave similar results.

2-Methyl-5-(4-methyl-4-hydroxyphenyl)-*p*-phenylenedibenzenesulfonamide.—Following the general directions for the addition of benzene to *p*-quinone dibenzenesulfonimide, *o*-cresol was added to 2-methyl-*p*-quinone dibenzenesulfonimide. The product was obtained in 52% yield. It formed white crystals, m. p. 189° (cor.) with decomposition.

Anal. Calcd. for $C_{25}H_{22}N_2O_5S_2$: C, 61.88; H, 4.80. Found: C, 61.49; H, 4.77.

Attempted addition of *o*-cresol and anisole to 2-chloro-*p*-phenylenedibenzenesulfonamide under the same conditions gave only tars.

URBANA, ILL.

RECEIVED JULY 31, 1950

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

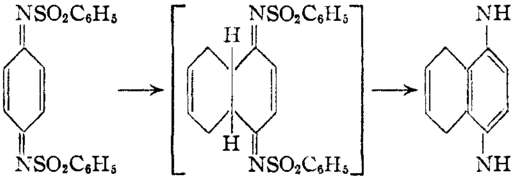
Quinone Imides. VI. Addition of Dienes to *p*-Quinone Sulfonimides

BY ROGER ADAMS AND C. ROBERT WALTER, JR.

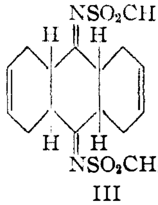
Diels–Alder reactions have been applied to *p*-quinone dibenzene- and dimethane-sulfonimides. They add one molecule of butadiene to give 5,8-dihydronaphthylene-1,4-disulfonamides. The latter on addition of one molecule of bromine and dehydrohalogenation give naphthylene-1,4-disulfonamides. 2,3-Diphenylbutadiene gives a stable mono-adduct with *p*-quinone dibenzenesulfonimide which is rearranged by halogen acid to 6,7-diphenyl-5,8-dihydronaphthylene-1,4-dibenzenesulfonamide. The methanesulfonimide does not react similarly. Two molecules of cyclopentadiene add and the products may be hydrogenated with saturation of the two carbon–carbon and two carbon–nitrogen double bonds. Anthracene does not act as a diene in the way it does with *p*-quinone but adds 1,4 to give 2-(9-anthryl)-*p*-phenylenedibenzenesulfonamide.

p-Quinone disulfonimides of various types exhibit reactions similar to *p*-quinones. They are reduced to the corresponding *p*-phenylenedisulfonamides, they add hydrogen chloride, and most of them also add amines and thiols.[1]

The application of the Diels–Alder reaction to the *p*-quinone disulfonimides has now been studied. When *p*-quinone dibenzenesulfonimide is heated in a sealed tube at 100–110° with butadiene in benzene, a product separates which has structure II. Even with excess of butadiene the same product is formed. The expected intermediate addition product (I) is apparently unstable under the conditions of the reaction and is converted completely by migration of two hydrogens into the aromatic compound, 5,8-dihydronaphthylene-1,4-dibenzenesulfonamide (II). The compound adds two atoms of bromine to the isolated double bond. This was assumed since *p*-quinone dibenzenesulfonamide does not react with bromine under the same conditions. The dibromo derivative thus formed upon treatment with ethanolic alkali loses two molecules of hydrogen bromide to produce naphthylene-1,4-dibenzenesulfonamide. This latter compound was identified by comparison with an authentic sample synthesized from 1,4-naphthylenediamine. *p*-Quinone dimethanesulfonamide reacts similarly and the corresponding 5,8-dihydronaphthylene-1,4-dimethanesulfonamide results which is converted through addition of bromine and elimination of hydrogen bromide to the fully aromatic analog. However, in the initial addition of butadiene to the *p*-quinone dimethanesulfonimide, some di-adduct was isolated, presumably with structure III, since its infrared spectrum shows the presence of carbon–nitrogen double bonds and no NH grouping.



I II



III

Unexpectedly, isoprene and dimethylbutadiene do not appear to behave like butadiene. Although reaction products formed which were purified to constant melting point, nevertheless they did not show the proper analysis for 1:1 or 2:1 adducts. Their structures have not yet been elucidated.

2,3-Diphenylbutadiene and *p*-quinone dibenzenesulfonimide react upon refluxing in benzene and a yellow compound results which is apparently the adduct analogous to I. Upon warming with a little mineral acid, rearrangement occurs with formation of 6,7-diphenylnaphthylene-1,4-dibenzenesulfonamide. *p*-Quinone dimethanesulfonimide, however, failed to react with 2,3-diphenylbutadiene under the same conditions.

Cyclopentadiene, which is an extremely reactive diene, adds to the *p*-quinone dibenzenesulfonimide in benzene solution at room temperature. The product is the di-adduct (IV) and in no attempt was it possible to isolate the mono-adduct even

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(1) (a) R. Adams and A. S. Nagarkatti, THIS JOURNAL, **72**, 4601 (1950); (b) R. Adams and J. L. Anderson, *ibid.*, **72**, 5154 (1950); (c) R. Adams and R. A. Wankel, *ibid.*, **73**, 131 (1951); (d) R. Adams and J. H. Looker, *ibid.*, **73**, 1145 (1951); (e) R. Adams and K. R. Eilar, *ibid.*, **73**, 1149 (1951).