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 $C_{26}H_{22}N_2O_6S_2$: 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]

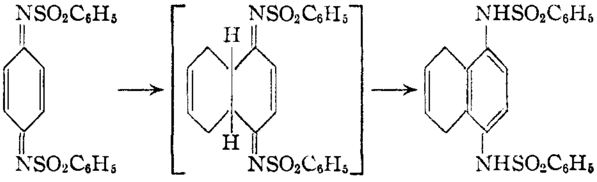
Quinone Imides. VI. Addition of Dienes to *p*-Quinone Sulfonimides

BY ROGER ADAMS AND C. ROBERT WALTER, JR.

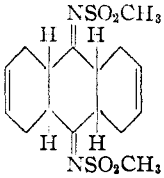
Diels-Alder reactions have been applied to *p*-quinone dibenzene- and dimethane-sulfonimides. They add one molecule of butadiene to give 5,8-dihydronaphthylene-1,4-disulfonamides. The latter on addition of one molecule of bromine and dehydrohalogenation give naphthylene-1,4-disulfonamides. 2,3-Diphenylbutadiene 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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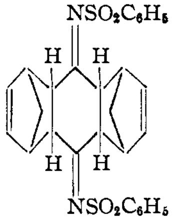
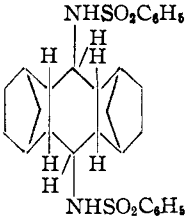
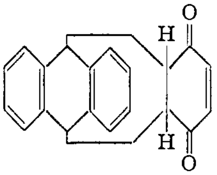
[1] (a) R. Adams and A. S. Nagarkatti, THIS JOURNAL, **72**, 4601 (1950); (b) R. Adams and J. L. Anderson, *ibid.*, **72**, 5154 (1950); (c) R. Adams and R. A. Wankel, *ibid.*, **73**, 131 (1951); (d) R. Adams and J. H. Looker, *ibid.*, **73**, 1145 (1951); (e) R. Adams and K. R. Eilar, *ibid.*, **73**, 1149 (1951).

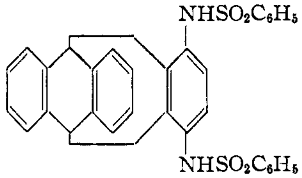
when equivalent amounts of diene and quinone diimide were used. The product shows no NH groups in its infrared spectrum but merely carbon–nitrogen double bonds. It readily absorbs four moles of hydrogen to completely saturate the two olefinic and two carbon–nitrogen double bonds and give V. The molecules corresponding to IV and V, using *p*-quinone dimethanesulfonimide, were also synthesized.

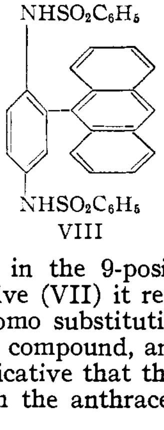

IV


V

The reaction of anthracene with *p*-quinone dibenzenesulfonimide occurs merely by refluxing the reactants in glacial acetic acid. By analogy to the addition of anthracene to *p*-quinone (VI) this product was assumed to be VII, formed by rearrangement of the initial addition product analogous to VI, to the benzene derivative. The product was shown to be aromatized by its infrared spectrum which indicated the presence of NH groups and absence of carbon–nitrogen double bonds. Compound VII was synthesized by an unequivocal method. When the quinone formed by oxidation of VI was converted to its dioxime, the latter reduced to the diamine and benzenesulfonated, the product (VII) was formed. It proved not to be identical with the compound resulting from anthracene and *p*-quinone dibenzenesulfonimide. The melting points and infrared spectra differed. It did not react with bromine. Another structure (VIII) was then postulated which was demonstrated to be correct. The Diels–Alder reaction apparently does not take place but instead a 1,4-addition of the anthracene to the quinone diimide. The attachment is assumed to be in the 9-position. Unlike the triptycene derivative (VII) it reacts with bromine to give a monobromo substitution product, probably the 10-bromo compound, and no dibromo adduct. This is indicative that the 9-position is the one through which the anthracene is attached to the diamide. The synthesis of VIII was achieved from *p*-quinone dibenzenesulfonimide and anthracene in carbon bisulfide as solvent with aluminum chloride as catalyst, following the procedure for adding aromatic compounds to quinone diimides described in an earlier paper.[1e] The compounds prepared by the two methods have identical melting points, identical infrared spectra and give the same monobromo compound on bromination.


VI


VII


VIII

Anthracene adds to *p*-quinone dimethanesulfonimide under the same conditions that it adds to the corresponding dibenzenesulfonimide. However, it did not add in carbon disulfide under the conditions of the Friedel–Crafts reaction.

p-Quinone dibenzenesulfonimide reacted with furan and chloroprene but no addition products could be characterized. It was reduced by bicyclohexenyl to *p*-phenylenedibenzenesulfonamide and no adduct formed. It oxidized diphenylisobenzofuran to *o*-dibenzoylbenzene.

Experimental

5,8-Dihydronaphthylene-1,4-dibenzenesulfonamide (A).—A mixture of 5 g. of *p*-quinone dibenzenesulfonimide,[1] 1.5 g. of butadiene and 15 ml. of benzene was placed in a sealed tube and heated at 100-110° for 9.5 hours. The crude product which weighed 3.8 g. was collected by filtration and recrystallized from approximately 2:1 pyridine-water or 2:1 dimethylformamide-water. The crystals were grayish-white and melted at 247-248° (cor.) (dec.). The yield was 2.7 g. (47.4%).

The compound was soluble in dilute aqueous alkali. An infrared absorption spectrum showed the presence of the -NH- grouping.

Anal. Calcd. for $C_{22}H_{20}N_2O_4S_2$: C, 59.98; H, 4.58; N, 6.36. Found: C, 60.04; H, 4.85; N, 6.60.

(B).—A mixture of 5.8 g. of *p*-quinone dibenzenesulfonimide, 1.5 g. of butadiene and 20 ml. of nitrobenzene was heated in a sealed tube at 140° for 8 hours. The solid, separated by filtration from the reaction mixture, was recrystallized by dissolving in hot pyridine and then adding water until incipient cloudiness. The product was washed with cold ethanol, m.p. 251-252° (cor.) (dec.). The yield was 2.1 g. (37%). It proved by analysis to be a pyridine salt.

Anal. Calcd. for $C_{22}H_{20}N_2O_4S_2 \cdot C_5H_5N$: C, 62.41; H, 4.85; N, 8.09. Found: C, 62.43; H, 4.68; N, 7.68.

The salt was shaken with 20% hydrochloric acid, and the product separated by filtration and washed with ethanol. It was recrystallized first by dissolving in 3:1 dimethylformamide–ethanol followed by addition of water to incipient turbidity, then from dimethylcellosolve. The cream-colored crystals melted at 247-248° (cor.) (dec.).

Anal. Calcd. for $C_{22}H_{20}N_2O_4S_2$: C, 59.98; H, 4.58. Found: C, 59.90, 59.83; H, 4.61, 4.62.

This product was not oxidized or dehydrogenated by the following treatments: (1) solution in 5% ethanolic potassium hydroxide and air; (2) chromic acid in acetic acid at 65-80°; (3) lead tetraacetate in acetic acid at 75-80°; (4) palladium in pyridine.

6,7-Dibromo-5,6,7,8-tetrahydronaphthylene-1,4-dibenzenesulfonamide.—A mixture of 0.3 g. of 5,8-dihydronaphthylene-1,4-dibenzenesulfonamide and 0.11 g. of bromine in 4 ml. of glacial acetic acid was warmed for about 15 minutes. The color disappeared. The material was separated by filtration, dissolved in dilute alkali, and reprecipitated by addition of hydrochloric acid. It was recrystallized from dilute acetone and washed with ethanol; m.p. 220° (cor.) (dec.). The yield was 0.15 g. (33%).

Anal. Calcd. for $C_{22}H_{20}Br_2N_2O_4S_2$: C, 44.01; H, 3.36; N, 4.67. Found: C, 43.87; H, 3.26; N, 4.57.

Naphthylene-1,4-dibenzenesulfonamide.—A solution of 0.2 g. of 6,7-dibromo-5,8-dihydronaphthylene-1,4-dibenzenesulfonamide in 25 ml. of 15% ethanolic potassium hydroxide was allowed to stand overnight and then warmed for 2 hours. The dark red solution was poured into ice containing hydrochloric acid. The resulting precipitate was collected, dissolved in dilute aqueous sodium hydroxide (Darco) and reprecipitated by pouring into ice and hydrochloric acid. It was purified by recrystallization from dilute ethanol, m.p. 251° (cor.) (dec.). The yield was 0.1 g. (65%).

There was no depression when a melting point was taken of this compound mixed with an authentic sample of naphthylene - 1,4 - dibenzenesulfonamide.[1c] The infrared absorption spectra were also identical.

Anal. Calcd. for $C_{22}H_{18}N_2O_4S_2$: C, 60.26; H, 4.14; N, 6.39. Found: C, 60.12; H, 4.18; N, 6.46.

By oxidation with lead tetraacetate, the corresponding quinone diimide resulted which was identical with that previously described.[1c]

5,8-Dihydronaphthylene-1,4-dimethanesulfonamide.—A suspension of 1.5 g. of *p*-quinone dimethanesulfonimide[1a] in 9 ml. of benzene and 0.6 g. of butadiene were heated in a sealed tube at 100° for 8 hours. After cooling, the mixture was filtered and 0.4 g. of *p*-quinone dimethanesulfonimide was recovered.

The filtrate was evaporated nearly to dryness and petroleum ether (b.p. 30–60°) was added. The solid, which separated, weighed 0.5 g. It proved to be a mixture of two compounds, presumably the mono- and di-adducts. They were separated by digestion with hot ethanol.

The ethanol insoluble portion of about 0.1 g. (5%) was recrystallized from acetic acid, m.p. 178.5° (cor.). This proved to be the diadduct. The infrared spectrum indicated the presence of a carbon-nitrogen double bond.

Anal. Calcd. for $C_{16}H_{22}N_2O_4S_2$: C, 51.87; H, 5.99; N, 7.56. Found: C, 51.72; H, 5.93; N, 7.84.

The ethanolic filtrate was concentrated and water was added. The white compound weighed 0.3 g. (17%) and was recrystallized from glacial acetic acid. The product did not melt sharply, but after much darkening and sintering, finally decomposed at 234-236°. Analysis showed it to be the mono-adduct. The infrared spectrum indicated the presence of the -NH- grouping.

Anal. Calcd. for $C_{12}H_{16}N_2O_4S_2$: C, 45.55; H, 5.10; N, 8.86. Found: C, 45.68; H, 5.25· N, 8.62.

In a second run using 3 g. of diimide, 1 g. of butadiene and 10 ml. of benzene heated in a sealed tube for 9 hours at 115-120°, the product was crystallized directly from glacial acetic acid. Only mono-adduct resulted, weighing 0.8 g. (22%).

Naphthylene-1,4-dimethanesulfonamide.—A mixture of 0.4 g. of 5,8-dihydronaphthylene-1,4-dimethanesulfonamide and 0.23 g. of bromine in 5 ml. of glacial acetic acid was heated on a steam-bath for 1 hour. The product which separated was recrystallized by adding water to a hot acetone solution until incipient cloudiness, m.p. 210° (cor.) (dec.). The yield was 0.3 g. (50%).

By treating the 6,7-dibromo-5,6,7,8-tetrahydronaphthylene-1,4-dimethanesulfonamide with ethanolic potassium hydroxide in the same manner as was employed for the corresponding dibromo dibenzenesulfonamide, hydrogen bromide was removed and the naphthylene-1,4-dimethanesulfonamide isolated in 76% yield. The product was purified by crystallization from glacial acetic acid, m.p. 260.5-261.5° (cor.) (dec.). The infrared spectrum indicated this compound to be identical with an authentic sample of naphthylene-1,4-dimethanesulfonamide.[1c] There was no depression when a melting point of this compound was mixed with an authentic sample of naphthylene-1,4-dimethanesulfonamide.[1c] By oxidation with lead tetraacetate, the corresponding quinone diimide resulted which was identical with that previously described.[1c]

Adduct of 2,3-Diphenylbutadiene to *p*-Quinone Dibenzenesulfonimide.—A mixture of 0.4 g. of 2,3-diphenylbutadiene, 0.74 g. of *p*-quinone dibenzenesulfonimide in 5 ml. of benzene was heated on a steam-bath for 20 hours. The solution was cooled and filtered to remove a small amount of solid which proved to be *p*-phenylenedibenzenesulfonamide.

The solvent was evaporated and petroleum ether (b.p. 30-60°) was added to the residue. It gradually became crystalline. The crude product weighed 1.0 g. (90%). This was recrystallized from glacial acetic acid and formed yellow crystals, m.p. 168-169° (cor.). The infrared spectrum indicated the presence of the carbon-nitrogen double bond.

Anal. Calcd. for $C_{34}H_{28}N_2O_4S_2$: C, 68.91; H, 4.76; N, 4.73. Found: C, 68.72; H, 4.76; N, 4.82.

Under similar conditions 2,3-diphenylbutadiene did not add to *p*-quinone dimethanesulfonimide.

Rearrangement of the Adduct of 2,3-Diphenylbutadiene with *p*-Quinone Dibenzenesulfonimide to 6,7-Diphenyl-5,8-dihydronaphthylene-1,4-dibenzenesulfonamide.—A solution of 75 mg. of the yellow adduct in 3 ml. of acetic acid was heated on a steam-bath and two drops of 48% hydrobromic acid then added. The color disappeared and on cooling a white precipitate formed. It was recrystallized from glacial acetic acid, m.p. 251-254° (cor.) (dec.) after some sintering.

Anal. Calcd. for $C_{34}H_{28}N_2O_4S_2$: C, 68.91; H, 4.76. Found: C, 68.93; H, 4.87.

Addition of Cyclopentadiene to *p*-Quinone Dibenzenesulfonimide.—A mixture of 2 g. of *p*-quinone dibenzenesulfonimide and 0.34 g. of cyclopentadiene was allowed to react at room temperature in 10 ml. of benzene. After standing a few hours a white product separated. The precipitate weighed 1.4 g. (52%). It was recrystallized from ethanol, m.p. 135-136° (cor.). It proved to be a diadduct. The infrared spectrum indicated the presence of a carbon-nitrogen double bond.

Anal. Calcd. for $C_{28}H_{26}N_2O_4S_2$: C, 64.84; H, 5.05; N, 5.40. Found: C, 64.68; H, 5.13; N, 5.39.

Experiments using equimolar quantities of *p*-quinone dibenzenesulfonimide and cyclopentadiene gave the same product.

Reduction of the Adduct of Cyclopentadiene to *p*-Quinone Dibenzenesulfonimide.—A suspension of 0.4 g. of adduct in 20 ml. of ethanol was hydrogenated under 48 p.s.i. at room temperature using 0.1 g. of platinum oxide as catalyst. The reduction was complete in 2 hours and 15 minutes. The product was collected by filtration and then extracted from the catalyst with hot ethanol. It was recrystallized by adding water to a hot ethanolic solution until incipient cloudiness. It did not melt sharply but gradually decomposed between 225 and 295°. The yield was 0.3 g. (74%). The infrared spectrum revealed the presence of -NH- groupings and showed no carbon-nitrogen double bonds.

Anal. Calcd. for $C_{28}H_{34}N_2O_4S_2$: C, 63.85; H, 6.51. Found: C, 64.15; H, 6.25.

Addition of Cyclopentadiene to *p*-Quinone Dimethanesulfonimide.—A mixture of 2 g. of *p*-quinone dimethanesulfonimide and 1.0 g. of cyclopentadiene in 10 ml. of benzene was refluxed for 1.5 hours on a steam-bath. After cooling and scratching, a white precipitate weighing 2.1 g. (70%) appeared. The di-adduct thus formed was purified from ethanol, m.p. 141-147° (cor.) (dec.). The infrared spectrum indicated the presence of a carbon-nitrogen double bond.

Anal. Calcd. for $C_{18}H_{22}N_2O_4S_2$: C, 54.80; H, 5.62; N, 7.10. Found: C, 54.90; H, 5.65; N, 7.14.

Reduction of Adduct of Cyclopentadiene to *p*-Quinone Dimethanesulfonimide.—A suspension of 0.5 g. of the adduct in 25 ml. of ethanol was hydrogenated under 44 p.s.i. at room temperature with 0.1 g. of platinum oxide. The reduction required 2 hours. The catalyst and product, which was essentially insoluble in cold ethanol, were collected by filtration and the product eluted with hot ethanol. It was purified from 70% ethanol, m.p. 251-252° (dec.) with preliminary softening and darkening from 225°. The yield was 0.5 g. (98%). The infrared spectrum indicated the presence of -NH- linkages and no carbon-nitrogen double bonds.

Anal. Calcd. for $C_{18}H_{30}N_2O_4S_2$: C, 53.70; H, 7.51; N, 6.96. Found: C, 53.92; H, 30.22; N, 7.17.

Addition of Anthracene to *p*-Quinone Dibenzenesulfonimide; 2-(9-Anthryl)-*p*-phenylenedibenzenesulfonamide (A).—A mixture of 1.8 g. of *p*-quinone dibenzenesulfonimide and 0.83 g. of anthracene in 10 ml. of acetic acid was refluxed for 1 hour, then cooled and filtered. The yield was 2.0 g. (76%). The precipitate was recrystallized by dissolving in hot dimethylformamide and then adding water to incipient turbidity. It formed cream-colored crystals, m.p. 246.5-247° (dec.).

Anal. Calcd. for $C_{32}H_{24}N_2O_4S_2$: C, 68.06; H, 4.28; N, 4.96. Found: C, 67.93; H, 4.55; N, 5.17.

B.—A mixture of 0.67 g. of aluminum chloride and 0.83 g. of anthracene in 15 ml. of carbon disulfide was stirred for

15 minutes while cooling in ice. Then 1.8 g. of *p*-quinone dibenzenesulfonimide was added all at once. The mixture was allowed to warm up to room temperature and stirred for 1.25 hours, then permitted to stand for several hours. It was poured into excess of hydrochloric acid and ice and the precipitate collected by filtration. The crude green product was digested with 5% aqueous sodium hydroxide, the solution filtered and the filtrate acidified with hydrochloric acid. The gray-white material was recrystallized from glacial acetic acid, m.p. 246-247° (dec.). The alkali-insoluble material proved to be undissolved product and was recrystallized from glacial acetic acid (Darco). The total yield was 0.8 g. (30.5%). The melting point of the mixture of this product with that formed by method A showed no depression. The infrared spectra of the products prepared by methods A and B were identical.

2-[9-(10-Bromoanthryl)]-*p*-phenylenedibenzenesulfonamide.—A mixture of 0.56 g. of 2-(9-anthryl)-*p*-phenylene-1,4-dibenzenesulfonamide, 0.16 g. of bromine, and 5 ml. of glacial acetic acid was warmed on a steam-bath for 2 hours. The product was then collected by filtration and weighed 0.4 g. (63%). It was recrystallized from glacial acetic acid; light-yellow crystals, m.p. 234-235° (cor.) (dec.).

Anal. Calcd. for $C_{32}H_{23}BrN_2O_4S_2$: C, 59.72; H, 3.60. Found: C, 59.47; H, 3.75.

This same compound was formed on bromination of samples of 2-(9-anthryl)-*p*-phenylenedibenzenesulfonamide produced either by methods A or B.

2-(9-Anthryl)-*p*-phenylenedimethanesulfonamide.—A mixture of 1.25 g. of *p*-quinone dimethanesulfonimide and 1.0 g. of anthracene in 7 ml. of acetic acid was heated under gentle reflux for 2 hours. On cooling a white solid separated. The yield was 2.0 g. (95%). It was recrystallized by adding water to a hot acetone solution until incipient cloudiness, m.p. 239-240° (cor.) (dec.).

Anal. Calcd. for $C_{22}H_{20}N_2O_4S_2$: C, 59.98; H, 4.58; N, 6.36. Found: C, 59.93; H, 4.74; N, 6.64.

Triptycene-2,5-dibenzenesulfonamide.—A solution of 21 g. of 2,5-triptaquinone[2] and 80 g. of hydroxylamine hydrochloride in 1900 ml. of ethanol was boiled for 2 hours. The product, formed by pouring the reaction mixture into water, did not appear to be pure.

A mixture of 2 g. of this product with 5.5 g. of hydroxylamine hydrochloride in 25 ml. of water was brought to the neutral point with 10% aqueous sodium hydroxide (about 30 ml.). Ethanol was added until complete solution was effected and the mixture then heated on a steam-bath for 1 hour. Ethanol was evaporated off until crystallization started, the mixture was cooled, and water added. The product weighed 1.7 g. After purification from glacial acetic acid it melted at 243° (cor.) (dec.).

The dioxime was reduced according to the directions of Bartlett.[2] The diamine dihydrochloride begins to darken above 224-229° (cor.) and then gradually decomposes. According to Bartlett the diamine dihydrochloride gradually decomposes above 210°.

A suspension of 0.5 g. of the diamine dihydrochloride in 15-20 ml. of 10% aqueous sodium hydroxide was treated with 0.5 g. of benzenesulfonyl chloride and the mixture stirred and allowed to stand for an hour before heating on a steam-bath for 1 hour. After cooling, it was acidified with hydrochloric acid and filtered. The white precipitate was purified by crystallization from glacial acetic acid, m.p. 298° (dec.).

Anal. Calcd. for $C_{32}H_{24}N_2O_4S_2$: C, 68.06; H, 4.28. Found: C, 67.96; H, 4.46.

Triptycene-1,4-dimethanesulfonamide.—To 0.5 g. of triptycene-1,4-diamine dihydrochloride in 15 ml. of pyridine was added 1.0 g. of methanesulfonyl chloride and the mixture allowed to stand overnight. It was then poured into ice and hydrochloric acid, and the product collected on a filter. After recrystallization from a 1:1 acetone-water mixture, the compound was pure; it gradually decomposed above 360°. The yield was 0.5 g. (70%). The compound was quite hygroscopic.

Anal. Calcd. for $C_{22}H_{20}N_2O_4S_2$: C, 59.98; H, 4.58. Found: C, 59.80; H, 4.60.

Reaction of Bicyclohexenyl with *p*-Quinone Dibenzenesulfonimide.—A mixture of 1 g. of *p*-quinone dibenzenesulfonimide and 0.4 g. of bicyclohexenyl in 7 ml. of *n*-butyl alcohol (or glacial acetic acid) was refluxed for eight hours, On cooling, the product, weighing 0.5 g., separated. After recrystallization from glacial acetic acid, it melted at 251-252.5° (cor.) (dec.) and proved to be *p*-phenylenedibenzenesulfonamide.

Reaction of 1,3-Diphenylisobenzofuran with *p*-Quinone Dibenzenesulfonimide.—A mixture of 0.5 g. of diphenylisobenzofuran and 0.7 g. of *p*-quinone dibenzenesulfonimide in 15 ml. of ethanol was heated under reflux for 5 hours. Complete solution gradually occurred. On cooling, a white crystalline product separated. The yield was 0.5 g. (94%). It was recrystallized from ethanol, m.p. 145° (cor.). The product proved to be *o*-dibenzoylbenzene, which did not depress the melting point of an authentic sample. Apparently an oxidation reaction had occurred rather than a Diels-Alder reaction.

URBANA, ILL.

RECEIVED AUGUST 2, 1950

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[2] P. D. Bartlett, THIS JOURNAL, **64**, 2649 (1942).

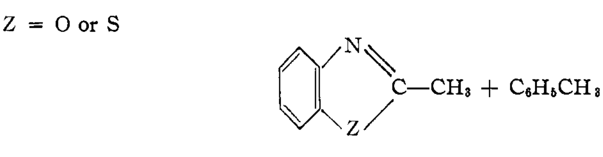
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF ST. JOHN'S UNIVERSITY]

Reaction of Benzyl Methyl Ketone with *o*-Aminophenol, *o*-Aminobenzenethiol and 1,8-Naphthalenediamine

BY FRANK J. KREYSA, VINCENT F. MATURI, JOHN J. FINN, JOHN J. MCCLARNON AND FLORA LOMBARDO

Direct heating of *o*-aminophenol, *o*-aminobenzenethiol and 1,8-naphthalenediamine with benzyl methyl ketone results in the formation of toluene and aromatic heterocyclic rings, *i.e.*, 2-methylbenzoxazole, 2-methylbenzothiazole and 2-methylperimidine, respectively.

The formation of benzimidazoles, presumably *via* intermediate benzimidazolines, when *o*-phenylenediamine or its monoalkyl derivatives are heated with ketones[1] suggests that similar formation of oxazole, thiazole and perimidine derivatives should occur from *o*-aminophenol, *o*-aminobenzenethiol and 1,8-naphthalenediamine, respectively. These derivatives have been found to be formed when the above substances were heated with benzyl methyl ketone, *e. g.*



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[1] Elderfield, Kreysa, Dunn and Humphreys, THIS JOURNAL, **70**, 40 (1948); Elderfield and Kreysa, *ibid.*, **70**, 44 (1948).