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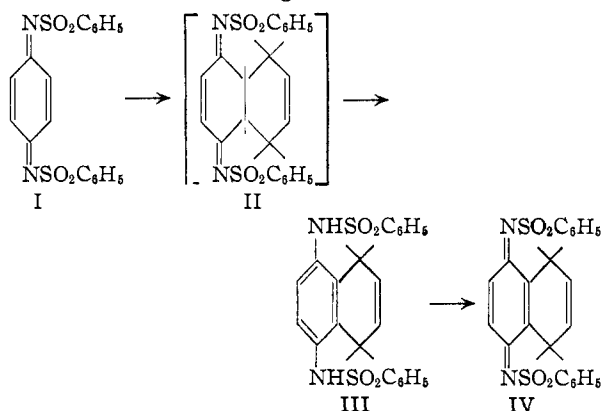
Quinone Imides. XI. Addition of Dienes to *p*-Quinonedibenzesulfonimide

BY ROGER ADAMS AND J. D. EDWARDS, JR.

The use of chloroform at room temperature as a medium for the addition of dienes to *p*-quinonedibenzesulfonamide led to improved yields of products and the synthesis of certain compounds not previously obtained. From butadiene, 2,3-dimethyl-1,3-butadiene and chloroprene, colorless mono-adducts result in which the quinone diimide ring is aromatized. Isoprene, on the other hand, gives a yellow mono-adduct in which the partial quinone structure is retained. By treatment with acid it is converted into the analogous aromatized product. Anthracene in boiling glacial acetic acid was shown previously to add 1,4- to the quinone diimide to give 2-(9-anthryl)-*p*-phenylenedibenzesulfonamide. When the reaction is conducted at room temperature in benzene, the anthracene reacts as a diene. A yellow mono-adduct is formed which upon rearrangement with acid results in the formation of triptycene-2,5-dibenzesulfonamide.

The addition of butadiene,<sup>1</sup> 2,3-diphenylbutadiene, cyclopentadiene and anthracene to *p*-quinonedibenzesulfonimide in boiling benzene or in some cases glacial acetic acid and nitrobenzene has been reported. The addition of isoprene, 2,3-dimethyl-1,3-butadiene and chloroprene failed to give the expected compounds. Further study has revealed that the addition reactions proceed much more smoothly by permitting the reactions to stand at room temperature in chloroform solution. Not only are the yields thus improved but in several instances the course of the reactions and the final products are different in character.

From butadiene and *p*-quinonedibenzesulfonimide (I), 5,8-dihydronaphthalene-1,4-dibenzesulfonamide (III) was formed in 80% yield. This colorless product had been prepared in the previous investigation and its structure established.<sup>1</sup> The chloroprene and 2,3-dimethyl-1,3-butadiene adducts have an analogous structure. The intermediate products (II) apparently rearrange subsequent to the addition of the diene. Infrared analyses confirmed the presence of NH linkages and absence of carbon-nitrogen double bonds.

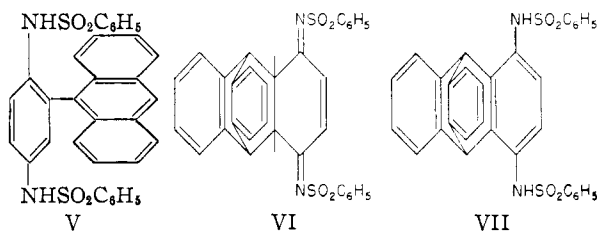


Using similar conditions, isoprene reacted with I to give a yellow mono-adduct. Infrared analysis indicated the presence of a carbon-nitrogen double bond. The product is therefore 5,8-dihydro-6-methyl-1,4-naphthoquinonedibenzesulfonimide, corresponding to structure II. Upon warming a solution of the product with a little mineral acid, rearrangement occurred instantly with the formation of a colorless compound, 5,8-dihydro-6-methyl-1,4-naphthalene-1,4-dibenzesulfonamide, analogous to the other diene adducts.

(1) R. Adams and C. R. Walter, *THIS JOURNAL*, **73**, 1152 (1951). For addition of dienes to 1,4-naphthoquinonedibenzesulfonimide, see R. Adams and W. Moje, *ibid.*, **74**, 2593 (1952).

Oxidation of 5,8-dihydronaphthalene-1,4-dibenzesulfonamide (III) with lead tetraacetate in glacial acetic acid yielded an orange crystalline compound (IV) which contained a carbon-nitrogen double bond as shown by infrared analysis. Upon reduction of IV with zinc and acetic acid, 5,8-dihydronaphthalene-1,4-dibenzesulfonamide (III) resulted. The structure of the oxidation product (IV) is therefore established as 5,8-dihydro-1,4-naphthoquinonedibenzesulfonimide.

In previous work the reaction of anthracene and I in the presence of refluxing glacial acetic acid was described and the structure of the product through a 1,4-addition demonstrated as 2-(9-anthryl)-*p*-phenylenedibenzesulfonamide (V). It has now been observed that when anthracene and I are allowed to stand in benzene solution at room temperature a product is formed slowly in which the anthracene has reacted as a normal diene. The yellow product was shown to have a carbon-nitrogen double bond by infrared analysis and therefore was assigned structure VI. Treatment with mineral acid caused rearrangement to a colorless compound which proved to be triptycene-2,5-dibenzesulfonamide (VII), previously prepared by an unequivocal synthesis.<sup>1</sup>



**Acknowledgment.**—The authors are indebted to Miss Elizabeth Petersen for the determination and interpretation of the infrared spectra and to Miss Emily Davis, Mrs. Katherine Pih and Mrs. Jean Fortney for the microanalyses.

Experimental<sup>2-4</sup>

**5,8-Dihydronaphthalene-1,4-dibenzesulfonimide.**—A solution of 2 g. of *p*-quinonedibenzesulfonimide (I) in 20 ml. of chloroform and 4 ml. of butadiene was allowed to stand at room temperature for three weeks during which time the color changed from dark to light yellow. The solution was filtered to remove a small amount of amorphous material and petroleum ether (b.p. 30–60°) then added until

(2) All melting points are corrected.

(3) The chloroform used in the experimental work was of analytical reagent grade dried over calcium chloride.

(4) The reaction times in the experiments reported below were entirely arbitrary. The mixture of reactants was allowed to stand at least until the initial deep yellow solutions had changed to light yellow.

slight turbidity was noted. After standing overnight the colorless crystals which formed were filtered and washed with petroleum ether (b.p. 30–60°). The yield was 1.80 g. (80%). The material was purified by recrystallization from glacial acetic acid, m.p. 247–248° (dec.) (previously reported 247–248°).<sup>1</sup>

*Anal.* Calcd. for  $C_{22}H_{20}N_2O_4S_2$ : C, 59.98; H, 4.58; N, 6.36. Found: C, 59.95; H, 4.65; N, 6.45.

**5,8-Dihydro-1,4-naphthoquinonedibzenzenesulfonimide.**—A suspension of 0.5 g. of powdered 5,8-dihydronaphthalene-1,4-dibzenzenesulfonamide in 15 ml. of glacial acetic acid was heated to 100° and then removed from the hot-plate. In one portion 0.6 g. of lead tetraacetate was then added. After stirring to complete solution, it was filtered and three drops of ethylene glycol added. On cooling 0.28 g. (56%) of a dark orange crystalline material formed. This was filtered, washed with ether and dried under a vacuum at room temperature. It was purified by crystallization from benzene-petroleum ether (b.p. 30–60°) and gave orange crystals, m.p. 237–239° (dec.) with color change to yellow at 160°.

*Anal.* Calcd. for  $C_{22}H_{18}O_4N_2S_2$ : C, 60.26; H, 4.14; N, 6.39. Found: C, 60.36; H, 4.27; N, 6.33.

This quinone imide is very unstable when exposed to air in the presence of acetic acid. Even pure dry samples on standing over a period of a few days decompose slowly.

Attempts to oxidize 5,8-dihydronaphthalene-1,4-dibzenzenesulfonamide at room temperature with lead tetraacetate in glacial acetic acid resulted in the recovery of starting material. Refluxing of a glacial acetic acid solution containing two mole equivalents of lead tetraacetate in attempts to obtain directly 1,4-naphthoquinonedibzenzenesulfonimide resulted only in extensive decomposition.

When a solution of 0.25 g. of this quinone diimide in 10 ml. of glacial acetic acid was treated with 0.2 g. of zinc dust and heated for 15 minutes on a steam-bath reduction occurred. After cooling to room temperature, the solid mixture was filtered and warmed with pyridine. The pyridine solution was filtered and water added dropwise until crystallization commenced. The colorless crystals weighed 0.2 g., melted at 247–248° (dec.) and were shown to be 5,8-dihydronaphthalene-1,4-dibzenzenesulfonamide.

**5,8-Dihydro-6-methyl-1,4-naphthoquinonedibzenzenesulfonimide.**—The reaction of 1 g. of I and 2 ml. of isoprene was carried out in the same manner as with butadiene. The yellow product which was obtained weighed 0.75 g. (63%). It was purified by crystallization from ethyl acetate-petroleum ether (b.p. 30–60°), yellow crystals, m.p. 146.5–147.5°.

An infrared absorption spectrum indicated the presence of a carbon-nitrogen double bond.

*Anal.* Calcd. for  $C_{23}H_{22}N_2O_4S_2$ : C, 60.77; H, 4.88; N, 6.16. Found: C, 60.96; H, 4.95; N, 6.34.

**5,8-Dihydro-6-methylnaphthalene-1,4-dibzenzenesulfonimide.**—To a warm solution of 0.1 g. of 5,8-dihydro-6-

methyl-1,4-naphthoquinonedibzenzenesulfonimide in 3 ml. of glacial acetic acid 2 drops of 48% hydrobromic acid was added. The yellow color disappeared immediately. After cooling, water was added dropwise until crystallization commenced. A quantitative yield of the rearranged product resulted. Recrystallization from ethyl acetate-petroleum ether (b.p. 30–60°) gave colorless needles, m.p. 188–190° (dec.).

Infrared analysis indicated the presence of the -NH- groupings.

*Anal.* Calcd. for  $C_{23}H_{22}N_2O_4S_2$ : C, 60.77; H, 4.88; N, 6.16. Found: C, 60.83; H, 5.15; N, 6.18.

**5,8-Dihydro-6,7-dimethylnaphthalene-1,4-dibzenzenesulfonimide.**—A solution of 1 g. of I and 2 ml. of 2,3-dimethyl-1,3-butadiene was allowed to stand in chloroform for 3.5 weeks. The product was isolated and purified in the manner described above. The yield was 1.2 g. (90%) of a colorless product which after purification from ethyl acetate-petroleum ether (b.p. 30–60°) melted at 200–201° (dec.).

Infrared absorption spectrum showed the presence of the -NH- grouping.

*Anal.* Calcd. for  $C_{24}H_{24}N_2O_4S_2$ : C, 61.51; H, 5.16; N, 5.98. Found: C, 61.56; H, 5.25; N, 5.91.

**6-Chloro-5,8-dihydronaphthalene-1,4-dibzenzenesulfonamide.**—A chloroform solution of 0.5 g. of *p*-quinonedibzenzenesulfonimide (I) and 0.2 g. of chloroprene was allowed to stand at room temperature for 3 months. Addition of petroleum ether gave 0.33 g. (52%) of a colorless crystalline compound. This was purified by recrystallization from ethyl acetate-petroleum ether (b.p. 30–60°), m.p. 215–218° (dec.).

*Anal.* Calcd. for  $C_{22}H_{19}ClN_2O_4S_2$ : C, 55.63; H, 4.03; N, 5.90. Found: C, 55.92; H, 4.14; N, 6.21.

**Adduct of Anthracene and *p*-Quinonedibzenzenesulfonimide.**—A solution of 1 g. of *p*-quinonedibzenzenesulfonimide (I) and 0.463 g. of anthracene in 30 ml. of dry thiophene-free benzene was allowed to stand for 2 months. The initial green color gradually changed to red with the formation of 0.4 g. (30%) of yellow crystalline material which was recrystallized from chloroform-petroleum ether (b.p. 30–60°). It was necessary to dry the product at 1 mm. for 48 hours at 180° to remove solvent, m.p. 192–195° (dec.).

*Anal.* Calcd. for  $C_{32}H_{24}N_2O_4S_2$ : C, 68.06; H, 4.28; N, 4.96. Found: C, 68.18; H, 4.37; N, 5.11.

This product has a great affinity for retaining different solvents and must be dried at a high temperature for a long period of time before it can be obtained solvent-free.

**Triptycene-2,5-dibzenzenesulfonamide.**—The anthracene mono adduct was rearranged in the same manner as the isoprene adduct to give a colorless product. The material was recrystallized from glacial acetic acid, m.p. 298° (dec.). This product was shown to be identical with triptycene-2,5-dibzenzenesulfonamide prepared by an unequivocal synthesis.<sup>1</sup>

URBANA, ILLINOIS

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