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

Quinone Imides. XII. Addition of Dienes to *p*-Quinonemonobenzenesulfonimide

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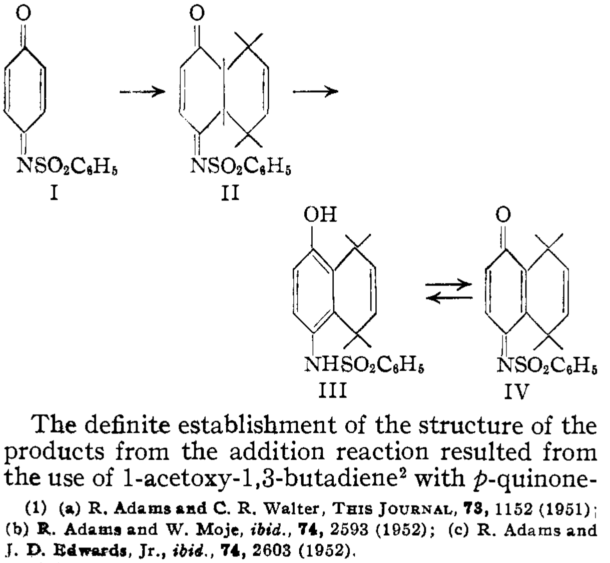
The Diels–Alder reactions of quinone imides have been extended to *p*-quinonemonobenzenesulfonimide. Mono-adducts in which no rearrangement has occurred are obtained with butadiene, isoprene and anthracene. By means of mineral acid the quinone imide ring moiety in these compounds is readily aromatized. The product thus obtained involving butadiene may be further oxidized to 5,8-dihydro-1,4-naphthoquinonemonobenzenesulfonimide. The structure of the mono-adduct from the addition of acetoxybutadiene has been demonstrated by deacetoxylation and aromatization to be 4-benzenesulfonamido-1-naphthol. When chloroprene and 2,3-dimethyl-1,3-butadiene are added, only products are isolated in which aromatization of the quinone imide moiety has occurred subsequent to the addition. Cyclopentadiene and, under specified conditions, butadiene give di-adducts. From the attempted addition of bicyclohexenyl only reduced starting material, *p*-benzenesulfonamidophenol, is isolated.

In previous investigations, it has been demonstrated that *p*-quinonedibenzenesulfonimide reacts very similarly to *p*-quinones with various dienes.[1] Mono or di-adducts may be formed. The study has now been extended to the addition of dienes to *p*-quinonemonobenzenesulfonimide.

The reaction of *p*-quinonemonobenzenesulfonimide (I) with butadiene and with isoprene at room temperature gave yellow mono-adducts. The infrared absorption spectra indicated the presence of carbon–oxygen and carbon–nitrogen double bonds. Aromatization of the quinone imide moieties in these mono-adducts with mineral acid gave colorless crystalline compounds which possessed the –NH and –OH groupings as shown by the infrared spectra. The mono-adduct from butadiene was therefore assumed to be 5,8-dihydro-1,4-naphthoquinonemonobenzenesulfonimide (II), which was converted to 4-benzenesulfonamido-5,8-dihydro-1-naphthol (III) by treatment with mineral acid. Preliminary attempts to completely aromatize this product to the known 4-benzenesulfonamido-1-naphthol failed.

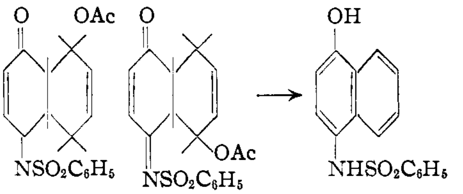
The mono-adduct from isoprene was a mixture of 5,8-dihydro-6- and 7-methyl-1,4-naphthoquinonemonosulfonimide which rearranged to a mixture of the corresponding dihydronaphthols. This was indicated by the melting points and infrared spectra of successive fractions during crystallization. Only one of the isomers was isolated pure.



I II III IV

The definite establishment of the structure of the products from the addition reaction resulted from the use of 1-acetoxy-1,3-butadiene[2] with *p*-quinonemonobenzenesulfonimide.[1b,1c] Reaction took place in chloroform at room temperature and a yellow crystalline monoadduct (IVa or V) was isolated. Infrared analysis showed the presence of carbon–nitrogen and carbon–oxygen double bonds as well as the acetoxyl grouping. Treatment of a glacial acetic acid solution of this mono-adduct with hydrobromic acid resulted in a colorless crystalline compound which proved to be 4-benzenesulfonamido-1-naphthol (VI)[3] as shown by the melting point of a mixture with an authentic sample and identical infrared spectra.

The mono-adduct was unstable to heat and its melting point behavior did not change on recrystallization. For this reason it was not possible to ascertain if the product was a single entity or a mixture of 5- and 8-acetoxy-5,8-dihydro-1,4-naphthoquinonemonobenzenesulfonimides (IVa and V). In either case 4-benzenesulfonamido-1-naphthol (VI) would result on deacetoxylation and aromatization.



IVa V VI

Oxidation of the rearranged butadiene adduct (III) with lead tetracetate gave an orange crystalline product (IV) which contained carbon–oxygen and carbon–nitrogen double bonds as evidenced by infrared analysis. On reduction with zinc and acetic acid, the original product (III) before oxidation was recovered. The structure of the oxidation product is therefore 5,8-dihydro-1,4-naphthoquinonemonobenzenesulfonimide (IV).

2,3-Dimethyl-1,3-butadiene and chloroprene reacted with *p*-quinonemonobenzenesulfonimide (I) to give colorless crystalline monoadducts. The chloroprene reaction required three months. Infrared analysis of the adducts showed the presence of the –NH and –OH groupings. The structure of the dimethylbutadiene adduct is therefore 4-benzenesulfonamido-5,8-dihydro-6,7-dimethyl-1-naphthol corresponding to formula III and that of the chloroprene adduct one or both of the possible isomers, 4-benzenesulfonamido(6 and/or 7)-chloro-5,8-dihydro-1-naphthol.

Since the butadiene mono-adduct (II) did not

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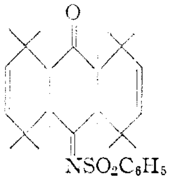
(1) (a) R. Adams and C. R. Walter, THIS JOURNAL, **73**, 1152 (1951); (b) R. Adams and W. Moje, *ibid.*, **74**, 2593 (1952); (c) R. Adams and J. D. Edwards, Jr., *ibid.*, **74**, 2603 (1952).

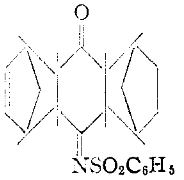
(2) H. J. Hagemeyer, Jr., and D. C. Hull, *Ind. Eng. Chem.*, **41**, 2920 (1949).

(3) R. Adams and R. A. Wankel, THIS JOURNAL, **73**, 131 (1951).

rearrange spontaneously to a dihydronaphthalene, an attempt was made to form the di-adduct. When *p*-quinonemonobenzenesulfonimide (I) and butadiene in benzene were heated at 100° in a sealed tube, a colorless crystalline di-adduct was isolated. Cyclopentadiene also added to *p*-quinonemonobenzenesulfonimide (I) in chloroform to give a colorless crystalline di-adduct. It was not possible to isolate a mono-adduct from this latter reaction even when equimolar quantities were used. The infrared spectra of these di-adducts indicated the presence of carbon–oxygen and carbon–nitrogen double bonds and no –NH or –OH groupings. The butadiene di-adduct is apparently 1,4,5,8-tetrahydro - 9,10 - anthraquinonemonobenzenesulfonimide (VIII) and the cyclopentadiene di-adduct 1,4,5,8 - tetrahydro - 1,4,5,8 - dimethano - 9,10 - anthraquinonemonobenzenesulfonimide (IX).

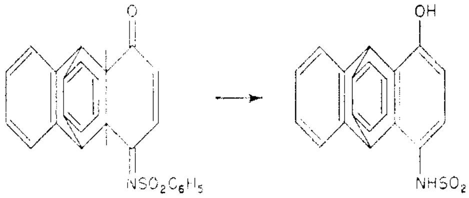


VIII



IX

The addition of anthracene to *p*-quinonemonobenzenesulfonimide (I) was accomplished by refluxing a chloroform solution of the reactants for 48 hours. The mono-adduct thus obtained was orange and the infrared spectrum indicated that carbon–nitrogen and carbon–oxygen double bonds were present. Treatment of a glacial acetic acid solution of the product with mineral acid gave a colorless product which contained the –NH and –OH groupings as shown by the infrared spectrum. The anthracene mono-adduct is assigned, therefore, structure X and the mineral acid rearranged product structure XI.



X XI

The attempted addition of bicyclohexenyl to *p*-quinonemonobenzenesulfonimide (I) afforded a mixture of resinous material and reduced starting material, *p*-benzenesulfonamidophenol. None of the expected adduct could be isolated.

Acknowledgment.—The authors wish to express their sincere thanks to Miss Elizabeth Petersen for the infrared analyses and to Miss Emily Davis, Mrs. Katherine Pih and Mrs. Jean Fortney for the microanalyses.

Experimental[4-6]

5,8-Dihydro-1,4-naphthoquinonemonobenzenesulfonimide.—The orange solution of 2 g. of *p*-quinonemonobenzenesulfonimide in 20 ml. of chloroform and 2 ml. of butadiene was allowed to stand one week at room temperature during which time the color changed to light yellow. The solution was filtered and concentrated to dryness *in vacuo* at room temperature. To the yellow residue a few ml. of ether was added and the light yellow precipitate was filtered. The crude product, which weighed 1.7 g. (70%), was recrystallized from ethyl acetate–petroleum ether (b.p. 30–60°) to give yellow crystals, m.p. 94–96°.

Anal. Calcd. for $C_{16}H_{15}NO_3S$: C, 63.77; H, 5.02; N, 4.65. Found: C, 63.87; H, 4.92; N, 4.48.

4-Benzenesulfonamido-5,8-dihydro-1-naphthol.—To a warm solution of 0.70 g. of 5,8-dihydro-1,4-naphthoquinonemonobenzenesulfonimide in 2 ml. of glacial acetic acid was added two drops of 48% hydrobromic acid. The solution immediately turned colorless and after cooling addition of a few drops of water induced crystallization. The colorless product was obtained in a quantitative yield and was recrystallized from glacial acetic acid, m.p. 194.5–195.5° (dec.).

Anal. Calcd. for $C_{16}H_{15}NO_3S$: C, 63.77; H, 5.02; N, 4.65. Found: C, 63.58; H, 4.97; N, 4.81.

5- and/or 8-Acetoxy-5,8-dihydro-1,4-naphthoquinonemonobenzenesulfonimide.—A mixture of a solution of 2 g. of *p*-quinonemonobenzenesulfonimide in 20 ml. of chloroform and 1 g. of 1-acetoxy-1,3-butadiene was allowed to stand for 3 days. Petroleum ether (b.p. 30–60°) was added until turbidity appeared. On standing overnight, 1.7 g. (58%) of a yellow material crystallized. The product was recrystallized from glacial acetic acid and then from ethyl acetate–petroleum ether (b.p. 30–60°). The yellow crystals melted at 155–160° (dec.).

Anal. Calcd. for $C_{18}H_{17}NO_5S$: C, 60.15; H, 4.77; N, 3.90. Found: C, 60.18; H, 4.88; N, 3.97.

4-Benzenesulfonamido-1-naphthol.—To a cool solution of 0.5 g. of the acetoxybutadiene adduct in 10 ml. of glacial acetic acid was added 2 drops of 48% hydrobromic acid. The solution was warmed gently on a steam-bath until the yellow coloration was discharged. Water was then added dropwise until crystallization commenced. The colorless product weighed 0.34 g. (80%). Recrystallization from ethyl acetate–petroleum ether (b.p. 30–60°) gave colorless crystals, m.p. 196–197° (lit. m.p. 193–194°).[4]

If the hydrobromic acid is added to a hot solution of the adduct, extensive decomposition occurs and little or no 4-benzenesulfonamido-1-naphthol could be isolated.

Anal. Calcd. for $C_{16}H_{13}NO_3S$: C, 64.20; H, 4.38. Found: C, 64.41; H, 4.53.

5,8-Dihydro-(6 and 7)-methyl-1,4-naphthoquinonemonobenzenesulfonimide.—A solution of 0.5 g. of *p*-quinonemonobenzenesulfonimide and 0.5 ml. of isoprene in 10 ml. of chloroform was allowed to stand for 3 weeks. Petroleum ether (b.p. 30–60°) was added to turbidity and after standing overnight 0.35 g. (56%) of a yellow crystalline material precipitated. After several recrystallizations from ethyl acetate–petroleum ether (b.p. 30–60°), the product melted at 111–114°.

Anal. Calcd. for $C_{17}H_{17}NO_3S$: C, 64.74; H, 5.43; N, 4.44. Found: C, 64.93; H, 5.64; N, 4.46.

4-Benzenesulfonamido-5,8-dihydro-(6 or 7)-methyl-1-naphthol.—When a glacial acetic acid solution of the isoprene adduct was treated with hydrobromic acid in the same manner as described for the butadiene adduct, a quantitative yield of the aromatized compound resulted. The product was repeatedly recrystallized from ethyl acetate–cyclohexane; m.p. 224–227° (dec.).

Anal. Calcd. for $C_{17}H_{17}NO_3S$: C, 64.74; H, 5.43; N, 4.41. Found: C, 64.49; H, 5.32; N, 4.51.

5,8 - Dihydro - 1,4-naphthoquinonemonobenzenesulfonimide.—A suspension of 1.18 g. of 4-benzenesulfonamido-5,8-dihydro-1-naphthol in 20 ml. of glacial acetic acid was treated at room temperature with 2 g. of lead tetraacetate. After standing for 3 hours with occasional stirring, ethylene glycol was added dropwise over a period of 10 minutes until a negative potassium iodide paper test was obtained. The orange crystalline precipitate which formed was filtered and dried. The crude product, which weighed 0.53 g. (48%), was recrystallized several times from glacial acetic acid, m.p. 135–137° (dec.). On standing for a period of several days slight decomposition occurred.

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(4) All melting points are corrected.

(5) The chloroform used in the experimental work was of Analytical Reagent grade dried over calcium chloride.

(6) 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 orange solution changed to light yellow.

Anal. Calcd. for $C_{16}H_{13}NO_3S$: C, 64.20; H, 4.38; N, 4.68. Found: C, 64.24; H, 4.61; N, 4.85.

Heating a glacial acetic acid solution of 1 mole equivalent of 4-benzenesulfonamido-5,8-dihydro-1-naphthol with 2 mole equivalents of lead tetraacetate gave a highly colored solution from which only a small quantity of 5,8-dihydro-1,4-naphthoquinonemonobenzenesulfonimide could be isolated. No 1,4-naphthoquinonemonobenzenesulfonimide was found.

A solution of 0.2 g. of 5,8-dihydro-1,4-naphthoquinonemonobenzenesulfonimide in 10 ml. of glacial acetic acid and 0.15 g. of zinc dust was heated on a steam-bath for 15 minutes. The color slowly disappeared after which the mixture was filtered while hot and water added dropwise to the acetic acid filtrate until crystallization commenced. On cooling, 0.18 g. (90%) of colorless crystals was obtained; m.p. 194–195° (dec.) which proved to be 4-benzenesulfonamido-5,8-dihydro-1-naphthol.

4-Benzenesulfonamido-5,8-dihydro-6,7-dimethyl-1-naphthol.—A solution of 1 g. of *p*-quinonemonobenzenesulfonimide and 1.5 ml. of 2,3-dimethyl-1,3-butadiene in 15 ml. of chloroform was allowed to stand 3 weeks. The white precipitate that formed was filtered and the filtrate was concentrated to 5 ml. Petroleum ether was then added and additional product obtained. The total yield was 1.1 g. (82%). Purification was achieved by recrystallization first from chloroform and then from ethyl acetate–petroleum ether (b.p. 30–60°), m.p. 204–206.5° (dec.).

Anal. Calcd. for $C_{18}H_{19}NO_3S$: C, 65.63; H, 5.81; N, 4.25. Found: C, 65.39; H, 5.83; N, 4.49.

4-Benzenesulfonamido-(6 and/or 7)-chloro-5,8-dihydro-1-naphthol.—From a solution of 0.5 g. of *p*-quinonemonobenzenesulfonimide and 1 ml. of chloroprene in 10 ml. of chloroform after standing at room temperature for 3 months, a tan precipitate deposited which weighed 0.21 g. (30%). The material was recrystallized several times from ethyl acetate–petroleum ether (b.p. 30–60°), m.p. 220–223° (dec.).

Anal. Calcd. for $C_{16}H_{14}ClNO_3S$: C, 57.22; H, 4.20; N, 4.17. Found: C, 57.52; H, 4.50; N, 4.14.

1,4,5,8-Tetrahydro-9,10-anthraquinonemonobenzenesulfonimide.—A solution of 2 g. of *p*-quinonemonobenzenesulfonimide and 4 ml. of butadiene in 15 ml. of dry thiophene-free benzene was heated for 24 hours at 100° in a sealed tube during which time the color changed from orange to light yellow. To the boiling benzene solution, cyclohexane was added until the volume was 100 ml. The solution was then concentrated *in vacuo* until turbid. After standing overnight the colorless crystals which formed were filtered and washed with cyclohexane. The product, which weighed 1.15 g. (40%), was purified by recrystallization from ethyl acetate–cyclohexane; m.p. 138–140°.

Anal. Calcd. for $C_{20}H_{21}NO_3S$: C, 67.58; H, 5.96; N, 3.94. Found: C, 67.62; H, 6.13; N, 3.89.

1,4,5,8-Tetrahydro-1,4,5,8-dimethano-9,10-anthraquinonemonobenzenesulfonimide.—Upon addition with stirring of 2.1 ml. of freshly-distilled cyclopentadiene to a solution of 2 g. of *p*-quinonemonobenzenesulfonimide in 15 ml. of chloroform, the mixture became warm and colorless. It was poured slowly with stirring into 70 ml. of cyclohexane and allowed to stand overnight. The crystals which formed weighed 2.5 g. (83%). They were purified by recrystallization from chloroform–cyclohexane to give colorless crystals, m.p. 153–153.5°.

Anal. Calcd. for $C_{20}H_{21}NO_3S$: C, 69.63; H, 5.58; N, 3.69. Found: C, 69.76; H, 5.55; N, 3.60.

Adduct of Anthracene to *p*-Quinonemonobenzenesulfonimide: 1,6-Dihydro-5-benzenesulfonimido-2-oxo-triptycene.—A solution of 2 g. of *p*-quinonemonobenzenesulfonimide and 2.7 g. of anthracene in 20 ml. of chloroform was refluxed for 48 hours. Upon addition of petroleum ether (b.p. 30–60°) to the dark brown solution, a yield of 1.8 g. (53%) of an orange crystalline material resulted. The product was recrystallized first from glacial acetic acid and then from ethyl acetate–petroleum ether (b.p. 30–60°), m.p. 179–181° (dec.)

Anal. Calcd. for $C_{26}H_{19}NO_3S$: C, 73.39; H, 4.50; N, 3.29. Found: C, 73.15; H, 4.37; N, 3.44.

5-Benzenesulfonamido-2-hydroxytriptycene.—The mono-anthracene adduct was rearranged with hydrobromic acid as previously described. The product was recrystallized from ethyl acetate–petroleum ether (b.p. 30–60°) or chloroform–petroleum ether.

Solvents are very tenaciously held by this substance. Both ethyl acetate and chloroform appear to give molecular compounds. By drying at 180° for 48 hours at 1 mm., it was possible to remove either solvent; white crystals, m.p. 230–231°.

Anal. Calcd. for $C_{26}H_{19}NO_3S$: C, 73.39; H, 4.50; N, 3.29. Found: C, 73.33; H, 4.42; N, 3.37.

Reaction of Bicyclohexenyl with *p*-Quinonemonobenzenesulfonimide.—Attempted addition of bicyclohexenyl to *p*-quinonemonobenzenesulfonimide by the general procedures previously described yielded only a gum and a small amount of *p*-benzenesulfonamidophenol.

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RECEIVED OCTOBER 18, 1951