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

Quinone Imides. XXXIV. Addition of Dienes to Substituted *p*-Quinonedibenzenesulfonimides

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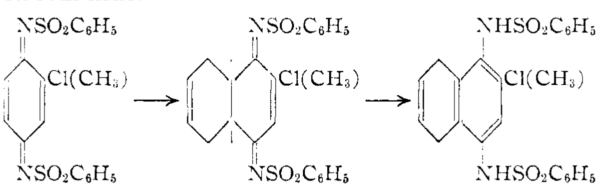
2-Chloro-, 2,5-dichloro-, 2-chloro-5-methyl-, 2-methyl- and 2,5-dimethyl-*p*-quinonedibenzenesulfonimides have been subjected to the Diels–Alder reaction with various dienes. The monosubstituted derivatives add one molecule of diene to the unsubstituted side of the nucleus. The dimethyl diimide adds only cyclopentadiene to give an unstable adduct. With the dichloro- or chloromethyl diimides, mono-adducts with angular chlorine result. Certain reactions of these monoadducts are described.

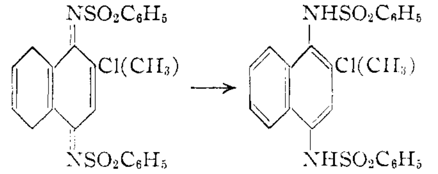
Previous studies[2] have demonstrated that dienes add readily to *p*-quinonedibenzenesulfonimides to give, with the exception of cyclopentadiene, mono-adducts. It has now been shown that if the quinone diimide is monosubstituted, the addition occurs on the unsubstituted side of the ring. The only previous example described of this class is the addition of dienes to 1,4-naphthoquinonedibenzenesulfonimide.[2b]



I II III

With butadiene and the chloro or methyl derivative I, the isolated products were III. Experiments in which material was isolated from the reaction mixture at different intervals of time demonstrated that lower-melting intermediates of type II formed first. The crude products in both reaction mixtures reached a minimum melting point and then gradually reached essentially a maximum, close to the melting points of the rearranged products III. 2,3-Dimethylbutadiene and cyclopentadiene reacted with compounds shown by I to give in each case stable intermediates of type II. The former adducts were rearranged by hydrobromic acid to compounds of type III, the latter were not.

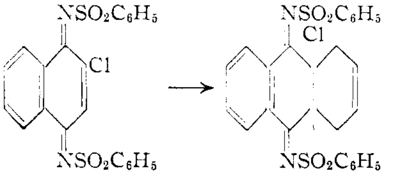
Upon oxidation of the two compounds III with lead tetraacetate, the diamides were converted to diimides IV.



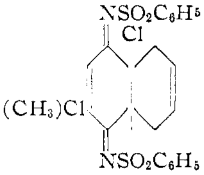
IV V

These products unlike the unsubstituted *homolog*[2c] rearranged upon recrystallization to compounds shown in V, identified by comparison with authentic products.

When groups are substituted on both sides of the quinone diimide ring, the addition of dienes proceeds more slowly and is dependent on the character of the groups present. Thus 2-chloro-1,4-naphthoquinonedibenzenesulfonimide (VI) reacted to yield a mixture of the adduct VII with an angular chlorine and reduced diimide.



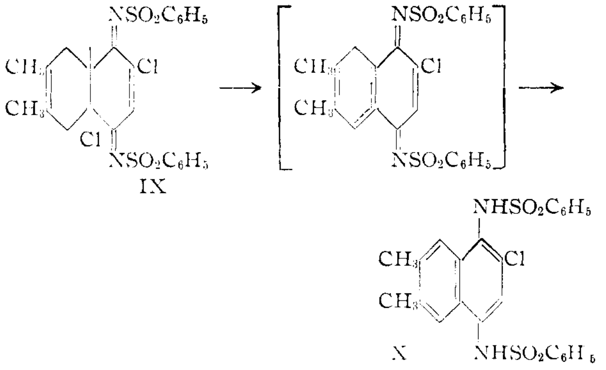
VI VII



VIII

Butadiene, dimethylbutadiene and cyclopentadiene reacted with 2,5-dichloro- or 2-chloro-5-methyl-*p*-quinonedibenzenesulfonimide to give mono-adducts of type VIII. From butadiene, the products are colorless, but from dimethylbutadiene and cyclopentadiene, are yellow. The infrared spectra of all are very similar. The ultraviolet and visible spectra of the butadiene and dimethylbutadiene adducts in chloroform solution were compared with the dimethylbutadiene adduct of the 2-chloro-*p*-quinonedibenzenesulfonimide (type II). The results are shown in Table I. In spite of the color differences, the general structure of the molecules appears to be the same.

When dimethylbutadiene was added to the 2,5-dichlorodiimide the main product IX was accompanied by a secondary product X formed obviously by elimination of a molecule of hydrogen chloride and rearrangement. The analysis, properties and spectral data indicate it to be a naphthalene derivative.



This loss of hydrogen chloride was not observed in the products formed by the reaction of dimethylbu-

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[1] An Abstract of a thesis submitted by Rolland W. P. Short to the Graduate College of the University of Illinois, 1953, in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

[2] (a) R. Adams and C. R. Walter, Jr., 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, 2605 (1952); (d) R. Adams and D. S. Acker, *ibid.*, **74**, 5872 (1952); (e) R. Adams and P. R. Shafer, *ibid.*, **75**, 667 (1953).

TABLE I

Diimide	Diene	Ultraviolet Å.(εmax)	Visible Å.(εmax)
2,5-Cl	Butadiene	2900	....
	Dimethylbutadiene	3000	4000–5000
2-Cl, 5-CH$_3$	Butadiene	2900	4000–4200 (slight)
	Dimethylbutadiene	2925	4000–4900
2-Cl	Dimethylbutadiene	2900	4000–5000

tadiene and the 2-chloro-5-methyl quinone diimide. When cyclopentadiene was added to the 2,5-dichloro diimide, some reduced diimide accompanied the main product.

The 2,5-dimethyl-*p*-quinonedibenzenesulfonimide did not react with butadiene or dimethylbutadiene under a variety of conditions. Cyclopentadiene gave an adduct which was so unstable it could not be recrystallized without dissociation. It was probably an unrearranged mono-adduct since it was obtained in a yield corresponding to a quantitative addition of one mole of diene to one mole of diimide, it was yellow, and it decomposed at a much lower temperature than the original diimide. Because of the unreactivity of the dimethyl diimide the structures of the adducts of the dienes with the 2-chloro-5-methyl derivatives would appear to be those with an angular chlorine.

The formation of stable adducts with angular chlorine in contrast to no adducts or very unstable adducts with angular methyl may be explained by comparison of the inductive and steric effects of the two groups. The steric effect of the chlorine atom is overcome by its inductive (−I) effect which enhances the positive charge on the quinoid ring and facilitates the approach of the negative end of the diene to give a stable adduct. On the other hand, the steric effect of the methyl group is enhanced by the inductive (+I) effect and a relatively poor dienophile is obtained.

Acknowledgment.—The authors are indebted to Mrs. Lucy Chang, Mrs. Esther Fett, Mrs. Katherine Pih and Mr. Joseph Nemeth for the microanalyses, to Miss Helen Miklas for the infrared determinations and interpretations and to Mrs. Rosemary Hill for the ultraviolet and visible spectra determinations.

Experimental

All melting points are corrected.

General Procedure for the Preparation of Adducts from Substituted *p*-Quinonedibenzenesulfonimides.—The diene was added to a solution or suspension of the substituted *p*-quinonedibenzenesulfonimide in dry chloroform and the resulting mixture allowed to stand at room temperature (see Table II). The chloroform solution was concentrated to a small volume (*ca.* 5 ml.) at room temperature and petroleum ether (b.p. 30–60°) was added to precipitate the crude adduct. Infrared spectra (see Table III) were employed to demonstrate whether the adducts were unrearranged or rearranged; the spectra were run in Nujol suspension using a Perkin–Elmer Model 21 Double Beam Spectrophotometer.

2-Chloro-*p*-quinonedibenzenesulfonimide and Butadiene; 2-Chloro-5,8-dihydro-1,4-naphthalenedibenzenesulfonamide.—To a solution of 4.0 g. of 2-chloro-*p*-quinonedibenzenesulfonimide[3] in 80 ml. of dry chloroform was added 10 ml. of butadiene. The resulting 90 ml. of solution was allowed to stand at room temperature. After specified periods of time, 20 ml. of solution (the fifth sample contained 10 ml.) was removed from the reaction mixture. The addition of 100 ml. of petroleum ether (b.p. 30–60°)

TABLE II: ADDUCTS FROM DIENES AND SUBSTITUTED *p*-QUINONEDIBENZENESULFONIMIDES

Type adduct	Diimide[a] (g.)	Diene[b] (g.)	Solvent, ml.	Days at room temp.	Yield, crude, %	Recryst. solvent	Color and crystal form	M.p. with dec., °C., pure	Adduct formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
III	2-Cl (1.0)	B (2.5)	25	5	92	HAc	White needles	227–228	$C_{22}H_{19}ClN_2O_4S_2$	55.63	55.55	4.03	4.06	5.90	5.90
VII[c]	2-Cl[d] (0.7)	B (2.5)	25	31	51	EtOAc	Yellow-tinted prisms	182–183	$C_{26}H_{21}ClN_2O_4S_2$	59.47	59.78	4.03	3.87	5.34	5.40
II	2-Cl (1.5)	D (0.88)	25	6	71	EtOAc–C_6H_{12}	Orange needles	165–166.5	$C_{24}H_{23}ClN_2O_4S_2$	57.30	57.33	4.61	4.62	5.57	5.70
II	2-Cl (1.0)	C (0.15)	35	4	96	EtOAc–C_6H_{12}	Yellow needles	151–153.5	$C_{23}H_{19}ClN_2O_4S_2$	56.72	56.82	3.93	3.95	5.75	5.55
III	2-CH$_3$ (1.5)	B (2.5)	25	5	91	HAc	White needles	233.5–234	$C_{23}H_{22}N_2O_4S_2$	60.77	60.56	4.88	4.65	6.16	6.16
II	2-CH$_3$ (1.5)	D (0.82)	25	6	97	CHCl$_3$–Pet. ether (b.p. 30–60°)[e]	Yellow needles	213–215	$C_{25}H_{26}N_2O_4S_2$	62.21	61.92	5.43	5.66	5.81	6.04
II	2-CH$_3$ (1.0)	C (0.16)	35	4	93	EtOAc–C_6H_{12}	Yellow needles	152.5–154.5	$C_{24}H_{22}N_2O_4S_2$	61.78	61.66	4.75	4.73	6.00	6.10
VIII[f]	2,5-diCl[k] (3.0)	B (5.0)	100	35	88	HAc	White needles	198.5–200	$C_{22}H_{18}Cl_2N_2O_4S_2$	51.87	52.05	3.56	3.60	5.50	5.42
VIII[g]	2,5-diCl (2.0)	D (1.09)	50	35	23.3	EtOAc	Yellow needles	185–186.5	$C_{24}H_{22}Cl_2N_2O_4S_2$	53.63	53.92	4.13	4.07	5.21	5.36
X[h,i]					17.3	HAc	White needles	239–240	$C_{24}H_{21}ClN_2O_4S_2$	57.53	57.50	4.23	4.27	5.59	5.55
VIII[j]	2,5-diCl (2.0)	C (0.87)	50	35	20	EtOAc	Yellow needles	156–157	$C_{23}H_{18}Cl_2N_2O_4S_2$	52.98	53.18	3.48	3.71	5.37	5.32
VIII	2-CH$_3$, 5-Cl[k] (2.0)	B (2.5)	25	35	60	EtOAc	Ivory needles	194–195	$C_{23}H_{21}ClN_2O_4S_2$	56.49	56.71	4.33	4.39	5.73	5.82
VIII	2-CH$_3$, 5-Cl (0.70)	D (0.27)	25	26	71	EtOAc	Yellow needles	203–204.5	$C_{25}H_{25}ClN_2O_4S_2$	58.07	58.20	4.87	4.82	5.42	5.26
VIII	2-CH$_3$, 5-Cl (0.70)	C (0.22)	25	27	93	EtOAc	Yellow crystals	159–160.5	$C_{24}H_{21}ClN_2O_4S_2$	57.53	57.65	4.22	3.96	5.59	5.80

[a] Substituted *p*-quinonedibenzenesulfonimides. [b] B = butadiene, D = 2,3-dimethylbutadiene and C = cyclopentadiene. [c] A 29% yield of reduced starting material was obtained as a precipitate in the reaction mixture. [d] 2-Chloro-1,4-naphthoquinonedibenzenesulfonimide [R. Adams and R. A. Wankel, THIS JOURNAL, **73**, 131 (1951)]. [e] Recrystallized at room temperature by dissolving in excess chloroform, adding the petroleum ether to the cloud point and concentrating until a substantial amount of crystals formed. [f] Chlorine analysis: calcd., 13.92; found, 13.97. [g] Isolated as the more insoluble product from the first recrystallization. [h] Isolated as the more soluble product from the first recrystallization. [i] Chlorine analysis: calcd., 7.08; found, 7.11. [j] A 10% yield of reduced starting material was obtained by extracting the gummy crude product with ethyl acetate and concentrating the resulting extract. [k] R. Adams, E. F. Elslager and K. F. Heumann, THIS JOURNAL, **74**, 2608 (1952).

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(3) R. Adams and A. S. Nagarkatti, THIS JOURNAL, **72**, 4601, (1950).

TABLE III

INFRARED ABSORPTION BANDS OF THE ADDUCTS IN CM.$^{-1}$

Adduct[a]	-NH-	Conj. C=N (+ conj. C=C + aromatic)	-SO_2-
III ($C_{22}H_{19}ClN_2O_4S_2$)	3245	1584(w)	1343, 1330, 1162
VII ($C_{26}H_{21}ClN_2O_4S_2$)	..	1625(s), 1586(s)	1330, 1322, 1317, 1162
II ($C_{24}H_{23}ClN_2O_4S_2$)	..	1597(s), 1569(w)	1327, 1156
II ($C_{23}H_{19}ClN_2O_4S_2$)	..	1581(s), 1560(m)	1323, 1314, 1157
III ($C_{23}H_{22}N_2O_4S_2$)	3195	....	1335, 1165
II ($C_{25}H_{26}N_2O_4S_2$)	..	1609(w), 1572(s)	1320, 1313, 1158
II ($C_{24}H_{22}N_2O_4S_2$)	..	1610(w), 1563(s)	1322, 1155
VIII ($C_{22}H_{18}Cl_2N_2O_4S_2$)	..	1637(m), 1595(m), 1553(s)	1340, 1319, 1165, 1157
VIII ($C_{24}H_{22}Cl_2N_2O_4S_2$)	..	1610(s), 1568(w)	1327, 1173, 1166
X ($C_{24}H_{21}ClN_2O_4S_2$)	3250	1597(m)	1343, 1312, 1168, 1158
VIII ($C_{23}H_{18}Cl_2N_2O_4S_2$)	..	1595(s)	1340, 1333, 1171
VIII ($C_{23}H_{21}ClN_2O_4S_2$)	..	1617(w), 1591(s)	1328, 1162
VIII ($C_{25}H_{25}ClN_2O_4S_2$)	..	1605(s), 1585(m)	1314, 1171
VIII ($C_{24}H_{21}ClN_2O_4S_2$)	..	1613(w), 1570(s)	1325, 1163

[a] In the same order as they appear in Table II. s = strong, m = medium, w = weak—referring to intensity of bands.

precipitated the crude adduct: 6 hr., m.p. 161–167° dec.; 12 hr., m.p. 156–206.5° dec.; 24 hr., m.p. 218–221° dec.; 48 hr., m.p. 227–230° dec.; 72 hr., m.p. 223–229° dec. The products in successive samples varied from yellow needles in the first to very pale yellow needles in the last. In previous studies, unrearranged mono-adducts always melted below either the starting diimide or the aromatized adduct.

Rearrangement of 2-Chloro-5,8-dihydro-1,4-naphthoquinonedibenzenesulfonimide; 2-Chloro-1,4-naphthalenedibenzenesulfonamide.—A suspension of 1.00 g. of 2-chloro-5,8-dihydro-1,4-naphthalenedibenzenesulfonamide and 0.92 g. of lead tetraacetate in 15 ml. of glacial acetic acid was stirred at room temperature. At the end of 26 hours, 5 drops of ethylene glycol was added and stirring continued an additional 10 minutes. The resulting red precipitate (containing some white solid) was washed with glacial acetic acid and petroleum ether (b.p. 30–60°). The orange acetic acid filtrate was added to 100 ml. of water to give an additional quantity of product. Total yield was 0.89 g. (90%). The crude product was probably 2-chloro-5,8-dihydro-1,4-naphthoquinonedibenzenesulfonimide. Upon recrystallization from glacial acetic acid, the color disappeared and colorless needles formed, m.p. 229–230° dec. (lit.[4] 228°).

Infrared analysis indicated that it was identical to an authentic sample.[4]

2-Chloro-6,7-dimethyl-5,8-dihydro-1,4-naphthalenedibenzenesulfonamide.—To a warm solution of 0.35 g. of 2-chloro-6,7-dimethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinonedibenzenesulfonimide (prepared from 2,3-dimethylbutadiene and 2-chloro-*p*-quinonedibenzenesulfonimide, see Table II) in 20 ml. of glacial acetic acid was added 4 drops of 48% hydrobromic acid. Upon the addition of the acid, the color of the solution changed from orange to amber. The solution was heated to boiling, water added to the cloud point and cooled. The resulting brown precipitate weighed 0.33 g. (97%). It was dissolved in 12 ml. of warm 2.5% aqueous sodium hydroxide, treated with Darco, and filtered through "Filter Cel." Acidification of the filtrate with concentrated hydrochloric acid gave a white precipitate which was recrystallized from glacial acetic acid–water to give white needles, m.p. 230.5–232° dec.

Anal. Calcd. for $C_{24}H_{23}ClN_2O_4S_2$: C, 57.30; H, 4.61; N, 5.57. Found: C, 57.41; H, 4.50; N, 5.41.

Infrared analysis indicated the presence of the NH band at 3225 cm.$^{-1}$.

2-Methyl-*p*-quinonedibenzenesulfonimide and Butadiene; 2-Methyl-5,8-dihydro-1,4-naphthalenedibenzenesulfonamide.—To a solution of 0.88 g. of 2-methyl-*p*-quinonedibenzenesulfonimide[3] in 20 ml. of reagent grade chloroform was added 3 ml. of butadiene and the resulting solution allowed to stand at room temperature. The solution was then concentrated to 5 ml. and the addition of 45 ml. of petroleum ether (b.p. 30–60°) precipitated the crude adduct. The results of five reactions at various periods of time were as follows: 6 hr., m.p. 163–166° dec.; 11 hr., m.p. 148–158° dec.; 26 hr., m.p. 145–154° dec.; 48 hr., 144–171°, resolidified and remelted at 209.5–237° dec.; 72 hr., m.p. 160–237° dec.

Rearrangement of 2-Methyl-5,8-dihydro-1,4-naphthoquinonedibenzenesulfonimide; 2-Methyl-1,4-naphthalenedibenzenesulfonamide.—2-Methyl-5,8-dihydro-1,4-naphthalenedibenzenesulfonamide was oxidized and rearranged by the same procedure described for the corresponding 2-chloro derivative. The total yield of the orange to yellow crude product, probably 2-methyl-5,8-dihydro-1,4-naphthoquinonedibenzenesulfonimide, was 1.48 g. (99%). Upon recrystallization from glacial acetic acid the color disappeared and colorless needles formed, m.p. 236–237° dec. (lit.[5] 236–237°).

2,6,7-Trimethyl-5,8-dihydro-1,4-naphthalenedibenzenesulfonamide.—2,6,7-Trimethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinonedibenzenesulfonimide (prepared from 2,3-dimethylbutadiene and 2-methyl-*p*-quinonedibenzenesulfonimide, see Table II) was rearranged in a similar manner to the corresponding 2-chloro-6,7-dimethyl derivative. The yield of product was 0.44 g. (81%). Recrystallization from glacial acetic acid–water gave white needles, m.p. 215.5–217° dec.

Anal. Calcd. for $C_{25}H_{26}N_2O_4S_2$: C, 62.21; H, 5.43; N, 5.81. Found: C, 62.28; H, 5.46; N, 5.84.

Infrared analysis indicated the NH band at 3215 cm.$^{-1}$.

2,5-Dimethyl-*p*-quinonedibenzenesulfonimides and Dienes. Method A. Butadiene.—A solution of 1.50 g. of 2,5-dimethyl-*p*-quinonedibenzenesulfonimide[3] and 4 ml. of butadiene or 0.88 g. of 2,3-dimethylbutadiene in 35 ml. of dry chloroform was allowed to stand at room temperature for one day and for 41 days. Only unchanged diimide was isolated in essentially quantitative yield.

Method B. Butadiene.—A mixture of 1.00 g. of 2,5-dimethyl-*p*-quinonedibenzenesulfonimide and 2 ml. of butadiene in 4 ml. of dry benzene in a 30-ml. sealed glass tube was heated at 99–102° for 72 hours. The only identifiable compound that was isolated from the reaction mixture was the starting diimide.

Method C. Cyclopentadiene.—A solution of 1.50 g. of 2,5-dimethyl-*p*-quinonedibenzenesulfonimide and 0.60 g. of cyclopentadiene in 30 ml. of dry chloroform was allowed to stand at room temperature. When the cyclopentadiene was added to the yellow solution of the imide, a transitory color (orange) was formed. After standing for one day, a trace of white solid was removed by filtration. Concentration of the filtrate at room temperature and addition of petroleum ether (b.p. 30–60°) precipitated 1.74 g. of yellow solid that darkened at 160°, turned black at 190° but did not melt below 360°. Recrystallization from hot ethyl acetate–petroleum ether (b.p. 30–60°) gave yellow needles that proved to be the starting diimide. An attempt to recrystallize by dissolving the compound in excess cold chloroform, adding petroleum ether (b.p. 80–100°) and allowing the solution to evaporate at room temperature until a substantial amount of crystals had formed yielded only starting material.

URBANA, ILLINOIS

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

(5) R. Adams and R. H. Mattson, unpublished work.