1-Fluoro-4-methylestra-1,3,5(10)-trien-17-one (IX).—A solution of 283 mg. of crude 1-amino-4-methylestra-1,3,5(10)-trien-17-one (VII) in 2.5 ml. of acetic acid, 3 ml. of water, and 7 ml. of 48% fluoroboric acid was cooled and treated with 0.7 g. of solid sodium hydroxide. The resulting solution was cooled to 2°, and a solution of 76 mg. of sodium nitrite in 2 ml. of water was added over a 5-min. period. Evolution of a gas was soon evident. The mixture was stirred at 0° for 30 min. and then warmed to room temperature over a 30-min. period. The mixture was poured into 400 ml. of water, and the precipitate was filtered and dried in air, yielding 274 mg. of crude material. This was chromatographed on alumina (Woelm, neutral, activity grade I). Elution with 10% ether in benzene afforded 83 mg. (29%) of 1-fluoro-4-methylestra-1,3,5-(10)-trien-17-one, m.p. 192–196°. An analytical sample recrystallized from methanol had m.p. 196–197°; $[\alpha]^{23}D$ +196° (*c* 0.6, $CHCl_3$); ν_{max} 1737, 1604, 1419, 1237, and 819 cm.$^{-1}$.

Anal. Calcd. for $C_{19}H_{23}FO$: C, 79.69; H, 8.10; F, 6.63. Found: C, 79.42; H, 8.23; F, 6.74.

Acknowledgment.—The authors wish to thank Mr. C. E. Childs and his staff of our Microanalytical Laboratory, Dr. J. M. Vandenbelt and his staff of our Physical Chemical Laboratory, and Mr. W. M. Pearlman of our High Pressure Laboratory for their valuable technical assistance. The authors also wish to thank Dr. G. W. Moersch and Dr. R. A. Scherrer for helpful discussions.

Base-Catalyzed Aromatization of *p*-Quinone Disulfonimide–Cyclopentadiene Adducts

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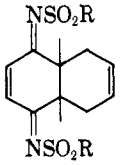
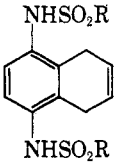
Simple monoadducts (IV) of *p*-quinone disulfonimides and cyclopentadiene were isomerized to their aromatic forms (V) by base catalysis. Structures of several quinone imide–cyclopentadiene adducts were thus confirmed. The alleged 4a-chloro-1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-bis(dimethylaminosulfonimide) (VI) of Adams and Shafer was shown to be the isomeric 6-chloro compound (IVg). Treatment of ring-unsubstituted *p*-quinone disulfonimides with equimolar amounts of cyclopentadiene has previously been shown to result only in the formation of the diadducts (III). When *p*-quinonedimethanesulfonimide was treated with an excess of cyclopentadiene in the presence of triethylamine catalyst, the aromatized monoadduct (VII) was obtained exclusively.

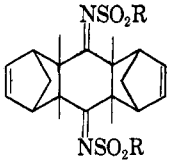
Quinone disulfonimides have been shown to undergo the Diels–Alder reaction with dienes to give either the simple adducts (I) or the aromatized adducts (II).[1–6]



I



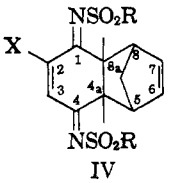
II



III

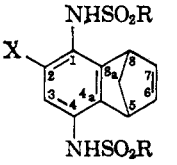
Simple adducts of dienes, other than cyclopentadiene, were caused to isomerize to the corresponding aromatized forms by treatment with catalytic amounts of hydrobromic acid.[1–3,5] Cyclopentadiene was shown to react with ring-unsubstituted *p*-quinone disulfonimides to give diadducts (III) exclusively[1] and with ring-substituted imides to give simple monoadducts (IV) which resisted isomerization to the aromatic forms upon treatment with acid catalyst.[2,5] Our initial interest in adducts of type IV was related to certain fungicidal activities of this series.

We have found that cyclopentadiene adducts of type IV can be isomerized to the aromatic forms (V) by treatment with a catalytic amount of amine base in an inert solvent. Thus, 2-chloro-4a,5,8,8a-tetrahydro-5,8-methano-1,4-naphthoquinonedimethanesulfonimide (IVa) was converted instantaneously to the corresponding 2-chloro-5,8-dihydro-5,8-methano-1,4-naphthalenedimethanesulfonamide (Va) by a catalytic amount of triethylamine in benzene solution. Similar aromatized adducts prepared in this way are 2-chloro-5,8-dihydro-5,8-methano-1,4-naphthalenebis(*p*-chlorobenzenesulfonamide) (Vb), 2-chloro-5,8-dihydro-5,8-methano-1,4-



IV

Compound	R	X	Yield, %
IVa	CH_3	Cl	84
b	*p*-ClC_6H_4	Cl	88
c	C_6H_5	Cl	96[5]
d	*n*-C_4H_9	Cl	86
e	CH_3	SCH_3	80
f	CH_3	SC_6H_{11}	...
g	$N(CH_3)_2$	Cl	34[4]



V

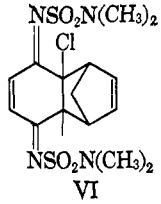
Compound	R	X	Yield, %
Va	CH_3	Cl	74
b	*p*-ClC_6H_4	Cl	89
c	C_6H_5	Cl	94
d	*n*-C_4H_9	Cl	46
e	CH_3	SCH_3	87
f	CH_3	SC_6H_{11}	58
g	$N(CH_3)_2$	Cl	55

(1) R. Adams and C. R. Walter, Jr., *J. Am. Chem. Soc.*, **73**, 1152 (1951).
(2) R. Adams and W. Moje, *ibid.*, **74**, 2593 (1952).
(3) R. Adams and J. D. Edwards, Jr., *ibid.*, **74**, 2603 (1952).
(4) R. Adams and P. R. Shafer, *ibid.*, **75**, 667 (1953).
(5) R. Adams and R. W. P. Short, *ibid.*, **76**, 2408 (1954).
(6) R. Adams and W. P. Samuels, *ibid.*, **77**, 5383 (1955).

naphthalenedibenzenesulfonamide (Vc), and 2-chloro-5,8-dihydro-5,8-methano-1,4-naphthalenedi-*n*-butanesulfonamide (Vd). Adduct IVa was also aromatized to Va in 70% yield by the exposure of a benzene solution of IVa to ultraviolet light for a period of 48 hr.

Adducts of 2-alkylthio-*p*-benzoquinonedimethanesulfonimides and cyclopentadiene were found to undergo reverse Diels–Alder reaction in the absence of excess cyclopentadiene. The base-catalyzed aromatization was used to characterize the unstable 2-methylthio-4a,5,8,8a-tetrahydro-5,8-methano-1,4-naphthoquinonedimethanesulfonimide (IVe) and 2-cyclohexylthio-4a,5,8,8a-tetrahydro-5,8-methano-1,4-naphthoquinonedimethanesulfonimide (IVf), giving 2-methylthio-5,8-dihydro-5,8-methano-1,4-naphthalenedimethanesulfonamide (Ve) and 2-cyclohexylthio-5,8-dihydro-5,8-methano-1,4-naphthalenedimethanesulfonamide (Vf), respectively. These reactions were accomplished in 60 and 90% yields by treatment of the alkylthioquinonedimethanesulfonimides with an excess of cyclopentadiene and a catalytic amount of triethylamine in benzene or chloroform solution.

Adams and Shafer[4] obtained two products by the treatment of 2-chloro-*p*-quinonebis(dimethylaminosulfonimide) with an excess of cyclopentadiene: a white solid, which proved to be the aromatized adduct (Vg), and a yellow isomer which did not aromatize upon treatment with acid. They suggested that the yellow isomer was the adduct VI formed by the addition of the



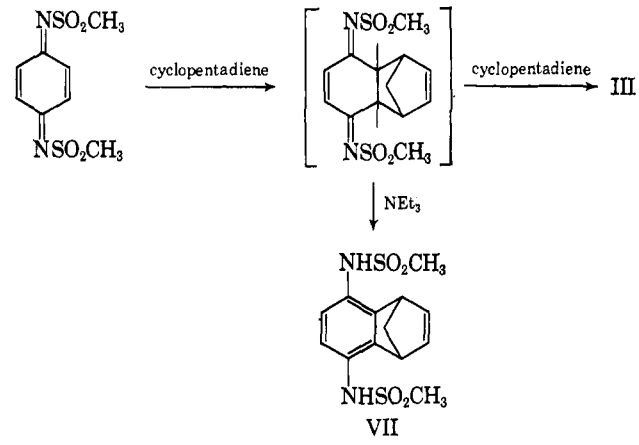
VI

cyclopentadiene molecule to the side of the quinone imide nucleus containing the chlorine atom. Upon repetition of the experiment, we also obtained the two products. However, when the yellow material was treated with base catalyst, a white crystalline substance identical with Vg was produced. The yellow isomer, therefore, was assigned structure IVg. Its failure to isomerize to the aromatic form on treatment with hydrobromic acid was merely the characteristic behavior of the simple cyclopentadiene adducts.

Although ring-unsubstituted *p*-quinone disulfonimides normally react with equimolar amounts of cyclopentadiene to give diadducts[1] (III) exclusively, we obtained a monoadduct, in aromatized form (VII), in 87% yield when either an equimolar amount or an excess of cyclopentadiene was added to *p*-quinonedimethanesulfonimide in an inert solvent in the presence of triethylamine catalyst.

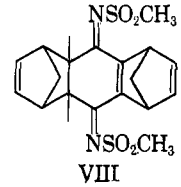
Thus, the rate of the base-catalyzed aromatization of the monoadduct is greater than that of the addition of the second molecule of cyclopentadiene to the monoadduct, and the addition of the first cyclopentadiene molecule is the rate-determining step. Cyclopentadiene monoadducts of ring-unsubstituted *p*-quinone disulfonimides have been otherwise inaccessible.

Oxidation of VII to the corresponding diimide with lead tetraacetate permitted the addition of a second

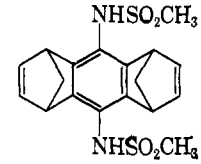


VII

molecule of cyclopentadiene to give the simple adduct (VIII) in the absence of base or the aromatized adduct (IX) when the addition was made in the presence of triethylamine catalyst.



VIII



IX

Experimental[7]

2-Chloro-4a,5,8,8a-tetrahydro-5,8-methano-1,4-naphthoquinonedimethanesulfonimide (IVa).—To a solution of 131.5 g. (0.443 mole) of 2-chloro-*p*-quinonedimethanesulfonimide[6] in 2.5 l. of chloroform was added 72 g. (1.1 moles) of cyclopentadiene. A transient dark red color was formed, and after 15 min. the color became pale yellow. The solution was then concentrated *in vacuo* to about 200 ml., diluted with carbon tetrachloride, and cooled to give 134.2 g. (84%) of light yellow crystals, m.p. 139–140° dec. Recrystallization from aqueous acetic acid gave the pure substance as light yellow crystals, m.p. 140–141° dec.

Anal. Calcd. for $C_{13}H_{15}ClN_2O_4S_2$: C, 43.03; H, 4.17; N, 7.72. Found: C, 43.11; H, 4.13; N, 7.57.

2-Chloro-5,8-dihydro-5,8-methano-1,4-naphthalenedimethanesulfonamide (Va). A.—To a boiling solution of 18.1 g. (0.0500 mole) of IVa in 250 ml. of benzene was added 5.60 g. (0.0553 mole) of triethylamine. The color of the solution changed immediately from pale yellow to amber. The gray solid, which crystallized as the solution cooled to room temperature, was collected on a filter and recrystallized from aqueous acetic acid (Norit) to give 10.9 g. (60%) of light tan crystalline solid, m.p. 210–212°. Three further recrystallizations from aqueous methanol gave the pure product as colorless crystals, m.p. 216.5–217.5°.

Anal. Calcd. for $C_{13}H_{15}ClN_2O_4S_2$: C, 43.03; H, 4.17; Cl, 9.77; N, 7.72; S, 17.67. Found: C, 43.33; H, 3.93; Cl, 9.65; N, 7.52; S, 17.58.

The infrared spectrum showed the presence of the –NH– linkage (3220–3270 $cm.^{-1}$).

B.—A solution of 5.00 g. (0.0138 mole) of IVa in 250 ml. of benzene was placed in a Pyrex flask and irradiated with a 275-w. G. E. sunlamp over a distance of 15 cm. for 48 hr. Upon standing at room temperature for several days thereafter, the solution yielded 3.72 g. (74%) of white solid. Recrystallization from glacial acetic acid gave a white solid, m.p. 216–218°.

The infrared spectrum of this substance and that of the substance prepared by procedure A were identical.

2-Chloro-*p*-phenylenebis(*p*-chlorobenzenesulfonamide).—To a stirred, ice-cold solution of 40.0 g. (0.186 mole) of chloro-*p*-phenylenediamine dihydrochloride in 400 ml. of pyridine was added a solution of 78.6 g. (0.372 mole) of *p*-chlorobenzene-

(7) All melting points are uncorrected. All cyclopentadiene was freshly prepared before use.

sulfonyl chloride in 80 ml. of pyridine. The mixture was allowed to stand at room temperature for 15 hr. and was then poured into ice and concentrated hydrochloric acid. The resulting crude substance was dissolved in a solution of 60 g. of sodium hydroxide in 1140 ml. of water and stirred for 30 min. with 30 g. of Norit at room temperature and filtered. The filtrate was acidified with dilute hydrochloric acid to give a white precipitate, which was recrystallized from glacial acetic acid to give 56.7 g. (62%) of the pure product as colorless crystals, m.p. 211–212°.

Anal. Calcd. for $C_{15}H_{13}Cl_3N_2O_4S_2$: C, 43.96; H, 2.66; N, 5.70. Found: C, 44.10; H, 2.76; N, 5.60.

2-Chloro-*p*-quinonebis(*p*-chlorobenzenesulfonimide).—This procedure exemplifies the general method used for the preparation of all of the diimides described in this paper.

To a well-stirred suspension of 56.3 g. (0.114 mole) of 2-chloro-*p*-phenylenebis(*p*-chlorobenzenesulfonamide) in 850 ml. of glacial acetic acid was added 65.8 g. (0.149 mole) of lead tetraacetate. A yellow color was apparent almost immediately. After the mixture had been stirred for 1 hr. at room temperature, 10 ml. of ethylene glycol was added to destroy excess lead tetraacetate, and the mixture was stirred for an additional 25 min. Water (850 ml.) was then added to precipitate 55.0 g. (98%) of yellow, crystalline solid. Recrystallization from glacial acetic acid gave the pure product as yellow crystals, m.p. 178–179° dec.

Anal. Calcd. for $C_{18}H_{11}Cl_3N_2O_4S_2$: C, 44.14; H, 2.26; N, 5.72. Found: C, 43.98; H, 2.33; N, 5.72.

2-Chloro-4a,5,8,8a-tetrahydro-5,8-methano-1,4-naphthoquinonebis(*p*-chlorobenzenesulfonimide) (IVb).—Cyclopentadiene (20 ml.) was added to a warm solution of 20.0 g. (0.0408 mole) of 2-chloro-*p*-quinonebis(*p*-chlorobenzenesulfonimide) in 200 ml. of chloroform. After the disappearance of the transient violet color, the solvent was removed by evaporation *in vacuo*, and the yellow, gummy residue was crystallized from cyclohexane–ethyl acetate to give 19.9 g. (88%) of yellow crystals, m.p. 153°.

Anal. Calcd. for $C_{23}H_{17}Cl_3N_2O_4S_2$: C, 49.69; H, 3.08; Cl, 19.14. Found: C, 49.59; H, 3.19; Cl, 18.82.

2-Chloro-5,8-dihydro-5,8-methano-1,4-naphthalenebis(*p*-chlorobenzenesulfonamide) (Vb).—Triethylamine (6 drops) was added to a well-stirred, boiling solution of 3.95 g. (0.00710 mole) of IVb in 80 ml. of benzene. The color of the solution changed immediately from yellow to amber. The reaction mixture was then allowed to cool to room temperature, and 3.53 g. (89%) of light tan solid was obtained. Recrystallization from glacial acetic acid (Norit) afforded colorless crystals, m.p. 242–243° dec.

Anal. Calcd. for $C_{23}H_{17}Cl_3N_2O_4S_2$: C, 49.69; H, 3.08; N, 5.04. Found: C, 49.83; H, 3.31; N, 4.63.

The infrared spectrum showed the presence of the –NH– linkage (3240 cm.$^{-1}$).

2-Chloro-5,8-dihydro-5,8-methano-1,4-naphthalenedibenzenesulfonamide (Vc). A.—Triethylamine (2 drops) was added to a solution of 1.35 g. (0.00278 mole) of IVc[5] in 25 ml. of chloroform. A dark brown coloration was immediately apparent. The mixture was allowed to stand at room temperature for 22 hr., during which time 0.68 g. (50%) of brown solid crystallized. Recrystallization from ethanol (Norit) gave light tan crystals, m.p. 246° dec.

Anal. Calcd. for $C_{23}H_{19}ClN_2O_4S_2$: C, 56.72; H, 3.93; N, 5.75. Found: C, 56.64; H, 3.86; N, 5.67.

The infrared spectrum showed the presence of the –NH– linkage (3240 cm.$^{-1}$).

B.—Cyclopentadiene (2 ml.) was added to a warm solution of 1.6 g. (0.0038 mole) of 2-chloro-*p*-quinonedibenzenesulfonimide[8] and 2 drops of triethylamine in 25 ml. of chloroform. A brown color was immediately apparent, and the reaction mixture was allowed to stand at room temperature for 22 hr., during which time 1.50 g. (94%) of brown crystals formed. Recrystallization from ethanol (Norit) gave colorless crystals, m.p. 247° dec.

Anal. Calcd. for $C_{23}H_{19}ClN_2O_4S_2$: C, 56.72; H, 3.93; N, 5.75. Found: C, 56.86; H, 3.77; N, 5.68.

The infrared spectrum was identical with that of the product obtained by procedure A.

***p*-Phenylenedi-*n*-butanesulfonamide.**—*n*-Butanesulfonyl chloride (69.7 g., 0.445 mole) was added over a period of 10 min. to a well-stirred, ice-cold solution of 24.1 g. (0.223 mole) of *p*-phenylenediamine in 230 ml. of pyridine. The mixture was then stirred at room temperature for 3 hr. and was poured into a mixture of ice and excess concentrated hydrochloric acid. The dark purple solid, thus obtained, was dissolved in a solution of 72 g. of sodium hydroxide in 1370 ml. of water. The solution was stirred with 36 g. of Norit for 20 min. at room temperature, filtered, and acidified with dilute hydrochloric acid to yield 64.0 g. (82.5%) of light tan solid. Recrystallization from glacial acetic acid (Norit) gave colorless platelets, m.p. 178–179°.

Anal. Calcd. for $C_{14}H_{24}N_2O_4S_2$: C, 48.25; H, 6.94; N, 8.04. Found: C, 48.94; H, 6.94; N, 7.96.

***p*-Quinonedi-*n*-butanesulfonimide.**—Lead tetraacetate oxidation of *p*-phenylenedi-*n*-butanesulfonamide afforded a 94% yield of the pure diimide as yellow platelets, m.p. 135–136° dec.

Anal. Calcd. for $C_{14}H_{22}N_2O_4S_2$: C, 48.53; H, 6.40; N, 8.09. Found: C, 48.96; H, 6.43; N, 8.16.

2-Chloro-*p*-phenylenedi-*n*-butanesulfonamide.—Concentrated hydrochloric acid (80 ml.) was added in one portion to a well-stirred suspension of 30.7 g. (0.0915 mole) of *p*-quinonedi-*n*-butanesulfonimide in 250 ml. of ethanol. The color disappeared after 1 min., and the white product began to crystallize. The mixture was diluted with 150 ml. of water to give 32.3 g. (95%) of white solid. Recrystallization from ethanol gave colorless needles, m.p. 134–135°.

Anal. Calcd. for $C_{14}H_{23}ClN_2O_4S_2$: C, 43.91; H, 6.05; N, 7.32. Found: C, 43.81; H, 5.78; N, 7.28.

2-Chloro-*p*-quinonedi-*n*-butanesulfonimide.—Lead tetraacetate oxidation of 2-chloro-*p*-phenylenedi-*n*-butanesulfonamide gave a quantitative yield of the diimide as a yellow solid, crystallizing from cyclohexane–carbon tetrachloride in yellow needles, m.p. 69–70°.

Anal. Calcd. for $C_{14}H_{21}ClN_2O_4S_2$: C, 44.14; H, 5.56; N, 7.36. Found: C, 44.37; H, 5.46; N, 7.17.

2-Chloro-4a,5,8,8a-tetrahydro-5,8-methano-1,4-naphthoquinonedi-*n*-butanesulfonimide (IVd).—Cyclopentadiene (15.2 g., 0.230 mole) was added to a solution of 11.0 g. (0.0289 mole) of 2-chloro-*p*-quinonedi-*n*-butanesulfonimide in 80 ml. of chloroform. The reaction was moderately exothermic and was accompanied by a transient violet color. The solvent was removed by evaporation *in vacuo*, and the residue solidified upon being triturated with ether to give 11.1 g. (86%) of pale yellow crystals, m.p. 110–111°. Two recrystallizations from benzene–ether gave pale yellow crystals, m.p. 112–113°.

Anal. Calcd. for $C_{19}H_{27}ClN_2O_4S_2$: C, 51.05; H, 6.09; N, 6.27. Found: C, 51.14; H, 5.99; N, 6.21.

2-Chloro-5,8-dihydro-5,8-methano-1,4-naphthalenedi-*n*-butanesulfonamide (Vd).—Triethylamine (6 drops) was added to a warm solution of 2.87 g. (0.00641 mole) of IVd in 25 ml. of benzene. A green color formed immediately, and after standing at room temperature for 1 hr., the solution exhibited an amber-red color. The benzene was removed by evaporation *in vacuo*, and the oily residue was crystallized from a minimum of hot, aqueous acetic acid (Norit) to give 1.32 g. (46%) of light tan crystals. Recrystallization from aqueous acetic acid gave colorless crystals, m.p. 138–139.5°.

Anal. Calcd. for $C_{19}H_{27}ClN_2O_4S_2$: C, 51.05; H, 6.09; N, 6.27. Found: C, 51.26; H, 6.08; N, 6.26.

The infrared spectrum showed the presence of the –NH– linkage (3245 cm.$^{-1}$).

2-Methylthio-*p*-phenylenedimethanesulfonamide.—To a cold (6°) solution of 26.2 g. (0.100 mole) of *p*-quinonedimethanesulfonimide[8] and 1 ml. of triethylamine in 3.5 l. of chloroform was added 12.0 g. (0.250 mole) of methanethiol. The yellow color of the solution became lighter immediately, and a white solid precipitated. Carbon tetrachloride (1 l.) was added, and 28.7 g. (92%) of white solid was obtained. Recrystallization from glacial acetic acid gave colorless needles, m.p. 166–167°.

Anal. Calcd. for $C_9H_{14}N_2O_4S_3$: C, 34.82; H, 4.55; N, 9.03. Found: C, 34.82; H, 4.38; N, 8.88.

2-Methylthio-*p*-quinonedimethanesulfonimide.—Lead tetraacetate oxidation converted 2-methylthio-*p*-phenylenedimethanesulfonamide to the diimide in 88% yield. Recrystallization from chloroform–carbon tetrachloride gave bright red crystals, m.p. 171° dec.

Anal. Calcd. for $C_9H_{12}N_2O_4S_3$: C, 35.05; H, 3.92; N, 9.09. Found: C, 34.95; H, 3.87; N, 8.85.

2-Methylthio-4a,5,8,8a-tetrahydro-5,8-methano-1,4-naphthoquinonedimethanesulfonimide (IVe).—Cyclopentadiene (30 ml.) was added to a solution of 6.20 g. (0.0200 mole) of 2-methylthio-*p*-quinonedimethanesulfonimide in 250 ml. of chloroform at room temperature. The color of the solution changed within 1 min.

(8) R. Adams and A. S. Nagarkatti, *J. Am. Chem. Soc.*, **72**, 4601 (1950).

from dark red to light orange. The chloroform was then removed by evaporation *in vacuo*, and the yellow, gummy residue was crystallized from nitromethane to give 6.03 g. (80%) of yellow solid. Attempts to recrystallize the substance from various solvents always resulted in the formation of a red color as the solutions were heated. This apparent reverse Diels–Alder reaction was finally avoided by the recrystallization of the crude material from ethanol containing a slight excess of cyclopentadiene to give a yellow solid, m.p. 159° dec. (with rapid decoloration from about 145°).

Anal. Calcd. for $C_{14}H_{18}N_2O_4S_3$: C, 44.90; H, 4.84; S, 25.68. Found: C, 45.50; H, 4.77; S, 24.95.

The infrared spectrum showed the ethylenic double bond stretching band at 1582 cm.$^{-1}$.

The solid product on standing a few hours underwent a spontaneous reverse Diels–Alder reaction as evidenced by its acquisition of a red color and by the presence of the characteristic odor of cyclopentadiene.

2-Methylthio-5,8-dihydro-5,8-methano-1,4-naphthalenedimethanesulfonamide (Ve).—Cyclopentadiene (40 ml.) was added to a solution of 9.25 g. (0.0300 mole) of 2-methylthio-*p*-quinonedimethanesulfonimide in 800 ml. of benzene. The color of the solution changed from a deep red to yellow over a period of 3 min. Triethylamine (5 ml.) was then added, and the solution was boiled under reflux for 20 min., during which time some crystalline product separated. After the mixture had been concentrated to 400 ml. and cooled, there was obtained 9.83 g. (87%) of light tan solid. Recrystallization from glacial acetic acid (Norit) gave colorless crystals, m.p. 243.5–244° dec.

Anal. Calcd. for $C_{14}H_{18}N_2O_4S_3$: C, 44.90; H, 4.84; N, 7.48. Found: C, 44.71; H, 4.79; N, 7.76.

The infrared spectrum showed the presence of the –NH– linkage (3245 cm.$^{-1}$).

2-Cyclohexylthio-*p*-phenylenedimethanesulfonamide.—A solution of 11.6 g. (0.100 mole) of cyclohexanethiol and 6 drops of triethylamine in 50 ml. of chloroform was added in one portion to a warm solution of 26.2 g. (0.100 mole) of *p*-quinonedimethanesulfonimide[8] in 1250 ml. of chloroform. A violet color formed immediately and persisted. After the solution had been allowed to stand at room temperature for 30 min., the solvent was removed by evaporation *in vacuo*, leaving a light tan solid residue. Recrystallization from ethanol (Norit) yielded 35.0 g. (93%) of tan crystals. Further recrystallization from glacial acetic acid (Norit) gave colorless crystals, m.p. 131–132°.

Anal. Calcd. for $C_{14}H_{22}N_2O_4S_3$: C, 44.42; H, 5.86; N, 7.40. Found: C, 44.42; H, 5.64; N, 7.63.

2-Cyclohexylthio-*p*-quinonedimethanesulfonimide.—Lead tetraacetate oxidation of 2-cyclohexylthio-*p*-phenylenedimethanesulfonamide afforded a 90% yield of the diimide as a red solid, crystallizing from carbon tetrachloride as red crystals, m.p. 149–150°.

Anal. Calcd. for $C_{14}H_{20}N_2O_4S_3$: C, 44.66; H, 5.35; N, 7.44. Found: C, 44.31; H, 5.11; N, 7.71.

2-Cyclohexylthio-5,8-dihydro-5,8-methano-1,4-naphthalenedimethanesulfonamide (Vf).—Cyclopentadiene (8.2 ml.) was added to a solution of 6.79 g. (0.0180 mole) of 2-cyclohexylthio-*p*-quinonedimethanesulfonimide in 100 ml. of chloroform. The addition resulted in a color change from violet to amber within 2 min.[9] Triethylamine (3 ml.) was added, and the mixture was allowed to remain at room temperature for 2 hr. The solvent was then removed by evaporation *in vacuo*, and the semisolid residue was crystallized from a minimum of hot, glacial acetic acid (Norit) to give 4.63 g. (58%) of light tan solid. Recrystallization from glacial acetic acid gave colorless crystals, m.p. 183.5–184°.

Anal. Calcd. for $C_{19}H_{26}N_2O_4S_3$: C, 51.57; H, 5.92; N, 6.33. Found: C, 51.33; H, 5.65; N, 6.56.

The infrared spectrum showed the presence of the –NH– linkage (3280 cm.$^{-1}$).

Characterization of Alleged 4a-Chloro-1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-bis(dimethylaminosulfonimide) (VI).—Treatment of 2-chloro-*p*-quinonebis(dimethylaminosulfonimide) with cyclopentadiene was repeated after the experiment of Adams and Shafer[4] with similar results. Two products were obtained: 2-chloro-5,8-dihydro-5,8-methano-1,4-naphthalenebis(dimethylaminosulfonamide) (Vg), m.p. 208.5–209.5° dec. (lit. 209.6–210.6° dec.), and a yellow crystalline isomer, m.p. 140–141° dec. (lit. 140–141° dec.). The infrared spectrum showed the same band at 1590 cm.$^{-1}$ attributed by the other authors to the carbon–nitrogen double bond.

To a warm, stirred solution of 3.00 g. (0.00712 mole) of the yellow isomer in 60 ml. of benzene was added 5 drops of triethylamine. The color of the solution changed from bright yellow to dark brown over a period of 3 min. The mixture was then boiled for 5 min., and upon cooling it yielded 0.65 g. of white solid. The filtrate was concentrated *in vacuo* to a dark brown, oily residue which was crystallized from nitromethane (Norit) to give 1.00 g. more of product, making the total yield 1.65 g. (55%). The combined portions were twice recrystallized from nitromethane (Norit) to give colorless crystals, m.p. 209.5–210.5° dec.

Anal. Calcd. for $C_{15}H_{21}ClN_4O_4S_2$: C, 42.80; H, 5.03; S, 15.23. Found: C, 42.75; H, 5.04; S, 15.35.

The infrared spectrum of this substance was identical with that of Vg.

5,8-Dihydro-5,8-methano-1,4-naphthalenedimethanesulfonamide (VII).—Cyclopentadiene (20 ml.) was added to a warm solution of 52.4 g. (0.200 mole) of *p*-quinonedimethanesulfonimide[8] and 1.7 ml. of triethylamine in 3 l. of chloroform. A dark brown color formed immediately, and the solution boiled spontaneously. After the reaction mixture had been allowed to stand at room temperature for 63 hr., a white solid had precipitated, and the supernatant liquid exhibited a cherry-red color. The solid was collected on a filter, washed with chloroform, and air-dried. The product (57.5 g., 88%), m.p. 211–212°, did not require further purification.

Anal. Calcd. for $C_{13}H_{16}N_2O_4S_2$: C, 47.54; H, 4.91; N, 8.53. Found: C, 47.79; H, 4.87; N, 8.35.

The infrared spectrum showed the presence of the –NH– linkage (3245 cm.$^{-1}$).

5,8-Dihydro-5,8-methano-1,4-naphthoquinonedimethanesulfonimide.—Lead tetraacetate oxidation of VII gave the diimide in 88% yield as a red solid, crystallizing from nitromethane as red crystals which decomposed without melting at 208°.

Anal. Calcd. for $C_{13}H_{14}N_2O_4S_2$: C, 47.84; H, 4.32; S, 19.65. Found: C, 47.83; H, 4.22; S, 19.65.

1,4,4a,5,8,9a-Hexahydro-1,4:5,8-dimethano-9,10-anthraquinonedimethanesulfonimide (VIII).—Cyclopentadiene (7 ml.) was added to a stirred suspension of 12.0 g. (0.0368 mole) of 5,8-dihydro-5,8-methano-1,4-naphthoquinonedimethanesulfonimide in 300 ml. of chloroform at room temperature. The color changed from dark red to light yellow over a period of about 2 min. The chloroform and excess cyclopentadiene were then removed by evaporation *in vacuo*, leaving 14.4 g. (100%) of product as a light yellow solid, which was twice recrystallized from ethanol to give light yellow crystals, m.p. *ca.* 182° dec.

Anal. Calcd. for $C_{18}H_{20}N_2O_4S_2$: C, 55.08; H, 5.14; S, 16.34. Found: C, 55.19; H, 5.16; S, 15.90.

1,4,5,8-Tetrahydro-1,4:5,8-dimethano-9,10-anthracenedimethanesulfonamide (IX). A.—Triethylamine (6 drops) was added to a boiling solution of 7.00 g. (0.0178 mole) of VIII in 100 ml. of chloroform. The solution was boiled under reflux for 32 hr., and upon cooling yielded 4.38 g. (63%) of light tan solid. Recrystallization from dimethylformamide gave a white solid which decomposed without melting from 300 to 320°.

Anal. Calcd. for $C_{18}H_{20}N_2O_4S_2$: C, 55.08; H, 5.14; S, 16.34. Found: C, 54.89; H, 5.20; S, 15.9.

The infrared spectrum showed the presence of the –NH– linkage (3240 cm.$^{-1}$).

B.—Cyclopentadiene (1.1 g., 0.017 mole) was added to a solution of 5.0 g. (0.016 mole) of 5,8-dihydro-5,8-methano-1,4-naphthoquinonedimethanesulfonimide and 6 drops of triethylamine in 200 ml. of chloroform with stirring. The solution was allowed to stand at room temperature for 20 min. during which time the color changed from red to yellow. The solution was then concentrated to yield 4.5 g. (72%) of tan crystals. Recrystallization from nitromethane gave a light tan solid which decomposed above 300°.

The infrared spectrum of this substance and that of the product prepared by procedure A were identical.

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(9) Attempts to isolate the simple adduct (IVf) resulted in reversal of the Diels–Alder reaction to give the red 2-cyclohexylthio-*p*-quinonedimethanesulfonimide and cyclopentadiene.