N-Sulfonyl-*N'*-(2,4-dinitrophenyl)-*p*-benzoquinonediimines

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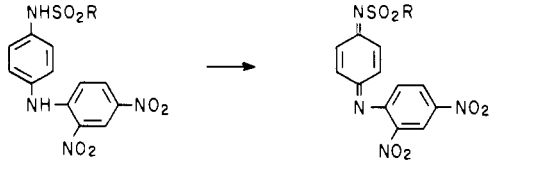
_N_-Sulfonyl-_N'_-(2,4-dinitrophenyl)-_p_-benzoquinonediimines were synthesized by the lead tetraacetate oxidation of the corresponding _N_-sulfonyl-_N'_-(2,4-dinitrophenyl)-_p_-phenylenediamines. Hydrogen chloride was shown to undergo 1,4-addition to the diimines, giving two isomeric adducts.

BENZOQUINONEDIIMINES, whose nitrogen atoms are substituted with electron-withdrawing groups such as sulfonyl, carbonyl (*1*), or thionophosphoryl (*2*), display stabilities comparable with the parent benzoquinones. In a search for fungicidally active quinonoid compounds, the 2,4-dinitrophenyl group was selected as another example of an electron-withdrawing group for placement on the quinoneimine nitrogen.

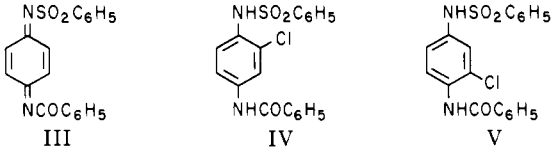
Synthesis of the benzoquinonediimines (II) was accomplished by the lead tetraacetate oxidation of the corresponding *p*-phenylenediamines (I) in glacial acetic acid. The *p*-phenylenediamines and benzoquinonediimines (all new) are described in Table I.



Ia, R = CH_3
b, R = *p*-$CH_3C_6H_4$
c, R = *p*-BrC_6H_4
d, R = 3,4-diClC_6H_3

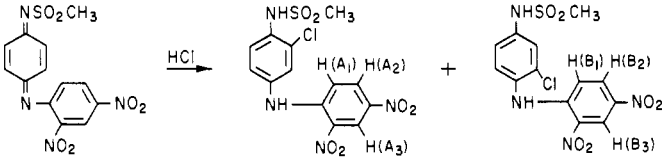
IIa, R = CH_3
b, R = *p*-$CH_3C_6H_4$
c, R = *p*-BrC_6H_4
d, R = 3,4-diClC_6H_3

Adams and Colgrove have shown (*3*) that the addition of hydrogen chloride to *N*-benzenesulfonyl-*N'*-benzoyl-*p*-benzoquinonediimine (III) results in a single monochloro adduct (IV) and not the other isomer (V). The authors



III IV V

attributed the selectivity of the addition to the difference in electron-withdrawing abilities of the two nitrogen substituents. The difference in electron-withdrawing abilities of the 2,4-dinitrophenyl group and the methylsulfonyl group in IIa might reasonably influence selective 1,4-addition of

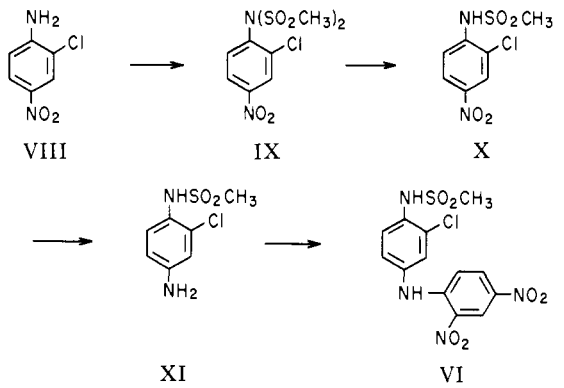


IIa VI VII

hydrogen chloride. Such was not the case, however, and two isomers were obtained in approximately equal amounts: yellow crystals, m.p. 202–4° C. (VI) and orange crystals, m.p. 202–5° C. (VII). The NMR spectra of the two isomers appeared to be similar, with the aromatic proton spectra resolvable into two ABC patterns corresponding to 1,2,4-placements of ring protons in each pattern. The spectra differ most in the position of $H_{(A_1)}$ and $H_{(B_1)}$. Protons A_2 and B_2 both appear as two doublets at −8.25δ; protons A_3 and B_3 show a doublet at −8.93δ. However, $H_{(B_1)}$ appears at −6.83δ, considerably upfield from $H_{(A_1)}$ at −7.23δ; the unexpectedly high shielding of $H_{(B_1)}$ most likely arises from the steric interaction of the chlorine atom in the orientation of the two rings. Assignment of structures was accomplished by unequivocal synthesis of 2,4-dinitro-3'-chloro-4'-methanesulfonamidodiphenylamine (VI) from 2-chloro-4-nitroaniline (VIII). Reaction of VIII with 1 mole of methanesulfonyl chloride in pyridine gave a mixture of 2-chloro-4-nitro-*N*,*N*-bis(methylsulfonyl)aniline (IX) and 2-chloro-4-nitromethanesulfonanilide (X). Hence, it was more convenient to convert VIII to IX completely and to prepare X by ethanolysis of IX. Hydrogenation then

Table I. Data on Diamines and Diimines

Cmpd.	Yield, %	Recryst. Solvent	M.P., °C.	Formula	% C Calcd.	% C Found	% H Calcd.	% H Found	% N Calcd.	% N Found
			N-SULFONYL-*N'*-(2,4-DINITROPHENYL)-*p*-PHENYLENEDIAMINES							
I,a	57	Acetonitrile	210–12.5	$C_{13}H_{12}N_4O_6S$	44.31	44.99	3.43	3.50	15.90	15.7
I,b	47	Nitromethane	253–5	$C_{19}H_{16}N_4O_6S$	53.26	53.06	3.77	3.65	13.08	13.0
I,c	53	Nitromethane	199–201	$C_{18}H_{13}BrN_4O_6S$	43.82	43.85	2.66	2.70	11.36	10.9
I,d	57	(1) Benzene (2) Ethanol	162–3.5	$C_{18}H_{12}Cl_2N_4O_6S$	44.73	44.84	2.50	2.34	11.59	11.41
			N-SULFONYL-*N'*-(2,4-DINITROPHENYL)-*p*-BENZOQUINONEDIIMINES							
II,a	57	Acetonitrile	202.5–3.5 (Orange-brown)	$C_{13}H_{10}N_4O_6S$	44.57	44.74	2.88	3.00	15.99	15.9
II,b	68	Methyl ethyl ketone	190–1 (Orange)	$C_{19}H_{14}N_4O_6S$	53.52	53.65	3.31	3.05	13.14	12.98
II,c	69	Acetonitrile	168–170 (Red-brown)	$C_{18}H_{11}BrN_4O_6S$	44.00	44.04	2.26	2.51	11.41	11.22
II,d	65	Nitromethane	183–4.5 (Orange)	$C_{18}H_{10}Cl_2N_4O_6S$	44.92	44.77	2.09	1.94	11.64	11.69



afforded 4-amino-2-chloromethanesulfonanilide (XI), which, when heated neat with 2,4-dinitrochlorobenzene, gave the 2,4 - dinitro - 3'- chloro - 4'- methanesulfonamidodiphenylamine (VI), which proved to be identical to the yellow isomer.

EXPERIMENTAL

***p*-Phenylenediamines (I).** The arene (or alkane)sulfonyl chloride (0.102 mole) was added dropwise to a stirred solution of 27.4 grams (0.100 mole) of 2,4-dinitro-4'-aminodiphenylamine in 200 ml. of pyridine, keeping the temperature below 10° C. When addition was complete, the reaction mixture was allowed to come to room temperature and was then poured into ice water. The crude product, which formed first as an oil and then solidified, was collected on a filter, air dried, and purified by recrystallization from the appropriate, polar solvent.

***p*-Benzoquinonediimines (II).** Lead tetraacetate (53.2 grams, 0.120 mole) was added to a suspension of 0.100 mole of the *p*-phenylenediamine (I) in 500 ml. of glacial acetic acid, and the mixture was stirred at room temperature for 1 hour and at 90° C. for an additional hour. After the mixture had been cooled again to room temperature, 8 ml. of ethylene glycol was added to destroy excess lead tetraacetate, and stirring was continued for 30 minutes. The reaction mixture was then poured into ice water, and the resulting precipitate was collected on a filter, dried, and recrystallized from the appropriate solvent.

2,4-Dinitro-3'(and 2')-chloro-4'-methanesulfonamidodiphenylamine (VI and VII). Hydrogen chloride was passed through a solution of 10.0 grams (0.0285 mole) of *N*-(2,4-dinitrophenyl) - *N'*- methylsulfonyl - *p* - benzoquinonediimine (IIa) in 600 ml. of methylene chloride for 0.5 hour. The solution changed from dark red to dark yellow during the first few minutes. After it had remained at room temperature for 3 hours, the solution was evaporated to dryness in vacuo to obtain a light orange, crystalline substance, which was stirred with methanol at room temperature. The insoluble, yellow isomer was collected on a filter in 25% yield. Evaporation of the solvent from the filtrate afforded the orange isomer in 18% yield. Recrystallization of the yellow isomer from acetonitrile gave yellow, fluffy crystals, m.p. 202–4° C. Anal. Calcd. for $C_{13}H_{11}ClN_4O_6S$: C, 40.37; H, 2.87; N, 14.49. Found: C, 40.40; H, 2.80; N, 14.3.

Recrystallization of the orange isomer from ethanol gave bright orange crystals, m.p. 202–5° C. Anal. Calcd. for $C_{13}H_{11}ClN_4O_6S$: C, 40.37; H, 2.87; N, 14.49. Found: C, 40.33; H, 2.86; N, 14.35. A mixture of the yellow and the orange crystals showed a melting point depression of 25° C.

2-Chloro-4-nitro-*N*,*N*-bis(methylsulfonyl)aniline (IX). Prepared from methanesulfonyl chloride and 2-chloro-4-nitroaniline. Colorless crystals, m.p. 164–6° C. Anal. Calcd. for $C_8H_9ClN_2O_6S_2$: C, 29.23; H, 2.76; N, 8.52. Found: C, 29.51; H, 2.69; N, 8.28.

2-Chloro-4-nitromethanesulfonanilide (*4*) (X). A solution of 27.3 grams (0.0830 mole) of 2-chloro-4-nitro-*N*,*N*-bis(methylsulfonyl)aniline (IX) in 200 ml. of absolute ethanol was added to an ethanolic solution of sodium ethoxide, prepared from 2.0 grams of sodium and 200 ml. of absolute ethanol. The reaction mixture was heated under reflux for 1 hour and cooled. Water (400 ml.) was then added, and the solution was acidified with concentrated hydrochloric acid. The cream-colored precipitate was collected on a filter, dried, and recrystallized from benzene to give pale yellow crystals, m.p. 156.5–8.5° C. (Lit. m.p. 159–61° C.). Anal. Calcd. for $C_7H_7ClN_2O_4S$: C, 33.54; H, 2.82; N, 11.18. Found: C, 33.88; H, 2.67; N, 11.15.

4-Amino-2-chloromethanesulfonanilide (XI). Prepared by catalytic (Adams' catalyst) reduction of 2-chloro-4-nitromethanesulfonanilide (X). Colorless crystals, m.p. 173.5–5.5° C. Anal. Calcd. for $C_7H_9ClN_2O_2S$: C, 38.09; H, 4.11; N, 12.70. Found: C, 38.26; H, 4.11; N, 12.7.

2,4- Dinitro-3'-chloro-4'-methanesulfonamidodiphenylamine (VI). A well-mixed combination of 2.2 grams (0.010 mole) of 4-amino-2-chloromethanesulfonanilide (XI) and 1.0 gram (0.0050 mole) of 2,4-dinitrochlorobenzene was heated with stirring on a hot plate for 5 minutes. The resulting melt was cooled, pulverized, washed with methanol, and collected on a filter. The crude substance was twice recrystallized from acetonitrile to give yellow crystals, m.p. 200–2° C. Anal. Calcd. for $C_{13}H_{11}ClN_4O_6S$: C, 40.37; H, 2.87; N, 14.49. Found: C, 40.34; H, 2.80; N, 14.7.

A mixture of this substance and the yellow isomer (VI) obtained in the addition of hydrogen chloride to *N*-(2,4-dinitrophenyl) - *N'* - methylsulfonyl - *p* - benzoquinonediimine (IIa) showed no melting point depression. The NMR and infrared spectra of this substance and that of the yellow isomer (VI) were identical. The NMR spectra were obtained in a Varian A-60 instrument with values reported in parts per million shift from tetramethylsilane; the spectra were obtained in acetone-dimethylsulfoxide solution. All melting points are uncorrected.

ACKNOWLEDGMENT

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LITERATURE CITED

(1) Adams, R., Reifschneider, W., *Bull. Soc. Chim. France* **1958**, p. 23.
(2) Dunbar, J.E. (to The Dow Chemical Co.), U. S. Patent **2,907,775** (Oct. 6, 1959).
(3) Adams, R., Colgrove, R.S., *J. Am. Chem. Soc.* **76**, 3584 (1954).
(4) Epstein, P.F., Dewald, C.L. (to Stauffer Chemical Co.), French Patent **1,315,371** (Jan. 18, 1963).

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