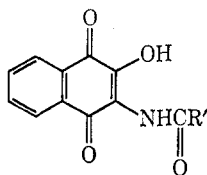


TABLE II
2-ACYLAMIDO-3-HYDROXY-1,4-NAPHTHOQUINONES



Registry no.	R'	Yield, %	Mp, °C	Formula	Anal., %						Uv absorption					
					Calcd			Found			pH 1		pH 11		Ethanol	
					C	H	N	C	H	N	λ_{max} , m μ	$\epsilon \times 10^{-3}$	λ_{max} , m μ	$\epsilon \times 10^{-3}$	λ_{max} , m μ	$\epsilon \times 10^{-3}$
22157-98-8	CH ₃	72 ^a	220-223	C ₁₃ H ₉ NO ₄	62.34	3.92	6.06	62.10	3.67	5.84	250	17.1	267	20.8	270	20.6
22188-53-0	CH ₂ (CH ₂) ₅	47 ^b	133-134	C ₁₇ H ₁₃ NO ₄	67.76	6.36	4.65	67.57	6.35	4.65	250	17.1	267	20.8	270	20.6
22157-99-9	CH ₂ (CH ₂) ₁₀	42 ^b	127-128	C ₂₂ H ₂₃ NO ₄	71.13	7.87	3.77	71.32	7.86	3.64	251	17.8	282	14.2	273	22.6
22158-00-5	CH ₃ (CH ₂) ₁₁	51 ^b	124-125	C ₂₃ H ₂₁ NO ₄	71.66	8.11	3.63	71.72	8.33	3.59	283	12.3	269	24.4	270	21.9
											304	20.4	268	23.4	270	21.9
											304	18.8	269	18.8	270	19.3

^a Prepared by procedure B (see Experimental Section). ^b Prepared by procedure A (see Experimental Section).

Procedure B.—A mixture of 10 g of II, 100 ml of glacial acetic acid, 25 ml of acetic anhydride, and 0.1 g of platinum oxide was hydrogenated at 4.2 kg/cm². After 2 hr, *ca.* 4 equiv of hydrogen were absorbed. The reaction mixture was then filtered and the filtrate was evaporated *in vacuo* at 30° to yield an off-white residue. This was dissolved in 100 ml of 2 *N* potassium hydroxide at room temperature and the red-brown solution was filtered after being stirred for 2 hr. Acidification of the filtrate with dilute hydrochloric acid yielded the desired product, which was isolated by filtration. The product IV (R' = CH₃) was usually of analytical quality and, in any event, was generally suitable for use in the following preparations without further purification.

General Preparation of 2-Alkylamino-3-hydroxy-1,4-naphthoquinones (I).—The acylamido compound (*ca.* 0.015 mol), dissolved in 125 ml of dry tetrahydrofuran, was added, at room temperature during 30 min, with stirring and under dry nitrogen, to a large excess (*ca.* 0.1 mol) of lithium aluminum hydride in 200 ml of dry tetrahydrofuran. The gray-green reaction mixture was then refluxed with stirring for 10 hr. The resulting mixture was chilled to about 5° and slowly hydrolyzed by the dropwise addition of 15 ml of water followed by 100 ml of 10% sulfuric acid. The bulk of the tetrahydrofuran was evaporated and the resulting intermediate was oxidized by passing a stream of air over the stirred solution, which rapidly turned purple. About 100 ml of water was added and the remaining tetrahydrofuran was removed *in vacuo*. The resulting solid and aqueous phases were extracted with ether. Better yields may be obtained by continuous extraction of the aqueous phase. The ether extracts were combined, dried over anhydrous sodium sulfate, filtered, and evaporated to dryness. Products of analytical purity are obtained by recrystallization from 95% ethanol.

2-Hydroxy-3-amino-1,4-naphthoquinone (VI). Procedure A.—A solution of 10.95 g (0.05 mol) of 2-hydroxy-3-nitro-1,4-naphthoquinone (II) in 200 ml of methanol was subjected to hydrogenation in a Parr shaker at 4.2 kg/cm² using platinum oxide as catalyst. *Ca.* 4 equiv of hydrogen were taken up within 30 min. (Color changes are indicated in procedure A of the general preparation for compounds IV.) On exposure to air, the colorless solution immediately turned purple as the intermediate was oxidized. The reaction mixture was warmed gently on the steam bath and filtered. The filtrate was concentrated to *ca.* one-half volume by evaporation under a stream of air while warming on a steam bath. After the filtrate had stood overnight at room temperature, dark red crystals were deposited. The crystals were collected by filtration and dried at 25° (0.1 mm) for 18 hr to yield 5.0 g (53%) of product, mp 242-245° dec.

Procedure B.—A solution of 10 g of sodium hydrosulfite in 100 ml of water was added to 3 g of 2-hydroxy-3-nitro-1,4-naphthoquinone (II) in 50 ml of ethanol at 50°. The reaction mixture was warmed for 15 min on the steam bath, whereupon some crystals began to separate. When the mixture was cooled and exposed to air, additional product separated. The product was collected by filtration and dried at reduced pressure to give 2.0 g (77%); mp 242-244° dec (lit. mp 130-140° dec;¹¹ darkened at 100°⁹); mol wt 189 (mass spectrum, 70 eV).

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The Behavior of Dithio Acids toward Nitro Derivatives of Chlorobenzene¹

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The crystalline thio ethers which are formed by the reaction of 2,4-dinitrochlorobenzene with alkali mercaptide have been used for identification of the latter.³

The present work was attempted to investigate the reaction of *gem*-dithiols with nitro derivatives of chlorobenzene. The dithiols and the nitro derivatives of chlorobenzene used here were di(sodiummercapto)methylene malononitrile (Ia), di(sodiummercapto)methylene methyl cyanoacetate (Ib), di(sodiummercapto)methylene ethyl cyanoacetate (Ic), di(sodiummercapto)methylene cyanoacetamide (Id), *o*- and *p*-nitrochlorobenzene, 2,4-dinitrochlorobenzene, and picryl chloride.

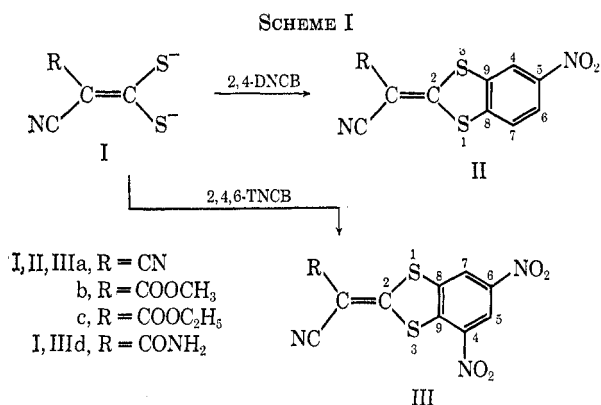
When 2,4-dinitrochlorobenzene (2,4-DNCB) reacted with Ia, Ib, and Ic, 2-dicyanomethylene-5-nitro-1,3-benzodithiole (IIa), 2-acetocarbonylcyanomethylene-5-nitro-1,3-benzodithiole (IIb), and 2-carbethoxycyano-5-nitro-1,3-benzodithiole (IIc), respectively, were obtained. The reaction of picryl chloride (2,4,6-TN-CB) with Ia, Ib, and Ic gave 2-dicyanomethylene-4,6-dinitro-1,3-benzodithiole (IIIa), 2-methoxycarbonylcyanomethylene-4,6-dinitro-1,3-benzodithiole (IIIb),

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(3) R. W. Bost, J. O. Turner, and R. D. Norton, *J. Amer. Chem. Soc.*, **54**, 1985 (1932).

and 2-carbomethoxycyano-4,6-dinitro-1,3-benzodithiole (IIIc), respectively (see Scheme I).



The elemental analysis of these compounds proved that one nitro group was removed in this reaction. This was confirmed also by the nitrite spot test (Liebermann reaction, see Experimental Section). The nitro group in question was considered to be in the 9 position and the 8 position of II and III, respectively. The 5 position of II and the 6 position of III were ruled out (see Scheme I), because they were impossible on the basis of bond angle. If the nitro group is eliminated according to the mode of von Richter rearrangement,⁴ the compound produced may have an unstable spiro form.⁵

The stability of II and III may be due in part to the aromaticity of the concerned hetero ring, which may arise from an electron-withdrawing effect, especially of the cyano group. The uv spectra of II and III were characteristic (see Table I).

TABLE I
ULTRAVIOLET DATA OF COMPOUNDS II AND III

Compd	$\lambda_{\text{max}}^{99\% \text{ ethanol}^1}$, m μ (log ϵ)
IIa	263.5 (3.95), 315 (sh, 3.60), 359 (sh, 4.10), 364 (4.21)
IIb	263.5 (3.97), 315 (sh, 3.76), 359 (sh, 4.18), 364 (4.19)
IIc	263.5 (3.93), 315 (3.72), 359 (sh, 4.16), 364.5 (4.20)
IIIa	253.5 (4.08), 292 (sh, 4.03), 314 (sh, 4.20), 325 (4.28), 334 (sh, 4.25), 408 (3.97)
IIIb	246 (4.03), 291 (sh, 3.96), 313.5 (sh, 4.08), 326 (4.10), 336 (4.10), 398 (3.96)
IIIc	250 (4.00), 292.5 (sh, 3.94), 313 (sh, 4.05), 326 (4.16), 336.5 (4.16), 398 (3.96)
IIId	255 (4.08), 292 (sh, 4.04), 314 (sh, 4.20), 324.5 (4.27), 333 (sh 4.24), 407 (4.00)

When di(sodiummercapto)methylene cyanoacetamide (Id) reacted with picryl chloride, 2-carbamoylcyno-4,6-dinitro-1,3-benzodithiole (IIId) was produced. Unlike picryl chloride, 2,4-DNCB did not afford the derivatives of type II; instead, 2,2',4,4'-tetranirodiphenyl sulfide and 2,4-bis(carbamoylcyanomethylene)-1,3-dithiacyclobutane (VI, a desaurine) were isolated in a 1:0.5 mol ratio. From elemental analysis, ir, and nmr, the above sulfide was assigned the structure 2,2',-

4,4'-tetranirodiphenyl sulfide. The structure of VI was determined in a similar way. The ir of VI showed a characteristic absorption of 1395 cm⁻¹.⁶ Furthermore, ir spectra of the desaurine (VI) coincided with those of the compound which was prepared from Id by Gompper's method.⁷

TABLE II
CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR COMPOUNDS II AND III^a

Compd	Temp, °C	δ Values in (CD ₃) ₂ SO
IIa	25	9.17 (m, 1, C-4 H), 8.55 (d, 2, C-6 and C-7 H, $J = 2$ cps)
IIb	100	9.20 (s, 1, C-4 H), 8.50 (d, 2, C-6 and C-7 H, $J = 2$ cps), 3.90 (s, 3, CH ₃)
IIc	130	8.50 (s, 1, C-4 H), 7.93 (s, 2, C-6 and C-7 H), 4.25 (q, 2, CH ₂ , $J = 7$ cps), 1.20 (t, 3, CH ₃ , $J = 7$ cps)
IIIa	25	9.30 (d, 1, C-5 H, $J = 2$ cps), 8.90 (d, 1, C-7 H, $J = 2$ cps)
IIIb	110	9.35 (d, 1, C-5 H, $J = 2$ cps), 8.98 (d, 1, C-7 H, $J = 2$ cps), 3.90 (s, 3, CH ₃)
IIIc	101	9.40 (d, 1, C-7 H, $J = 2$ cps), 9.02 (d, 1, C-5 H, $J = 2$ cps), 4.43 (q, 2, CH ₂ , $J = 6$ cps), 1.39 (t, 3, CH ₃ , $J = 6$ cps)
IIId	82	8.85 (d, 1, C-7 H, $J = 2$ cps), 8.58 (d, 1, C-5 H, $J = 2$ cps), 7.20 (br, 2, NH ₂)

^a Recorded on a JNM-C-60 high-resolution nmr spectrometer operating at 60 Mcps.

The reaction mechanism of the formation of VI may be elucidated by assuming an activated complex V⁸ (see Scheme II). The nmr spectrum of II showed peaks at δ 8.50–9.17 (one proton, C-4) and 7.93–8.55 (two protons, C-6 and C-7) (see Table II). It may be considered, from the nmr data, that the (S)₂C=C(CN)R group has a large electron-withdrawing effect on the benzene ring. In other words, R and cyano groups may have a large effect on sulfur atoms of the *gem*-dithiol. The estimated reaction speeds of III were 50–60 min, 20–30 min, and 10–20 min, respectively, when the R groups were cyano, ester, and amide (see Experimental Section).

The reaction of ethyl cyanoacetate with carbon disulfide in concentrated NH₄OH solution (28%) occurred only when the mixture was stirred at room temperature to give di(ammoniomercapto)methylene cyanoacetamide. However, the reaction of cyanoacetamide with carbon disulfide in concentrated NH₄OH solution could be made to occur by refluxing the mixture at 60–70° to give the same product.⁹

These experiments support the conclusion that electron density on sulfur atoms of the *gem*-dithiol I is in the order CONH₂ > COOR > CN (reversed order of electron-withdrawing effect).

When Id reacts with 2,4-DNCB, an activated complex (IV) is chiefly in the conformation in which the negatively charged sulfur atom is far away from the *ortho* nitro group owing to electrostatic repulsion.

On the other hand, when Id reacts with picryl chloride, IV easily transfers to a stable compound (IIId) which resulted from removal of one of two *ortho* nitro groups.

(4) V. von Richter, *Ber.*, **8**, 1418 (1875).

(5) R. J. Pollit and B. C. Saunders, *J. Chem. Soc.*, 1132 (1964); a compound which is similar to the O isolog of activated complex V was reported to have been isolated but unstable.

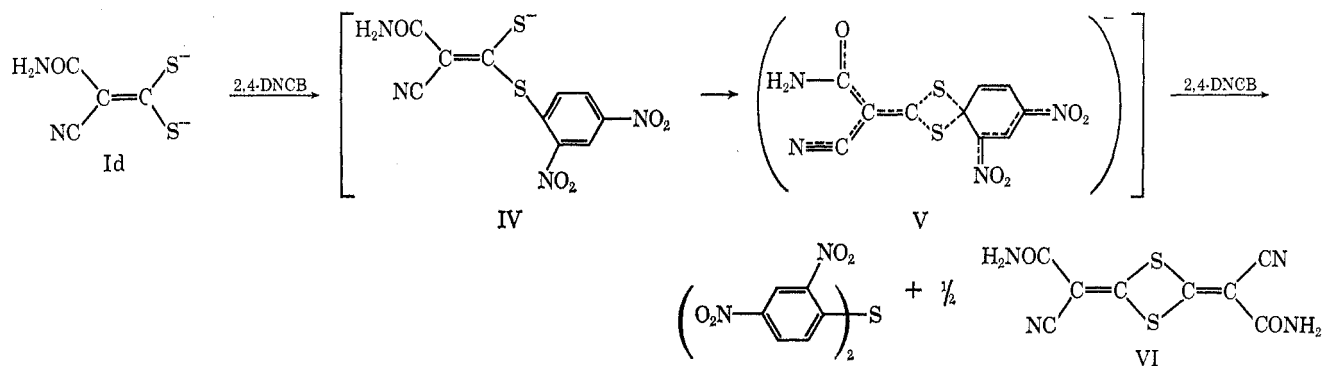
(6) P. Yates and D. R. Moore, *J. Amer. Chem. Soc.*, **20**, 5577 (1958).

(7) R. Gompper and W. Töpfel, *Chem. Ber.*, 2861 (1962).

(8) R. Seltzer, *J. Org. Chem.*, **33**, 3900 (1968).

(9) Details concerning the reaction will be reported in a separate paper.

SCHEME II



o-Nitrochlorobenzene and *p*-nitrochlorobenzene did not react with I either under the same reaction conditions or under reflux for *ca.* 20 hr.

Experimental Section

Preparation of Ia, Ib, Ic, and Id.—Ia, Ib, and Ic were prepared by Söderback's method.¹⁰ Compound Ia [$\text{Na}_2\text{S}_2\text{C}_2(\text{CN})_2 \cdot 3\text{H}_2\text{O}$, light yellow plates] was prepared by the reaction of malononitrile, carbon disulfide, and sodium ethoxide. Compound Ib [$\text{Na}_2\text{S}_2\text{C}_2(\text{CN})\text{COOCH}_3 \cdot 2\text{H}_2\text{O}$, yellow needles] was prepared from methyl cyanoacetate, carbon disulfide, and sodium ethoxide. Compound Ic [$\text{Na}_2\text{S}_2\text{C}_2(\text{CN})\text{COOC}_2\text{H}_5 \cdot 5\text{H}_2\text{O}$, light yellow needles] was prepared from ethyl cyanoacetate, carbon disulfide, and sodium ethoxide.

A mixture of ethyl cyanoacetate (120 g, *ca.* 1 mol), carbon disulfide (161 g, 2.1 mol), and aqueous ammonia (360 ml, 28%) was stirred at 25° for *ca.* 8 hr. The light yellow, solid product was collected, washed with ether, and dried. When the crude product was recrystallized from acetone-water, 82.5 g of light yellow plates [Id, $(\text{NH}_4)_2\text{S}_2\text{C}_2(\text{CN})\text{CONH}_2$] was obtained:⁹ yield *ca.* 40%; mp 145° (in sealed tube).

Preparation of IIa, IIb, and IIc. **Isolation of IIa.**—To a mixture of Ia (8 g, 0.033 mol) and water (100 ml) was added alcoholic 2,4-DNCB solution (7 g of 2,4-DNCB in 100 ml of 99% ethanol) slowly under stirring. The stirring was continued for several additional hours after the addition was complete. The reaction mixture was refluxed for 1.5 hr, and the solid product was collected and washed with water and ether. Recrystallization from pyridine yielded light yellow needles (IIa, *ca.* 7 g): yield 80%; mp 284–285°; ir (KBr) 3040 (m, aromatic CH), 2200 (s, conjugated CN), 1600 (s, conjugated C=C), 1570 (w, benzene ring), 1543 (vs, asymmetric NO_2), 1495 (m, benzene ring), and 1335 cm^{-1} (s, symmetric NO_2).

Anal. Calcd for $\text{C}_{10}\text{H}_8\text{N}_4\text{S}_2\text{O}_4$: C, 45.97; H, 1.15; N, 16.09; S, 24.52; mol wt, 261. Found: C, 45.88; H, 1.33; N, 16.09; S, 24.69; mol wt, 255 (vapor pressure osmometer, in acetone).

Isolation of IIb.—Alcoholic 2,4-DNCB solution (20 g of 2,4-DNCB in 60 ml of ethanol) was added to the mixture of Ib (24 g, 0.099 mol), ethanol (40 ml), and water (100 ml). The same method as that used in the preparation of IIa was applied. The crude product was recrystallized from pyridine to give light yellow needles (IIb, 24 g): yield 87%; mp 295–296°; ir (KBr) 3085 (s, aromatic CH), 2950 (w, CH_3), 2200 (s, conjugated CN), 1680 (vs, conjugated CO), 1595 (m, conjugated C=C), 1570 (m, benzene ring), 1525 (vs, asymmetric NO_2), 1495 (vs, benzene ring), and 1353 cm^{-1} (s, symmetric NO_2).

Anal. Calcd for $\text{C}_{11}\text{H}_8\text{N}_4\text{S}_2\text{O}_4$: C, 44.89; H, 2.04; N, 9.52; S, 21.77; mol wt, 294. Found: C, 44.50; H, 1.99; N, 9.50; S, 21.65; mol wt, 290.5 (vapor-pressure osmometer, in acetone).

Isolation of IIc.—Compound IIc was prepared by the same method as above from Ic (8 g, 0.025 mol) water (100 ml), and alcoholic 2,4-DNCB solution (100 ml). Recrystallization from pyridine yielded light needles (IIc, 6 g): yield 78%; mp 254–255°; ir (KBr) 3080 (s, aromatic CH), 2200 (s, conjugated CN), 1680 (vs, conjugated CO), 1600 (m, conjugated C=C), 1580 (m, benzene ring), 1537 (s, asymmetric NO_2), 1497 (s, benzene ring), and 1353 cm^{-1} (s, symmetric NO_2).

Anal. Calcd for $\text{C}_{12}\text{H}_8\text{N}_4\text{S}_2\text{O}_4$: C, 46.76; H, 2.62; N, 9.09; S, 20.80; mol wt, 308.20. Found: C, 46.72; H, 2.66; N, 9.24; S, 20.68; mol wt, 305 (vapor pressure osmometer, Rast method).

Compounds IIa, IIb, and IIc were easily soluble in pyridine and dimethyl sulfoxide, and scarcely soluble in acetone and alcohol.

Preparation of IIIa, IIIb, IIIc, and IIId. **Isolation of IIIa.**—To the mixture of Ia (8 g, 0.033 mol) and water (100 ml) was added alcoholic 2,4,6-TNCB solution (2,4,6-TNCB, 14 g) slowly under stirring. After the mixture was stirred for 2 hr, a brown product was filtered and recrystallized from pyridine yielded 10 g of orange prisms (IIIa): yield 98%; mp 279–280°; ir (KBr) 3080 (s, aromatic CH), 2200 (s, conjugated CN), 1600 (m, conjugated C=C), 1585 (m, benzene ring), 1530 (s, asymmetric NO_2), 1470 (s, benzene ring), and 1343 cm^{-1} (vs, symmetric NO_2).

Anal. Calcd for $\text{C}_{10}\text{H}_2\text{N}_4\text{S}_2\text{O}_4$: C, 39.21; H, 0.65; N, 18.30; S, 20.93; mol wt, 306. Found: C, 39.00; H, 0.70; N, 18.55; S, 20.68; mol wt, 295 (vapor pressure osmometer, in acetone).

Isolation of IIIb.—Compound IIIb was prepared in the same method as above from Ib (6 g, 0.024 mol) and 2,4,6-TNCB (8 g, 0.035 mol). The crude yellow product was collected after the solution was stirred for 30 min and recrystallized from pyridine to give 8 g of yellow needles (IIIb): yield 98%; mp 265–266°; ir (KBr) 3080 (s, aromatic CH), 2950 (m, CH_3), 2200 (s, conjugated CN), 1700 (vs, conjugated CO), 1600 (m, conjugated C=C), 1585 (s, benzene ring), 1530 (vs, asymmetric NO_2), 1495 (s, benzene ring), and 1343 cm^{-1} (vs, symmetric NO_2).

Anal. Calcd for $\text{C}_{11}\text{H}_5\text{N}_4\text{S}_2\text{O}_6$: C, 38.93; H, 1.47; N, 12.39; S, 18.88; mol wt, 339. Found: C, 39.01; H, 1.43; N, 12.45; S, 18.83; mol wt, 328 (vapor pressure osmometer, in acetone).

Isolation of IIIc.—Compound Ic (6 g, 0.018 mol) and 2,4,6-TNCB (5 g, 0.02 mol) was allowed to react for *ca.* 20 min as above. The yellow product was filtered and recrystallized from pyridine to give 6 g of yellow needles (IIIc): yield 95%; mp 247–248°; ir (KBr) 3080 (s, aromatic CH), 2980 (w, CH), 2200 (s, conjugated CN), 1695 (vs, conjugated CO), 1598 (s, conjugated C=C), 1580 (s, benzene ring), 1530 (vs, asymmetric NO_2), 1495 (s, benzene ring), and 1340 cm^{-1} (vs, symmetric NO_2).

Anal. Calcd for $\text{C}_{12}\text{H}_7\text{N}_4\text{S}_2\text{O}_6$: C, 40.79; H, 1.98; N, 11.90; S, 18.13; mol wt, 353. Found: C, 40.59; H, 1.83; N, 11.65; S, 18.03; mol wt, 348 (vapor pressure osmometer, in acetone).

Isolation of IIId.—The solution of Id (5 g, 0.026 mol) and sodium hydroxide (1.1 g) was heated on the water bath until emission of ammonia gas finished out. To this solution was added 2,4,6-TNCB (8 g, 0.035 mol) in the same way as in the isolation of IIIa, IIIb, and IIIc. The stirring was stopped after 10 min. The yellow product was collected and recrystallized from pyridine to give 8 g of yellow needles (IIIId): yield 95%; mp 292–293°; ir (KBr) 3090 (s, aromatic CH), 2200 (s, conjugated CN), 1675 (vs, conjugated CO), 1600 (s, conjugated C=C), 1590 (vs, benzene ring), 1530 (vs, asymmetric NO_2), 1470 (vs, benzene ring), and 1340 cm^{-1} (vs, symmetric NO_2).

Anal. Calcd for $\text{C}_{10}\text{H}_4\text{N}_4\text{S}_2\text{O}_5$: C, 37.03; H, 1.23; N, 17.28; S, 19.75; mol wt, 324. Found: C, 36.99; H, 1.36; N, 17.04; S, 19.51; mol wt, 320 (vapor pressure osmometer, in acetone).

Estimation of the Reaction Speed of IIIa, IIIb, IIIc, and IIId.—Compound I (0.033 mol) was allowed to react with 2,4,6-

(10) E. Söderback, *Acta Chem. Scand.*, **19**, 554 (1965).

TNCB (0.035 mol) in the same method as that used in the above preparation. The stirring continued for 5 hr. The reaction almost went to completion. Then the crude product was filtered, washed with water and ether, and dried. The product was weighed: IIIa, *ca.* 10.0 g; IIIb, *ca.* 11.0 g; IIIc, 11.0 g; IIIId, *ca.* 10.0 g.

Under the above reaction conditions, the finished time of reaction was measured: IIIa, 50–60 min; IIIb, 20–30 min; IIIc, 20–30 min; IIIId, 10–20 min (experimental errors within $\pm 8\%$).

Test of Confirmation for Nitrite Ion.—Phenol (*ca.* 50 mg) and concentrated H_2SO_4 (a few drops) were mixed in a test tube. When the filtrate of the reaction mixture mentioned in the isolation of compounds II and III was added, violet color appeared instantly and disappeared after 30–40 min.

Isolation of VI.—The mixture of Id (5 g, 0.026 mol) and sodium hydroxide (1.1 g) was treated as mentioned in the isolation of IIIId. The reaction mixture was added to 2,4-DNCB (12 g, 0.06 mol) and stirred for 1 hr. The crude product was filtered and dissolved in hot pyridine, and the hot pyridine was filtered. The filtrate was diluted with water until it was turbid, and filtered. Yellow prisms (7.5 g) were obtained: yield 79%; mp 198–199° (lit.⁸ mp 196–198°); ir (KBr) 3110 (s, aromatic CH), 1600 (vs, benzene ring), 1530 (vs, asymmetric NO_2), and 1350 cm^{-1} (vs, symmetric NO_2); nmr (CD_3SOCD_3) δ 8.95 (d, 2, $J = 3$ cps, C-3 and C-3' H), 8.45 (q, 2, $J = 9$ cps, C-5 and C-5' H), and 7.25 (d, 2, $J = 9$ cps, C-6 and C-6' H). Elemental analysis gave the molecular formula $C_{12}H_6N_4SO_3$. From the above analytical results, the compound was assigned the structure 4,4'-tetraniro-diphenyl sulfide.

In addition, the residue from which the above hot pyridine-containing sulfide was filtered was recrystallized from dimethyl sulfoxide to give 3.8 g of colorless prisms: yield 79%; mp $< 300^\circ$; uv mas (99% EtOH) 317.5 $m\mu$ (sh, log ϵ 3.45), 331 (log ϵ 3.95), and 346 (log ϵ 4.08); mass spectrum (75 eV) m/e (rel intensity) 126 (50), its value coincided with one-half of the parent peak; ir (KBr) 3370 (s), 3300 (w), 3250 (w), and 3150 (m), all assigned to the stretching of NH_2 ; 2220 (s, CN), 1680 (s, CO), 1660 (vs, NH_2), 1530 (vs, conjugated $C=C$), and 1395 cm^{-1} (vs, probable ring stretching); nmr (CD_3SOCD_3) δ 8.35 (br, 4, NH_2); the protons were counted by dissolving 1 mol of VI and 1 mol of *p*-bromobenzoic acid in $(CD_3)_2SO$.

Anal. Calcd for $C_8H_4N_4S_2O_2$: C, 38.11; H, 1.60; N, 22.22; S, 25.40; mol wt, 252. Found: C, 37.92; H, 1.77; N, 21.98; S, 25.65; mol wt, 252 (vapor pressure osmometer, mass spectrum).

Registry No.—IIa, 22158-01-6; IIb, 22158-02-7; IIc, 22158-03-8; IIIa, 22158-04-9; IIIb, 22158-05-0; IIIc, 22158-06-1; IIIId, 22158-07-2; VI, 22158-08-3.

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