

Nucleophilic Substitution on Dialkoxy Disulfides. II.¹⁾ Reactions with Hydrazine Derivatives

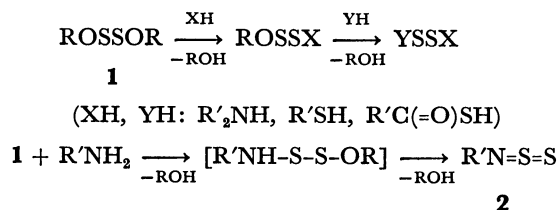
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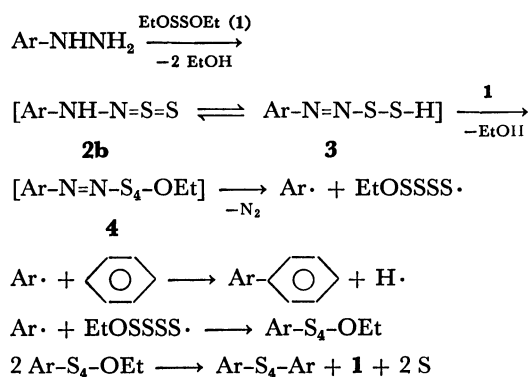
Synopsis. Diethoxy disulfide (**1**) reacted with arylhydrazines to give arylbenzenes, diaryl sulfides, and aryl ethoxy tetrasulfides. The reaction of **1** with hydrazobenzenes gave azobenzenes in quantitative yields. The treatment of **1** with 1,5-diphenylthiocarbonohydrazide or 1,5-diarylthiocarbazones afforded 2,3-diaryltetrazolium-5-thiolates.

Dialkoxy disulfides (**1**) are reactive toward some nucleophilic reagents.^{2,3)} Previously, we have also found that the alkoxyl group of **1** is readily displaced by secondary amines,¹⁾ thiols,¹⁾ or thiocarboxylic acids⁴⁾ to give several unsymmetrical polysulfides. Further, the reaction of primary amines with **1** afforded *N*-thiosulfinylamine (**2a**) by the intramolecular elimination of alcohol (Scheme 1).¹⁾ We have now studied the reaction of **1** with hydrazine derivatives, and found that not only the substitution of the alkoxyl group, but also the elimination of sulfur and nitrogen, takes place.



Scheme 1.

4-Nitrophenylhydrazine was allowed to react with **1** in refluxing benzene. Ethanol was eliminated, and 4-nitrobiphenyl, ethoxy 4-nitrophenyl tetrasulfide, and bis(4-nitrophenyl) disulfide were obtained. The other monosubstituted hydrazines reacted similarly. The results are shown in Table 1. Considering the formation of the thiosulfinyl compound (**2a**) from **1** and primary amines, it seems reasonable to assume that the reaction of **1** with hydrazines proceed *via* a thiosulfinyl intermediate (**2b**) in the following way: arylhydrazines and **1** initially afford **2b**, followed by the transfer of a proton to give an azo intermediate (**3**).



Scheme 2.

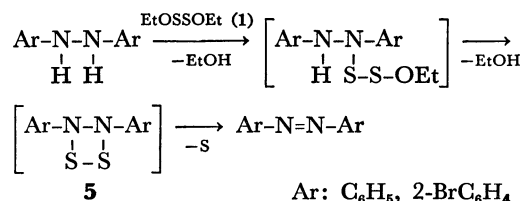
TABLE 1. REACTION OF DIETHOXY DISULFIDE (**1**) WITH MONOSUBSTITUTED HYDRAZINE

Hydrazine (ArNHNH ₂) Ar	Benzene reflux- ing time h	Products Isolated yield/%		
		Ar-C ₆ H ₅	Ar-S ₄ -OEt	Ar-S _x -Ar
4-NO ₂ C ₆ H ₄	10	21	29	13 (x=2) ^{a)}
2-ClC ₆ H ₄	30	27	10	48 (x=4)
4-BrC ₆ H ₄	20	0 ^{b)}	5 ^{b)}	39 (x=4) ^{a)}
C ₆ H ₅	12	8 ^{b)}	0 ^{b)}	37 (x=4)
4-CH ₃ C ₆ H ₄	15	20	0 ^{b)}	31 (x=4)
2-C ₁₀ H ₇	15	5 ^{b)}	0 ^{b)}	47 (x=4)

a) Diaryl tetrasulfides are relatively unstable compounds, and especially careful handling is necessary for bis(4-bromophenyl) tetrasulfide to prevent its thermal decomposition to the disulfide during recrystallization. Presumably, the formation of bis(4-nitrophenyl) disulfide is due to the elimination of sulfur from the tetrasulfide during the operation. b) In these cases, the complete separation of the products by chromatography is extremely difficult. The low yields of the biphenyl and aryl ethoxy tetrasulfide are mainly the result of the loss of these products during the operation.

The azo intermediate (**3**) then replaces the ethoxy group in **1** to give the intermediate arylazo ethoxy tetrasulfide (**4**) (Scheme 2). The formation of the aryl radical by the decomposition of diazonium salts is well known.⁵⁾ Therefore, the intermediate, **4**, presumably decomposes to the aryl radical with the evolution of nitrogen, and the resulting radical reacts immediately with benzene (solvent) or the ethoxy tetrasulfanyl radical to give biphenyl or aryl ethoxy tetrasulfides respectively. Symmetrical diaryl sulfides would be formed by the thermal decomposition of aryl ethoxy tetrasulfides.

On the other hand, hydrazobenzene reacted with **1** to give azobenzene in a quantitative yield, with the elimination of ethanol and sulfur. 2,2'-Dibromohydrazobenzene reacted similarly. It can be assumed that hydrazobenzene reacts with **1** to give a cyclic disulfide (**5**), followed by the elimination of sulfur to form azobenzene (Scheme 3). In these reactions, the sulfur of **1** serves as an oxidizing agent, whereas divalent sulfur compounds such as dialkyl sulfoxylates

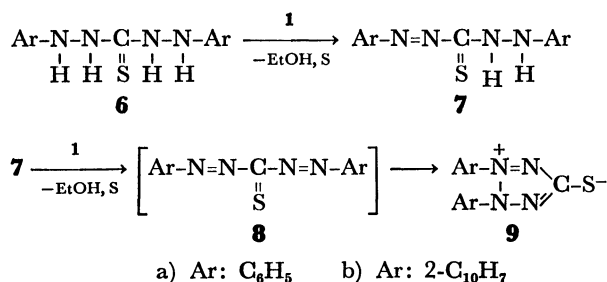
Ar: C₆H₅, 2-BrC₆H₄

Scheme 3.

are known as reducing agents.^{6,7} Such conflicting dual properties of sulfur compounds has aroused interest.

In contrast to hydrazobenzene or phenylhydrazine, 1,1-diphenylhydrazine and **1** gave diphenylamine with ethanol and sulfur. However, the mechanism of the reaction has not yet been elucidated.

A related compound of hydrazine 1,5-diphenylthiocarbonohydrazide (**6a**) reacted with 2 mols of **1** to give 2,3-diphenyltetrazolium-5-thiolate (**9a**).⁸ Similarly, 1,5-diphenylthiocarbazon (**7a**) or 1,5-di-2-naphthylthiocarbazon (**7b**) reacted readily with **1** to give **9a** or 2,3-di-2-naphthyltetrazolium-5-thiolate (**9b**). It is considered that these reactions proceed via azo compounds (**7,8**), much like the formation of azobenzene from hydrazobenzene.



Scheme 4.

Experimental

The IR spectra were measured with a Hitachi 260-10 spectrometer. The NMR spectra were determined in a CDCl₃ solution with a JEOL JNM-PMX-60 spectrometer. The mass spectra were obtained on a Hitachi RMU-7 M at 70 eV. Diethoxy disulfide (**1**)³ and 2,2'-dibromohydrazobenzene⁹ were prepared by the method of the literature.

Reaction of 1 with Arylhydrazine. A solution of arylhydrazine (0.02 mol) and **1** (0.04 mol) in 50 cm³ of benzene was refluxed for 10–30 h. The reaction mixture was then evaporated, and the residue was chromatographed on silica gel, using hexane or benzene–hexane (1:2) as an eluent, to give arylbenzene, aryl ethoxy tetrasulfide, and diaryl sulfide. Ethoxy 4-nitrophenyl tetrasulfide: light yellow liq.; NMR (CDCl₃) δ 1.32 (m, 3H), 3.93 (m, 2H), 7.36–8.40 (aromatic, 4H); MS *m/e* 295 (M⁺). Found: N, 4.80; S, 43.74%. Calcd for C₈H₉NO₃S₄: N, 4.74; S, 43.41%. Bis-(4-nitrophenyl) disulfide, mp 180 °C. Found: C, 46.90; H, 2.68%. Calcd for C₁₂H₈N₂O₄S₂: C, 46.74; H, 2.62%. 2-Chlorophenyl ethoxy tetrasulfide; light yellow liq., NMR (CDCl₃) δ 1.28 (m, 3H), 3.98 (m, 2H), 7.03–8.00 (aromatic, 4H). Found: C, 33.48; H, 2.92%. Calcd for C₈H₉OClS₄: C, 33.73; H, 3.18%. Bis(2-chlorophenyl) tetrasulfide, light yellow liq. Found: C, 41.10; H, 2.50%. Calcd for C₁₂H₈Cl₂S₄: C, 41.02; H, 2.30%. 4-Bromophenyl ethoxy tetrasulfide; light yellow liq., NMR (CDCl₃) δ 1.30 (m, 3H), 3.95 (m, 2H), 7.20–7.67 (aromatic, 4H). Found: C, 28.92; H, 2.52%. Calcd for C₈H₉OBrS₄: C, 29.18; H, 2.75%. Bis(4-bromophenyl) tetrasulfide, light yellow liq. Found: C, 32.95; H, 2.01%. Calcd for C₁₂H₈Br₂S₄: C, 32.74; H, 1.83%. Diphenyl tetrasulfide, light yellow liq. Found: C, 50.88; H, 3.66%. Calcd for C₁₂H₁₀S₄: C, 51.03; H, 3.57%. Ditolyl tetrasulfide, light yellow liq. Found: C, 54.03; H, 4.32%. Calcd for C₁₄H₁₄S₄: C, 54.15; H, 4.55%. Dinaphthyl tetrasulfide, light yellow liq. Found: C, 62.56; H, 3.41%. Calcd for C₂₀H₁₄S₄: C, 62.79; H, 3.69%.

Reaction of 1 with Hydrazobenzene.

A solution of 9.2 g

(0.05 mol) of hydrazobenzene and 7.7 g (0.05 mol) of **1** in 50 cm³ of benzene was refluxed for 20 h. The color of the solution turned red. The reaction mixture was then evaporated, and 60 cm³ of hexane was added. The precipitated sulfur (2.3 g) was filtered off, and the filtrate was evaporated. The residue was chromatographed on silica gel, using hexane as an eluent, to give 9.03 g (99%) of azobenzene (mp 67–68 °C) and 0.2 g of sulfur. A total of 2.5 g (78%) of sulfur was obtained. Similarly, 2,2'-dibromohydrazobenzene (3.42 g, 0.01 mol) and **1** (1.54 g, 0.01 mol) gave 2,2'-dibromoazobenzene (3.35 g, 99%) by column chromatography. 2,2'-Dibromoazobenzene; mp 131–132 °C; reddish orange needles from ethanol. A total of 0.63 g (98%) of sulfur was obtained.

Reaction of 1 with 1,1-Diphenylhydrazine. To a suspension of 2.21 g (0.01 mol) of 1,1-diphenylhydrazine hydrochloride in 30 cm³ of benzene, a solution of 1.51 g (0.01 mol) of triethylamine was added. After that, a solution of 1.54 g (0.01 mol) of **1** in 10 cm³ of benzene was added to the reaction mixture and the mixture was refluxed for 3 h. Triethylamine hydrochloride was then filtered off, and the filtrate was evaporated. The residue was chromatographed on silica gel, using benzene–hexane (1:2) as an eluent, to give 1.36 g (80%) of diphenylamine; mp 52 °C.

Reaction of 1 with 1,5-Diphenylthiocarbonohydrazide (6a). A suspension of 2.58 g (0.01 mol) of **6a** and 3.08 g (0.02 mol) of **1** in 50 cm³ of benzene was refluxed for 3 h. The color of the solution gradually turned reddish brown. Upon cooling to room temperature, a red solid precipitated from the solution. This red solid was collected and was recrystallized from ethanol to give 2.1 g (83%) of **9a** as red needles; mp 180 °C dec (lit.⁹ 180 °C); MS *m/e* 254 (M⁺, 18), 226 (M⁺–N₂, 18), 167 (11), 105 (25), 77 (100); IR (KBr) 1320 cm^{–1} (very strong). Found: C, 61.25; H, 4.01%. Calcd for C₁₃H₁₀N₄S: C, 61.40; H, 3.96%.

Reaction of 1 with 1,5-Diphenylthiocarbazon (7a). A suspension of 2.56 g (0.01 mol) of **7a** and 1.54 g (0.01 mol) of **1** in 50 cm³ of benzene was refluxed for 0.5 h. The color of the suspension immediately turned from dark green to red. A red solid was collected and recrystallized to give 2.38 g (94%) of **9a**. Similarly, 1,5-di-2-naphthylthiocarbazon (**7b**) (1.1 g, 0.003 mol) and **1** (0.48 g, 0.003 mol) gave **9b** (0.8 g, 73%); red prisms from ethanol; mp 167–168 °C dec; MS *m/e* 354 (M⁺, 11), 326 (M⁺–N₂, 18), 267 (15), 131 (18), 127 (100); IR (KBr) 1310 cm^{–1} (very strong). Found: C, 71.33; H, 4.14; N, 15.66%. Calcd for C₂₁H₁₄N₄S: C, 71.16; H, 3.98%; N, 15.81%.

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