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Derivatives of Cyclic Disulfides. III.[1] A New Method of Deoxygenation of Thiolsulfinates and Thiolsulfonates with Inorganic Cyanide

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Synopsis. The reaction of rigid cyclic thiolsulfinates and thiolsulfonates such as 1,2-dithiaacenaphthene *S*-oxide and *S,S*-dioxide with inorganic cyanide afforded the corresponding reduced 1,2-dithiaacenaphthene, but not the open-chain *p*-tolyl benzenethiolsulfonate. This was explained by the proximity effect due to the rigidly confined S–S bond at peri-position of the naphthalene ring.

In the nucleophilic substitution reactions of atomic centers such as carbon, sulfur, and transition metal atoms, cyanide is known to show peculiar behavior as an excellent nucleophile.[3] It sometimes acts as a reducing agent and picks up oxygen, being oxidized to isocyanate despite its poor deoxygenative ability.[4] This was found to be the case in the reaction of 1,2-dithiaacenaphthene *S*-mono and *S,S*-dioxides.

The present investigation was undertaken to clarify the reaction of these disulfide derivatives, *i.e.*, thiolsulfinates, thiolsulfonates, and the related open-chain analogues with cyanide ion.

Results and Discussion

Many studies have been made on the heterolytic S-S bond cleavages of disulfides and their oxygenated derivatives by various types of nucleophiles. The S-S bond in disulfide undergoes facile scission by the action of CN^- to give the thiocyanate and the thiolate, while the thiolsulfonate gives the sulfinate and the thiocyanate.[5]

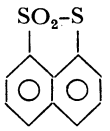
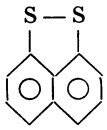
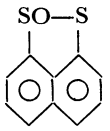
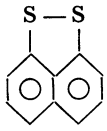
The reaction of *p*-tolyl benzenethiolsulfonate with sodium cyanide gives the products, which are identical with those reported[6] (Table 1). Cyanide ion simply attacks the S-S bond to afford sodium benzenesulfinate and *p*-tolylthiocyanate with no detectable amount of reduction product. On the other hand, a similar treatment of phenyl benzenethiolsulfinate with NaCN in MeOH at room temperature readily affords the transient sulfenate which subsequently reacts with the other partner, *i.e.*, thiocyanate, eventually giving the corresponding disulfide and NaOCN.

$$\mathrm{PhSO\text{-}SPh + CN^- \rightarrow PhSO^- + PhSCN \rightarrow}$$

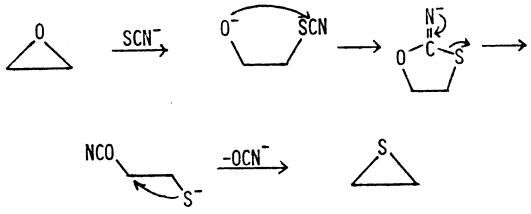
$$\mathrm{PhSO\text{-}C(\overset{\curvearrowright}{S}Ph)(\overset{\curvearrowleft}{\|}N^-) \rightarrow PhSOCN + {}^-SPh \rightarrow PhS\text{-}SPh + OCN^-}$$

In contrast to the reaction of the open-chain *p*-tolyl benzenethiolsulfonate, 1,2-dithiaacenaphthene *S,S*-dioxide yields the reduced 1,2-dithiaacenaphthene when treated with NaCN in MeOH. This finding demonstrates that in the reduction of 1,2-dithiaacenaphthene *S,S*-dioxide the proximity effect due to the rigidly confined two sulfur atoms at peri-position is effectively in operation at the reduction stage where the oxygen atom of the sulfinate moiety and the carbon atom of the thiocyanate group are forced to approach each other sufficiently to react intramolecularly to form the intermediate(I) which upon the elimination of OCN^- gives the reduced disulfide. With regard to the elimination of OCN^- the above deoxygenation resembles the pathway for the formation of thiirane from the corresponding epoxide and SCN^-.[7]

Table 1. Reaction of thiolsulfinates and thiolsulfonates with NaCN[a] in MeOH at room temperature

Substrate	Reaction time	Reduced product	(%)	Other product (%)
	2 days		(48) (72)[c]	NaOCN[b]
	2 days		(83)	NaOCN
PhSO-SPh	0.5 hr	PhSSPh	(74)	NaOCN
$PhSO_2SPh$	1 hr	—		(Tol-S)$_2$ (9), Tol-SCN (24), $PhSO_2Na$ (86)

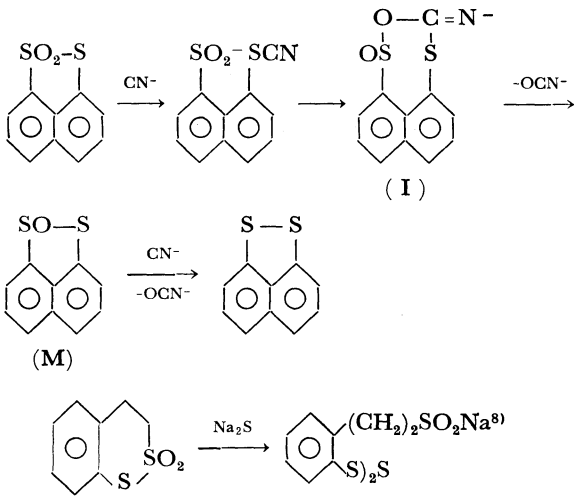
a) 1 equiv. of NaCN. b) Yields were not determined. c) 2 equiv. of NaCN.



The fact that in the course of the reaction a spot due to 1,2-dithiaacenaphthene *S*-monoxide(M) was observed in thin layer chromatography supports the mechanism in which the reaction proceeds through the monoxide as a stable intermediate which in turn can be readily reduced to the corresponding disulfide in a good yield (Table I). The overall reaction pathway is outlined below.

Srivastava and Field reported that the alicyclic thiolsulfonate reacts with Na_2S to afford the trisulfide without giving any reduction product.[8]

However, with the rigidly confined thiolsulfonate even a reduction *via* the initial displacement reaction takes place smoothly, eventually producing the corresponding



disulfide in an 86% yield. This would also show the characteristic aspect of this rigidly confined thiolsulfonate.

Comparing the reaction time for the open-chain compounds with that for the rigid cyclic analogues, we see that the latter is less reactive. This implies that the S-S bond rigidly confined at peri-positions of naphthalene nucleus should be less reactive toward an attack of nucleophile as compared with the open-chain compound. In fact the deoxygenation of 1,2-dithiaacenaphthene oxides by trimethyl phosphite is 100 times slower than that of phenyl benzenethiolsulfinate and the thiolsulfonate.[9]

Experimental

Materials. 1,2-Dithiaacenaphthene *S,S*-dioxide was prepared according to the reported procedure.[10] The monoxide was obtained in good yield either by the sodium metaperiodate oxidation of 1,2-dithiaacenaphthene or the deoxygenation of 1,2-dithiaacenaphthene *S,S*-dioxide with trimethyl phosphite; mp 82.5—83.5 °C.

Deoxygenation of Thiosulfinates and Thiosulfonates. Deoxygenation of 1,2-dithiaacenaphthene *S,S*-dioxide and *S*-monoxide by NaCN was carried out in MeOH at room temperature for 2 days. After the solvent was removed on a rotary evaporator, the preparative tlc using benzene afforded 1,2-dithiaacenaphthene. Identification of NaOCN was made by a comparison of its IR spectrum with that of the authentic sample(2240 cm^{-1}: C N).

References

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