DERIVATIVES OF 1,2-DITHIOLE-3-THIONES. XII.
THE REACTIONS OF 1,2-DITHIOLE-3-THIONE WITH BIS-ARYLSULFONYLDIAZOMETHANE

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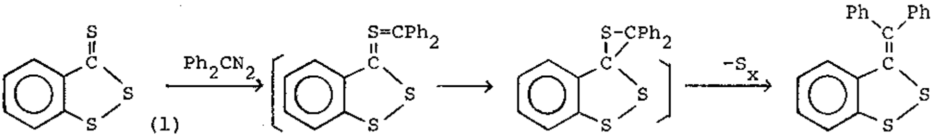
4,5-Benzo-1,2-dithiole-3-thione reacted with bis-sulfonyldiazomethane to give the rearranged products of a new type. The same was found to take place for 1,3-dithiole-2-thione.

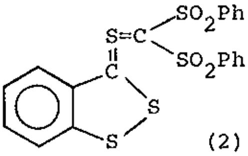
The formation of three-membered thiacycles by the reaction of thiocarbonyl compounds with carbene intermediates has attracted considerable attention.[1] However, the analogous reactions of 1,2-dithiole-3-thiones with diphenyldiazomethane were found to produce the corresponding 1,2-dithiole-3-diphenylmethylene presumably by ring closure to a thiirane ring followed by sulfur extrusion.[2]



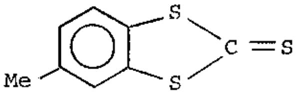
When the phenyl groups about the diazo linkage were substituted by arylsulfonyl groups, a presently unknown type of rearrangement was found to occur. In this communication, we wish to present the results of the reexamination of the reaction between the thiones and bis-sulfonyldiazomethanes.

Earlier, 4,5-benzo-1,2-dithiole-3-thione(1) was reported to react with bis-phenyl- and tolylsulfonyldiazomethane in the presence of a catalytic amount of copper(II) acetylacetonate in refluxing benzene to form adducts(4 and 5) in 78 and 60 % yields, respectively, without accompanying with desulfuration.[3] Similarly, the treatment of benzo-1,3-dithiole-2-thione(3) with bis-phenylsulfonyldiazomethane gave an adduct(6) in 70 % yield. Based on the limited data available at the time the products thus obtained were assumed as having ylide structure like 2 in the case of 1,2-dithiole-3-thione.

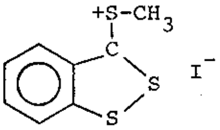
Since then, compounds with ylide structure have been documented to be thermally labile and should undergo either cyclization to give a thiirane or further desulfuration to form a olefin.[4] However, over 90 % of the adduct(4) was recovered unchanged even when treated in refluxing benzene for 3 hr and only a trace amount of a red-colored precipitate(8) was obtained; thus the adduct is quite stable with respect to drastic heating. Furthermore, the spectroscopic behavior of the adduct in the presence of hydrochloric acid was found incompatible with the thiocarbonyl ylide structure(2); such a ylide would normally be protonated on its negatively charged carbon atom and consequently the UV absorption band due to 4 should be shifted toward that of the model compound(7, λ_{max} 412nm, ε 5240 in DMF)[5] but this was not the case and no significant change in the absorption maximum and intensity was observed. These observations mean clearly that the previously advocated assignments are incorrect.



(2)

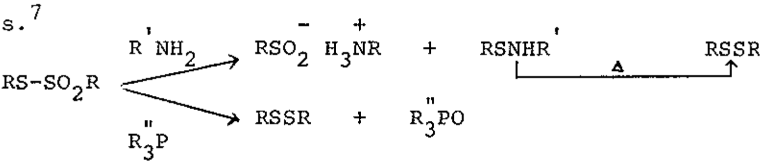


(3)



(7)

In order to shed further light on the structural assignments for these adducts(4, 5, and 6), the reactions with various nucleophiles such as t-$BuNH_2$, phosphines, and OH^- were performed. As the results in Table 1 show, red-colored precipitates are common products throughout the reactions examined here. It is well known that thiolsulfonates react with amines to give sulfinic acids, and sulfenamides or disulfides,[6] and with phosphines to afford disulfides and phosphine oxides.[7]

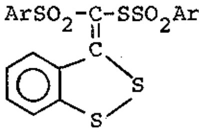


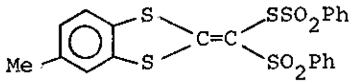
$$RS\text{-}SO_2R \xrightarrow{R'NH_2} RSO_2^- \; H_3\overset{+}{N}R' + RSNHR' \xrightarrow{\Delta} RSSR$$
$$RS\text{-}SO_2R \xrightarrow{R''_3P} RSSR + R''_3PO$$

Meanwhile, there is controversy concerning hydrolysis products; thiolsulfonates are reported to be hydrolyzed by alkali usually to a mixture of the disulfides and sulfinic acids. However, those bearing a relatively electronegative group at the thiol sulfur could be attacked on the sulfonyl sulfur atom especially by small, hard nucleophiles such as OH^- to yield the sulfonic acids.[8]

In fact, the latter is just the case for our compounds.

Accordingly, the chemical behaviors all can best be rationalized by assuming the adducts(4, 5, and 6) containing an $S\text{-}SO_2$ unit in the molecules, and support dimeric 8, 9, and 10 as the structures of red-colored precipitates.[9]


(4) Ar=Ph
(5) Ar=Tol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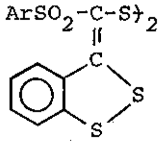

(8) Ar=Ph
(9) Ar=Tol

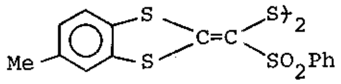

(10)

Table 1. The Reactions of the Adducts(4, 5, and 6)

a) with $t\text{-BuNH}_2$ in refluxing benzene for 1 hr.

compound	a	dimer(%)	$t\text{-Bu}\overset{+}{N}H_3\bar{O}_2SAr$(%)	recoved(%)
4[b]	1.0	46.8[e]	43.2	40
5[c]	excess	49.9[f]	60	0
6[d]	excess	8.8[g]	7	78

b) with triphenylphosphine in benzene for 4 hr at room temperature.

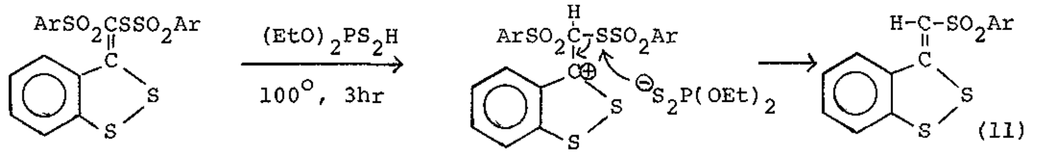
compound	a	dimer	Ph_3PO	$(ArS)_2$	recoved.
5	1.0	30.6[f]	90	35.9	45
6	1.0	38.9[g]	80	40	40
6[h]	excess	66.3[g]	195	41.9	0

c) with KOH in MeOH at room temperature for 30 min.

compound	dimer	arenesulfonic acid
4	53.5[e]	70
5	88[f]	83

(a)mole ratio to the compound; (b) λ_{max}459nm, ε 13800(DMF); (c) λ_{max} 447nm, ε 12000(DMF); (d) λ_{max}388nm, ε 17000(DMF); (e) (8):λ_{max}436nm, ε9800(DMF); (f) (9):λ_{max}425nm, ε9100(DMF); (g) (10):λ_{max}377nm, ε10400(DMF); (h) the reaction with $n\text{-Bu}_3P$.

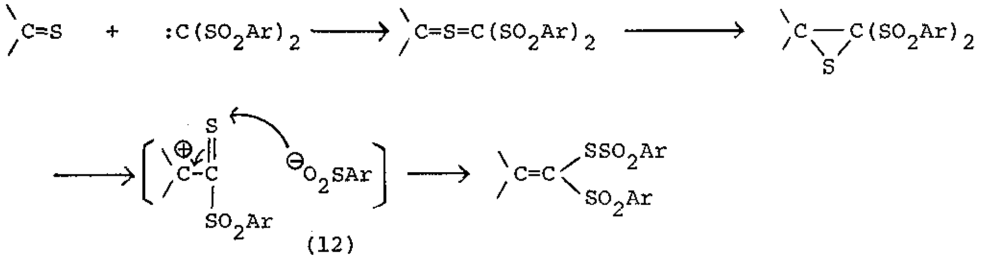
Furthermore, on the basis of the revised structures the reaction of 4 and 5 with a reducing agent, O, O'-diethyl dithiophosphoric acid, eventually leading to the formation of the corresponding 1,2-dithiole-3-arylsulfonylmethylene(11), can easily be understood to proceed along a path such as illustrated below.



a: Ph
b: Tol

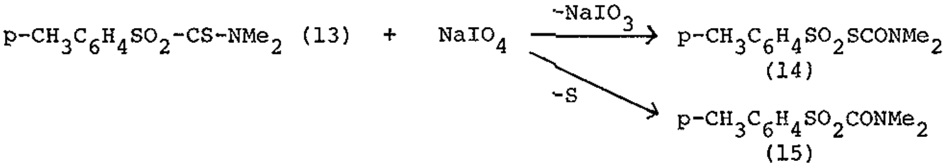
a: 78%
b: 79%

The formation of these thiolsulfonates(4, 5, and 6) would be explicable in terms of a plausible mechanism depicted below; the reaction, after the formation of an unstable thiocarbonyl ylide, undergoes cyclization and then elimination of a sulfonate anion to give an intimate ion-pair(12), subsequently followed by the recombination of the ion-pair, affording observed thiolsulfonates.



(12)

Recently, the literature analogy was reported for the oxidation of C-tosylthioformamide(13), which led to S-tosyl-N,N-dimethylthiourethane(14) by the rearrangement, rather than 15 by the loss of a sulfur atom.[10]



$$p\text{-}CH_3C_6H_4SO_2\text{-}CS\text{-}NMe_2\ (13) + NaIO_4 \xrightarrow{-NaIO_3} p\text{-}CH_3C_6H_4SO_2SCONMe_2\ (14)$$

$$\xrightarrow{-S} p\text{-}CH_3C_6H_4SO_2CONMe_2\ (15)$$

References and Notes

1) J.P. Snyder, J. Amer. Chem. Soc., 1974, 96, 5005; A. Schönberg and R. von Ardenne, Chem. Ber., 1968, 101, 346.

2) S. Tamagaki, R. Ichihara, and S. Oae, Bull. Chem. Soc. Japan, 1975, 48, 355.

3) S. Tamagaki and S. Oae, Tetrahedron Lett., 1972, 1159.

4) J. Buter, S. Wassenaar, and R.M. Kellogg, *J. Org. Chem.*, 1972, **37**, 4045.

5) A.W. Johnson, 'Ylid Chemistry', Academic Press, New York, 1966, pp. 304; B.M. Trost and L.S. Melvin, Jr., 'Sulfur Ylides', Academic Press, New York, 1975.

6) J.E. Dunbar and J.H. Rogers, *J. Org. Chem.*, 1966, **31**, 2842; N.E. Heimer and L. Field, *ibid.*, 1970, **35**, 3012.

7) S. Hayashi, *Chem. Pharm. Bull.(Tokyo)*,1967, **18**, 1310.

8) L. Bauer and J. Cymermen, *J. Chem. Soc.*, 1950, 109.

9) (4): mp 138-139°; Calcd for $C_{20}H_{14}O_4S_5$:C, 50.18; H, 2.94%. Found:C, 50.15; H, 2.73%.

(5): mp 163-164°; Calcd for $C_{22}H_{18}O_4S_5$:C, 52.10; H, 3.56%. Found:C, 51.88; H, 3.53%.

(6): mp 164-165°; Calcd for $C_{21}H_{16}O_4S_5$:C, 51.20; H, 3.27%. Found:C, 51.55; H, 3.31%.

(8): dec. 202°; Calcd for $C_{14}H_9O_2S_4$:C, 49.86; H, 2.69%; Found:C, 49.34; H, 2.76%.

(9): dec. 180°; Calcd for $C_{15}H_{11}O_2S_4$:C, 51.28; H, 3.13%. Found:C, 51.12; H, 3.22%.

(10): dec. 210°; Calcd for $C_{15}H_{11}O_2S_4$:C, 51.28; H, 3.13%. Found:C, 51.12; H, 3.22%.

(11a): mp 175°; Calcd for $C_{14}H_{10}O_2S_3$:C, 54.90; H, 3.29%. Found:C, 55.20; H, 3.34%.

(11b): mp 185°; calcd for $C_{15}H_{12}O_2S_3$:C, 56.25; N, 3.75%. Found:C, 56.31; H, 3.77%.

10) N.H. Nilsson and A. Senning, *Angew. Chem.*, 1972, **84**, 293.

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