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Cyclic Disulfides. The Reaction of 1,2-Dithiaacenaphthene with Carbenoids

Seizo TAMAGAKI and Shigeru OAE
Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sumiyoshi-ku, Osaka

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The chemistry of five-membered disulfides has drawn considerable interest mainly because of their characteristic properties in biological reactions and their special role in metabolic sequences.[1] Recently, the electronic features of the five-membered cyclic disulfides have been made clear on the basis of semi-empirical molecular orbital calculations, and the implications on the chemical reactivity have been discussed.[2] At the dihedral angle of 0° around the S–S bond the π-p orbitals of the lone-pairs on the two sulfur atoms are arranged parallel to each other, resulting in a larger splitting of the lone-pair energy levels than in disulfides containing non-parallel-allied lone pairs. Accordingly, electron pairs at the higher level may be expected to display a greater reactivity toward the electrophilic reagents than the less-splitting lone-pairs of the sulfur atom in open-chain disulfides.

The reaction of diaryl disulfide with the methylene formed by the photolysis of diazomethane has been investigated by German chemists and found to proceed in the following manner.[3,4]

$$\text{Ar-S-S-Ar} + \text{CH}_2\text{N}_2 \xrightarrow{h\nu} \text{Ar-S-CH}_2\text{-S-Ar}^{3)}$$

$$\text{Ph-S-S-Ph} + \text{Ph}_2\text{CN}_2 \xrightarrow{h\nu} \text{Ph-S-CPh}_2\text{-S-Ph}^{4)}$$

The similar insertion reaction of five-membered cyclic disulfide is interesting; we carried out the reaction of 1,2-dithiaacenaphthene with bis(arenesulfonyl)diazomethane or with diphenyldiazomethane in the presence of a catalytic amount of copper acetylacetonate.

Experimental

Reaction of 1,2-Dithiaacenaphthene with Bis(toluenesulfonyl)-diazomethane. A mixture of 1,2-dithiaacenaphthene (190 mg) and bis(toluenesulfonyl)diazomethane (350 mg) was refluxed for 15 min in the presence of 15 mg of copper acetylacetonate. After cooling, the solvent was evaporated to afford crystals, which were then recrystallized from benzene (450 mg: 88%) to give, finally, colorless crystals of (A): mp 148—148.5°C. Found: C, 58.36; H, 3.95%. Calcd for $C_{14}H_{14}S_2O_4$: C, 58.60; H, 3.91%.

Decomposition of (A). Compound (A) (140 mg) was decomposed in a test tube at 150°C. Then, the reaction mixture was extracted with hot *n*-hexane. After the evaporation of the solvent, the crystals (60 mg) were sublimated under reduced pressure to afford a carbonyl compound (B): mp 132—133°C. Found: C, 60.64; H, 2.85%. Cacld for $C_{11}H_{16}S_2O$: C, 60.50; H, 2.75%.

Reaction of 1,2-Dithiaacenaphthene with Diphenyldiazomethane. In a similar fashion, the reaction of 350 mg of diphenyldiazomethane with 1,2-dithiaacenaphthene (200 mg) gave 350 mg (91%) of crystals upon recrystallization from benzene-hexane; mp 180—181°C. Found: C, 77.65; H, 4.45%. Calcd for $C_{23}H_{16}S_2$: C, 77.52; H, 4.49%.

Results and Discussion

Diphenyl disulfide was allowed to react with an equimolar amount of bis(toluenesulfonyl)diazomethane in the presence of a catalytic amount of copper acetylacetonate to afford crystals melting at 169—170°C. This structure is at present yet unidentified. However, it is apparent that the reaction mixture did not contain disulfide linkage. Besides, from the reaction mixture no product was isolated which corresponds to the insertion product.

Contrary to the above reaction, the copper salt-

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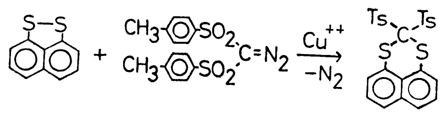
[1] L. J. Reed, "Organic Sulfur Compounds," Vol. 1, Pergamon Press, Oxford (1969), p. 443.

[2] H. Yamabe, H. Kato, and T. Yonezawa, This Bulletin, **44**, 604 (1971).

[3] N. Petragnari and G. Schill, *Chem. Ber.*, **103**, 2271 (1970).

[4] A. Schönberg and T. Stalpp, *ibid.*, **63**, 3102 (1930).

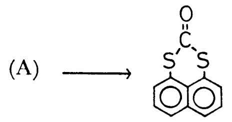
catalyzed reaction of 1,2-dithiaacenaphthene with bis(toluenesulfonyl)diazomethane took place smoothly and was completed within 5 min in refluxing benzene; then the reaction gave crystals (A) with a decomposition temperature of 148—148.5°C. On the basis of the IR and NMR spectra, the compound obtained is considered to be an insertion adduct formed from bis(toluenesulfonyl)diazomethane and 1,2-dithiaacenaphthene as is shown below.



(A)

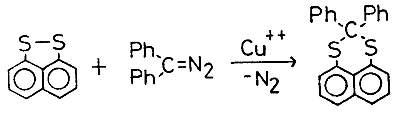
The IR spectrum showed bands at 1355 and 1175 cm^{-1} corresponding to the stretching frequencies of the sulfonyl group, while the NMR spectrum of the compound fully confirmed the (A) structure. The signals due to two methyl groups appear at δ 2.51 as singlet, and those of 14 aromatic hydrogens as a multiplet centered at δ 7.58.

The pyrolysis of (A) at its decomposition temperature gave carbonyl compound (B). The structure of the resulting compound was confirmed by IR, NMR, MS, and elemental analysis. The IR spectrum showed a strong band at 1610 cm^{-1} corresponding to that of the carbonyl groups. The mass spectrum showed a peak at *m/e* 218 as the molecular peak, followed by an intense peak of *m/e* 190 and with a metastable peak appearing at *m/e* 165.0 due to decarboxylation.



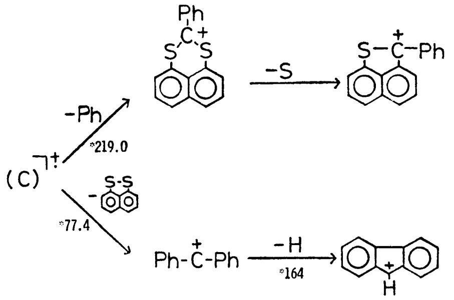
(B)

Similarly, upon heating of a benzene solution of an equimolar mixture of 1,2-dithiaacenaphthene and diphenyldiazomethane in the presence of copper salts, a reaction took place promptly and the diphenylmethylene insertion product (C) was obtained as the sole product nearly quantitatively:



(C)

The structure of (C) was confirmed similarly on the basis of IR, MS, and elemental analysis. The mass spectrum showed a peak at *m/e* 356 as calculated from the expected structure (C):

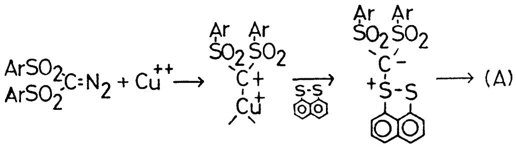


(* indicates the metastable peak)

Unlike 1,2-dithiaacenaphthene, diphenyl disulfide did not give any similar product, as had been anticipated.

All these observations suggest that the reactions of carbenoids are essentially electrophilic. Thus, the effect of lone-pair lone-pair repulsion is evidently demonstrated by the above experiments; that is, the fact that the carbenoids react with 1,2-dithiaacenaphthene readily and not with diphenyl disulfide implies that the five-membered disulfide is much more reactive toward the electrophilic reagents than are the ordinary disulfides.

The formation of the metal carbenoid on the copper salts of acetylacetonate may be followed by the nucleophilic attack of 1,2-dithiaacenaphthene on the carbenoid carbon atom, resulting in the formation of ylide.[5] The mechanism of the carbenoid reaction may be represented as is shown below:



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[5] S. Searles, Jr., and R. E. Wann, *Tetrahedron Lett.*, **1965**, 2899