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REACTIONS OF CYCLIC DISULFIDES WITH CARBENES; DESULFURIZATION AND INSERTION

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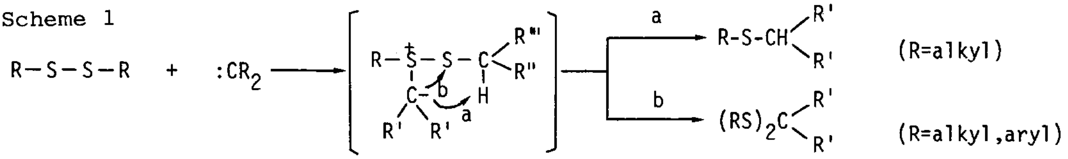
Summary: Reactions of several cyclic disulfides with carbenes generated by catalytic and photochemical decompositions of diazo compounds have been studied. Carbenes reacted with cyclic disulfides yielding 1,3-dithiane quantitatively as S-S insertion reaction, while the selective desulfurization results in the reaction of disulfides with bulky substituents. The carbene reaction is sensitive to bulkiness of disulfides.

The influence of steric effect of carbnene reaction very often changes the reaction courses. Typical of this general problem is in ability to have β-elimination of sulfur ylide. There have been only a few reports on the reaction of disulfide with carbenes, in contrast to vast amount of sulfide-carbene reactions. We have already shown that the reaction of dialkyl disulfides with carbenes predominantly affords the sulfur ylide followed by cyclic β-elimination to give olefin. Diaryl disulfide ineffficiently reacted with carbene to afford the S-S insertion product.[1,2] Of the few examples known of S-S insertion on the reaction of acyclic disulfide with carbene, no detail studies involve dithiaacenaphthene.[3-5]

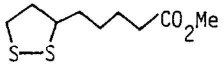
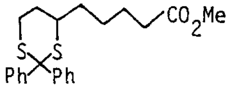
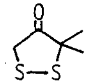
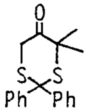
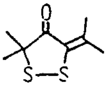
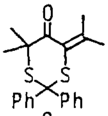
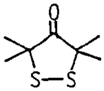
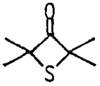
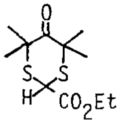
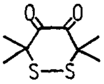
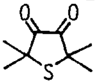
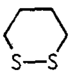
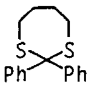
Scheme 1



One uses the cyclic disulfides in the reaction of carbene, a number of possibility can be realized. Here we report the reactions of cyclic disulfides with carbenes in which the selective S-S insertion and desulfurization took place depending on both the structures of disulfides and carbenes used.

In a typical procedure, to a mixture of 1.1 mmol of α-lipoic acid methyl ester 1 and 2.6 mmol of diphenyl diazomethane in 10 ml of dichloromethane was added 0.02 mmol of cuprous chloride at room temperature. Nitrogen evolution ceased in two to three hours. The mixture was filtered to removed CuCl, and the products were separated by silica gel column chromatography (eluent: benzene). The stable sulfur ylide can not be isolated but 1,3-dithiane 7 was obtained unexpectedly high yield as the S-S insertion product along with tetraphenylazine.

Table 1 Reaction of Cyclic Disulfide with Carbene in Dichloromethane at Room Temperature

Run	Substrate		Diazo Compd.	Catalyst	Product and Yield(Conv. Yield)		
1		1	N_2CPh_2	CuCl		7[6]	100%(100%)
2		2	N_2CPh_2	CuCl		8[7]	68%(100%)
3		3	N_2CPh_2	CuCl		9[8]	66%(100%)
4		4	N_2CPh_2	CuCl		10	28%(100%)
5		4	N_2CPh_2	$[Rh(OAc)_2]_2$ [a]		10	29%(100%)
6		4	$N_2C(CO_2Me)_2$	$h\nu$ [b]		10	33%(100%)
7		4	N_2CHCO_2Et	CuCl		11[9]	69%(69%)
8		5	N_2CPh_2	$[Rh(OAc)_2]_2$ [a]		12	30%(100%)
9		5	$N_2C(CO_2Me)_2$	$h\nu$ [b]		12	29%(100%)
10		6	N_2CPh_2	CuCl		13	89%(89%)

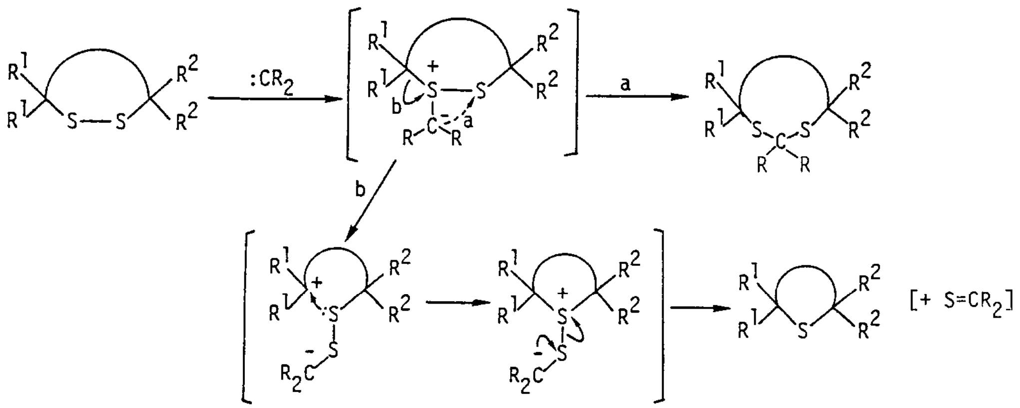
a) 0.01 equiv. of $[Rh(OAc)_2]_2$ was added to disulfides. b) Carbene was generated by irradiation with high pressure mercury lamp in pyrex tube.

Analogous reactions were attempted using disulfides 2 and 3 in place of α-lipoic acid methyl ester. The formation of 1,3-dithiane is somewhat lower yield but higher conversion yield, probably by steric effects on sulfur. In contrast to disulfides 1-3, the disulfide 4 reacted with diphenyl diazomethane in the presence of cuprous chloride under the same reaction condtions as those employed with 1 yielding desulfurization product, thietanone 10. The thietanone 10 was also obtained from the reaction of the disulfide 4 with biscarbomethoxycarbene. In turn, the reaction with carboethoxycarbene caused the formation of 1,3-dithiane 11, but none of thietanone formation.

The reaction of disulfide 5 with diphenylcarbene or biscarbomethyoxycarbene gave thiolane 12 in 30% yield along with 70% of recovered substrates (Run 8 and 9). The 1,3-dithiepane 13 was obtained as a sole product in 89% yield in the reaction of disulfide 6 with diphenylcarbene. These results clearly indicate that the desulfurization requires both sterically hindered disulfide and carbene; it does not depend on the generating method of carbene. The formation of S-S insertion product 11 may consist with less hindered or highly reactive carbene. There is no β-elimination product in the reaction of cyclic disulfide.

We now propose that these reactions involve the sequence of steps shown in scheme 2, namely sulfur ylide formation followed by 1,3-rearrangement with S-S bond cleavage (a type), or with C-S bond cleavage (b type). Clearly the b type rearrangement occurs in hindered sulfur ylide, and a type rearrangement in less hindered one.

Scheme 2



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2) W. Ando, T.Yagihara, S. Tozune, I. Imai, J. Suzuki, T. Toyama, S. Nakaido, and T. Migita, J. Org. Chem., 37, 1721 (1972).

3) A. Schönberg and T. Stalpp, Chem. Ber., 63, 3102 (1930).

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6) 7; mp. 66-67°C. ^{13}C NMR(δ,$CDCl_3$) 24.8(t), 25.6(t), 29.9(t), 32.3(t), 33.9(t), 35.5(t), 42.7(d), 51.5(q), 64.5(s), 127.3(d), 128.6(d), 130.3(d), 141.4(d), 144.2(d), 173.9(d).

7) 8; IR(cm^{-1},KBr) 1695(C=O). ^{1}H NMR(δ,$CDCl_3$) 1.53(s,6H), 3.66(s,2H), 7.51-8.11(m,10H).

8) 9; mp. 95-96°C. IR(cm^{-1},KBr) 1570(C=C), 1665(C=O). ^{1}H NMR(δ,$CDCl_3$) 1.53(s,6H), 1.97(s,3H), 2.01(s,3H), 7.50-8.09(m,10H). ^{13}C NMR(δ,$CDCl_3$) 23.1(q), 23.3(q), 27.4(q), 53.1(s), 65.1(s), 125.0(s), 127.7(d), 128.0(d), 128.7(d), 143.6(s), 146.9(s), 200.4(s).

9) 11; mp. 109-110°C. ^{1}H NMR(δ,$CDCl_3$) 1.33(t,3H), 3.62(bs,3H), 3.68(bs,3H), 4.31(q,2H), 4.96(s,1H).

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