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FORMATION OF DITHIOETHER DICATIONS OF CYCLIC DITHIOETHERS IN CONCENTRATED SULFURIC ACID

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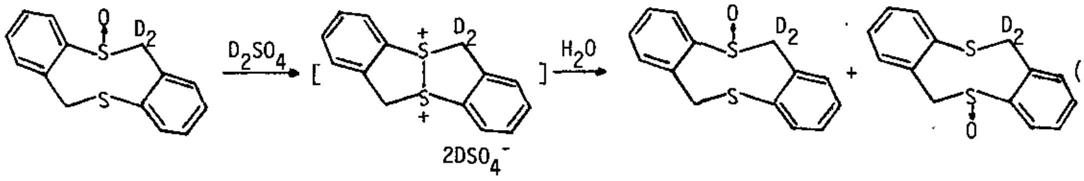
Abstract - The dithioether dications of 5H,7H-dibenzo[b,g][1,5]dithiocin, 6H,12H-dibenzo[b,f][1,5]dithiocin, and 1,6-dithiacyclodecane were formed in the reaction of the corresponding S-oxides with conc. H_2SO_4.

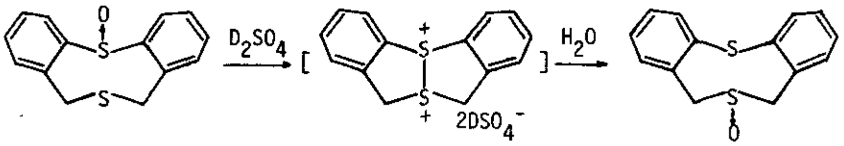
We recently reported that the dithioether dication of 1,5-dithiacyclooctane was formed in a reaction of the corresponding S-oxide with conc. H_2SO_4 and actually isolated in crystalline form.[1] The dication of thianthrene, which has been extensively studied by Shine et al. does not contain an intramolecular S-S bond.[2] However, the dication of cyclic dithioether having benzylic methylene group has never been reported. Autenrieth and Bruning suggested formation of the dithioether dication by a reaction of 5,7,12,14-tetrahydrodibenzo[c,h][1,6]dithiecin bearing benzylic methylene group with bromine,[3] whereby the product obtained was solely the disulfide due to the C-S bond cleavage and not the dication.[4, 5] We now report the ^1H and ^{13}C n.m.r. spectroscopic evidences for formation of the dithioether dications in the reaction of dibenzodithiocin S-oxides (1) and (3), 1,6-dithiacyclodecane S-oxide (7) and their deuteriated derivatives with conc. H_2SO_4.

6,12-Dihydrodibenzo[b,f][1,5]dithiocin S-oxide (1)[6], 5H,7H-dibenzo[b,g][1,5]dithiocin S-oxides (3) and (5)[7], 5,7,12,14-tetrahydrodibenzo[c,h][1,6]dithiecin S-oxide (6)[8], 1,6-dithiacyclodecane S-oxide (7)[9], and the corresponding deuteriated derivatives (1a)[10] and (7a)[11] were prepared by general methods. When (1) was dissolved in conc. D_2SO_4(98%), the solution became yellow. Then the reaction was followed immediately by both ^1H and ^{13}C n.m.r. spectroscopies. In the ^1H n.m.r., two methylene signals adjacent to the sulfenyl groups for (1) in $CDCl_3$



(1a) $^2H_2$-(2) (1a) (1b)

(Eq. 1)



(3) (4) (5)

(Eq. 2)

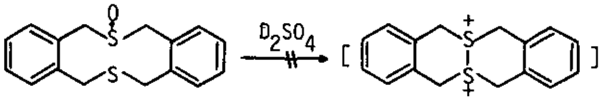
disappeared and new AB quartet peaks appeared which must be the benzylic methylene of (2), while in ^{13}C n.m.r., two signals due to the corresponding methylene carbon atoms in (1) in $CDCl_3$, coalesced into one signal in D_2SO_4. Both ^1H and ^{13}C n.m.r. data are shown in Table 1. Treatment of the D_2SO_4 solution of (1) with ice-H_2O and work up afforded only the original monosulfoxide (1) in 82% isolated yield. Similar treatment of (1a) in D_2SO_4 led to similar changes in the ^1H n.m.r. spectra. Hydrolysis of the D_2SO_4 solution of (1a) led to 80% recovery of the S-oxide. The ^1H n.m.r. spectra indicate that it is a complete 1:1 mixture of the 6,6- and 12,12-dideuteriated S-oxides (1a) and (1b). Furthermore, no H-D exchange of (1a) with the solvent H_2SO_4 was observed during the reaction (Eq. 1). These results indicate clearly that (1) and (1a) are converted into the symmetrical intermediate dication (2). In a similar way, the reaction of (3) with conc. D_2SO_4 was also followed by ^1H n.m.r. spectroscopy, and the spectra suggested formation of the dication (4) in D_2SO_4. Treatment of this solution with H_2O afforded the oxygen migrated sulfoxide (5) in good yield and the compound (3) was not obtained at all (Eq. 2).[12]

Meanwhile, when dithiecin S-oxide (6) as a ten-membered homolog of (1) was similarly dissolved in D_2SO_4, and taken its ^1H n.m.r. spectrum, we found that the spectrum showed very complex signals probably due to the C-S bond cleavage. Actually the products obtained were composed of a complex mixture which was not investigated further. On the other hand, dissolution of the compound (7) in conc. D_2SO_4 afforded the corresponding dithioether dication (8). The ^1H n.m.r. spectra are assigned as shown in Table 1. Treatment of the tetradeuteriated

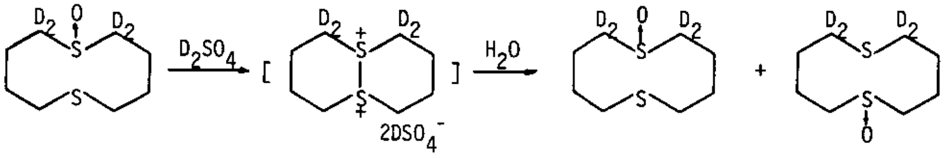
Table 1. N.m.r. data for (1)-(5) and (7)-(8)[a]

(1)[b]	7.64-6.77(m,8H,Ph), 5.11,4.08(ABq,J 14Hz,CH_2SO), 4.15,3.96(ABq,J 14Hz,CH_2S)
(1a)	7.65-6.76(m,8H,Ph), 4.13,3.95(ABq,J 14Hz,CH_2S)
(2)[c]	7.82-6.96(m,8H,Ph), 5.61,5.17(ABq,J 15.6Hz,CH_2S^+)
(3)[d]	8.30-8.01(m,2H,Ph), 7.69-7.01(m,6H,Ph), 4.56,3.87(ABq,J 15Hz,CH_2S)
(4)[e]	7.92-6.98(m,8H,Ph), 5.57,5.20(ABq,J 15Hz,CH_2S^+)
(5)[f]	7.96-7.15(m,8H,Ph), 5.64,4.18(ABq,J 12Hz,CH_2SO), 4.06,3.82(ABq,J 13Hz,CH_2SO)
(7)	3.72-2.91(m,4H,CH_2SO), 2.89-2.62(m,4H,CH_2S), 2.27-1.57(m,8H,CH_2)
(7a)	2.87-2.62(m,4H,CH_2S), 2.27-1.57(m,8H,CH_2)
(8)	4.14-3.29(br.m,8H,CH_2S^+), 2.32-1.25(br.m,8H,CH_2)

[a] ^1H and ^{13}C data (δ) for (1),(1a),(3),(5),(7), and (7a) in $CDCl_3$, relative to Me_4Si; data for (2),(4), and (8) in D_2SO_4 relative to sodium 4,4-dimethyl-4-silapentane-sulfonate (DSS). [b] ^{13}C: δ 61.3 and 35.6 for methylene carbon. [c] ^{13}C: δ 63.6 for methylene carbon. [d] Boat-chair form (100%).[12] [e] Twist-boat form(100%). [f] Twist-boat form (78%) and Boat-chair form (22%).

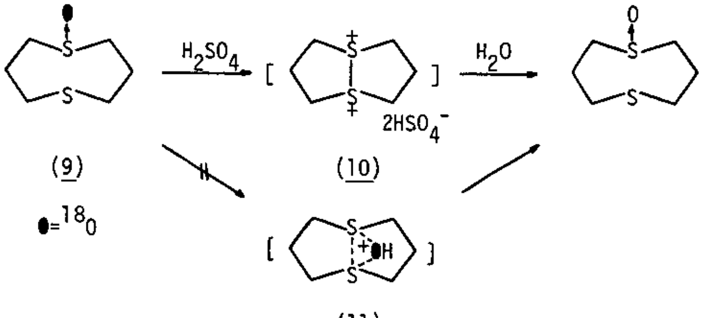


(6)



(Eq.3)

(7a) $^2H_4$-(8) (7a) (7b)



(Eq.4)

(11)

compound (7a) in D_2SO_4 gave similar changes as (7) in the ^1H n.m.r. spectra and 1:1 mixture of 2,2,10,10- and 5,5,7,7-tetradeuteriated S-oxides (7a) and (7b) were obtained by hydrolysis of the D_2SO_4 solution (Eq. 3).

Although both our present and previous results seem to display formation of dithioether dications generated from the corresponding sulfoxides in conc. H_2SO_4, other possible formation of symmetrical oxydisulfonium salts such as (11) is unable to eliminate. Therefore, in order to confirm the formation of symmmetrical dication by ^{18}O-tracer experiment, we prepared ^{18}O-labelled 1,5-dithiacyclooctane *S*-oxide (9){^{18}O content 42 excess atom%}[13] and dissolved it in conc. H_2SO_4. Then upon treatment initially with cold anhydrous diethyl ether and subsequently with ordinary ice-water, no ^{18}O was incorporated into the recovered *S*-oxide (confirmed by mass spectroscopy). The result eliminates clearly the formation of (11) and is consistent with conversion of (9) to the dication (10) (Eq. 4).

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6. (1): mp 119°C. i.r.(KBr) 1038 cm^{-1}. Anal. Calcd for $C_{14}H_{12}OS_2$; C, 64.58; H, 4.64%. Found: C, 64.41; H, 4.63%.
7. (3): mp 195-196°C. i.r.(KBr) 1078, 1040 cm^{-1}. Anal. Calcd for $C_{14}H_{12}OS_2$: C, 64.58; H, 4.64%. Found: C, 64.50; H, 4.61%. (5): mp 178-180°C. i.r.(KBr) 1075, 1040 cm^{-1}. Anal. Calcd for $C_{14}H_{12}OS_2$: C, 64.58; H, 4.64%. Found: C, 64.51; H, 4.65%.
8. (6): mp 279-281°C. i.r.(KBr) 1039 cm^{-1}. Anal. Calcd for $C_{16}H_{16}OS_2$: C, 66.62; H, 5.59%. Found: C, 66.52; H, 5.55%.
9. (7): mp 69-70°C. i.r.(KBr) 1030 cm^{-1}.
10. The deuteriation was accomplished by heating (1) with NaOD-D_2O-tetrahydrofuran in a sealed tube at 85°C for 7 h; deuterium content of (1a) was $>$95 atom%.
11. H-D Exchange of (7) could be carried out in NaOD-D_2O at 100°C for overnight under nitrogen; deuterium content of (7a) was $>$ 95 atom%.
12. Recently, Akiba et al. reported the same result on this dication: K. Okada, K. Ohkata, and K. Akiba, Abstract of the 13th Symposium on Organic Sulfur and Phosphorus Chemistry, Japan, 1985, p. 1.
13. ^{18}O-Labelled compound was prepared by the method of S. Oae, Y. Ohnishi, S. Kozuka, and W. Tagaki, *Bull. Chem. Soc. Jpn.*, 1966, **39**, 364.

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