FORMATION OF DITHIOETHER DICATIONS OF CYCLIC DITHIOETHERS
IN CONCENTRATED SULFURIC ACID

Hisashi Fujihara, Akira Kawada, and Naomichi Furukawa*
Department of Chemistry, The University of Tsukuba,
Sakura-mura, Niihari-gun, Ibaraki 305, Japan

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

We recently reported that the dithioether dication of 1,5-dithiacyclooctane was
formed in a reaction of the corresponding S-oxide with conc. H2SO4 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 dithio-
ether 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 13C 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.
H2SO4.

6,12-Dihydrodibenzo[b,f][1,5]dithiocin S-oxide (1), 5H,7H-dibenzo[b,g][1,5]
dithiocin S-oxides (3) and (5), 5,7,12,14-tetrahydrodibenzo[c,h][1,6]dithiecin
S-oxide (6), 1,6-dithiacyclodecane S-oxide (7) and the corresponding deuteriated
derivatives (1a) and (7a) were prepared by general methods. When (1) was
dissolved in conc. D2SO4(98%), the solution became yellow. Then the reaction
was followed immediately by both 1H and 13C n.m.r. spectroscopies. In the 1H
n.m.r., two methylene signals adjacent to the sulfenyl groups for (1) in CDCl3
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$_2$SO$_4$. Both $^1$H and $^{13}$C n.m.r. data are shown in Table 1. Treatment of the D$_2$SO$_4$ solution of (1) with ice-H$_2$O and work up afforded only the original monosulfoxide (1) in 82% isolated yield. Similar treatment of (1a) in D$_2$SO$_4$ led to similar changes in the $^1$H n.m.r. spectra. Hydrolysis of the D$_2$SO$_4$ solution of (1a) led to 80% recovery of the S-oxide. The $^1$H 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$_2$SO$_4$ 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$_2$SO$_4$ was also followed by $^1$H n.m.r. spectroscopy, and the spectra suggested formation of the dication (4) in D$_2$SO$_4$. Treatment of this solution with H$_2$O afforded the oxygen migrated sulfoxide (5) in good yield and the compound (3) was not obtained at all (Eq. 2).

Meanwhile, when dithiecin S-oxide (6) as a ten-membered homolog of (1) was similarly dissolved in D$_2$SO$_4$, and taken its $^1$H 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$_2$SO$_4$ afforded the corresponding dithioether dication (8). The $^1$H 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)\textsuperscript{a}

\begin{tabular}{l}
(1)\textsuperscript{b} 7.64-6.77 (m, 8H, Ph), 5.11, 4.08 (ABq, J 14 Hz, CH\textsubscript{2}SO), 4.15, 3.96 (ABq, J 14 Hz, CH\textsubscript{2}S) \\
(la) 7.65-6.76 (m, 8H, Ph), 4.13, 3.95 (ABq, J 14 Hz, CH\textsubscript{2}SO) \\
(2)\textsuperscript{c} 7.82-6.96 (m, 8H, Ph), 5.61, 5.17 (ABq, J 15.6 Hz, CH\textsubscript{2}S\textsuperscript{+}) \\
(3)\textsuperscript{d} 8.30-8.01 (m, 2H, Ph), 7.69-7.01 (m, 6H, Ph), 4.56, 3.87 (ABq, J 15 Hz, CH\textsubscript{2}S) \\
(4)\textsuperscript{e} 7.92-6.98 (m, 8H, Ph), 5.57, 5.20 (ABq, J 15 Hz, CH\textsubscript{2}S\textsuperscript{+}) \\
(5)\textsuperscript{f} 7.96-7.15 (m, 8H, Ph), 5.64, 4.18 (ABq, J 12 Hz, CH\textsubscript{2}SO), 4.06, 3.82 (ABq, J 13 Hz, CH\textsubscript{2}SO) \\
(7) 3.72-2.91 (m, 4H, CH\textsubscript{2}SO), 2.89-2.62 (m, 4H, CH\textsubscript{2}S), 2.27-1.57 (m, 8H, CH\textsubscript{2}) \\
(7a) 2.87-2.62 (m, 4H, CH\textsubscript{2}S), 2.27-1.57 (m, 8H, CH\textsubscript{2}) \\
(8) 4.14-3.29 (br. m, 8H, CH\textsubscript{2}S\textsuperscript{+}), 2.32-1.25 (br. m, 8H, CH\textsubscript{2}) \\
\end{tabular}

\textsuperscript{a} \textsuperscript{1H} and \textsuperscript{13C} data (6) for (1), (la), (3), (5), (7), and (7a) in CDCl\textsubscript{3}, relative to Me\textsubscript{4}Si; data for (2), (4), and (8) in D\textsubscript{2}SO\textsubscript{4} relative to sodium 4,4-dimethyl-4-sila- pentane-sulfonate (DSS). \textsuperscript{b} \textsuperscript{13C}: \textsuperscript{6} 61.3 and 35.6 for methylene carbon. \textsuperscript{c} \textsuperscript{13C}: \textsuperscript{6} 63.6 for methylene carbon. \textsuperscript{d} Boat-chair form (100%). \textsuperscript{e} Twist-boat form (100%). \textsuperscript{f} Twist-boat form (78%) and Boat-chair form (22%).

\[ \xrightarrow{D_{2}SO_{4}} \]

\[ \xrightarrow{H_{2}SO_{4}} \]

\[ \xrightarrow{H_{2}O} \]

compound (7a) in D\textsubscript{2}SO\textsubscript{4} gave similar changes as (7) in the \textsuperscript{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\textsubscript{2}SO\textsubscript{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\textsubscript{2}SO\textsubscript{4},
other possible formation of symmetrical oxydisulfonium salts such as \((11)\) is unable to eliminate. Therefore, in order to confirm the formation of symmetrical dication by \(^{18}O\)-tracer experiment, we prepared \(^{18}O\)-labelled 1,5-dithiaacyclooctane \(S\)-oxide \((9)\) \(^{18}O\) content 42 excess atom% 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).

REFERENCES

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\(_2\)O-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\(_2\)O at 100°C for overnight under nitrogen; deuterium content of \((7a)\) was >95 atom%.

Received, 19th August, 1985