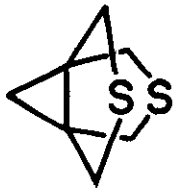
PROPELLANES. LXV. DITHIA[3.3.n]PROPELLANES, THEIR METAL SALT COMPLEXES, SULFILIMINES AND SULFOXIDES.*

Ishai Sataty, Michael Peled and David Ginsburg

Department of Chemistry, Technion - Israel Institute of Technology, Haifa.

Abstract — The structures of the title compounds and those of various derivatives have been studied.

We were interested in a comparison of dithiapropellanes within a homologous series, particularly with respect to the angle between the planes formed between the two thioether rings. It has been claimed that propellanes in general may be compared to clamps and that in a homologous series, "pinching" the "clamp", i.e. lowering the size of one ring, the other two being kept constant, the angle between the latter ought to increase.[1] We had available compounds 1-3[2] and 4[3] and have shown that a "Klammer" effect indeed occurs within the series (albeit 4 contains a cyclohexene ring rather than a fully reduced one).[4]



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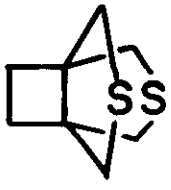

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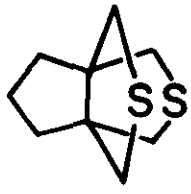

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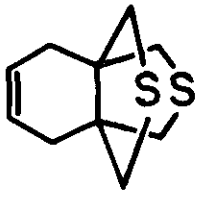

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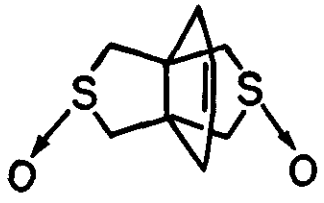
* Part LXIV. P. Ashkenazi and D. Ginsburg, Heterocycles, 1982, 18, 45.

We also prepared complexes with metal salts, sulfoxides and sulfilimines of some of these substrates and of 5 in order to study their configurations about sulfur. Such a rich array of structures is obtained for complexes with metal salts that no common denominator is found for the various substrates. These will be reported elsewhere.[5]

Oxidation of a substrate of type 1-5 may afford two configurationally different mono-sulfoxides and that of 1-4 may afford three configurationally different bis-sulfoxides. Bis-isomer 6 crystallized with 1 mole of water. Its X-ray structural determination showed that it



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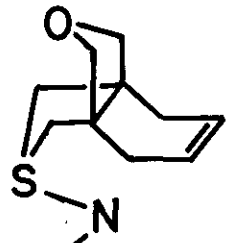

p-$MeC_6H_4SO_2$

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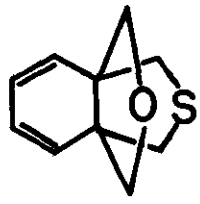

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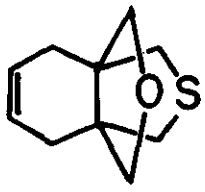

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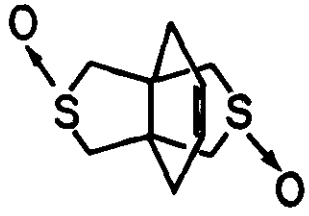

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was the syn- anti- bis-sulfoxide (with respect to the cyclohexene ring)whilst the X-ray structure of 7 showed it was the anti-anti-isomer. Its crystals did not contain water. The X-ray results will be published elsewhere.[5] The third, syn-syn-isomer was not isolated at all.

Two configurationally isomeric sulfilimines were formed from 5 by reaction with chloramine-T in the ratio of 1:3. The X-ray structure of one of the isomers showed it to be 8. Hence 9 has the S-N bond in the direction syn to the ether ring rather than anti as in 8. When the oxa-thiapropelladiene 10 was treated with N-phenyltriazolinedione it reacted exclusively syn to the thioether ring, i.e. anti to the ether ring.[6] Although the behavior of the pair 8, 9 reacting with chloramine-T is not analogous to that of 10 reacting in a Diels-Alder reaction, it is of

interest to compare the two reactions at least from the steric viewpoint. In the latter case the mode of attack may be understood on steric grounds although the quantitative formation of only one isomer is not obvious a priori. For the former case one obtains twice 9 as compared to 8. It isn't obvious why 9 should necessarily be the thermodynamically more stable of the two. Thermal equilibration by heating either 8 or 9, separately (see experimental section) gives nearly a 1:1 equilibrium mixture of the two, very slightly in favor of 9 (55% as compared to 45% after heating to 160° for 5hr).

Experimental

IR spectra were recorded on a Perkin-Elmer 237 spectrometer, NMR spectra on a Varian T-60 or a Bruker WP-60 instrument and mass spectra on a Varian MAT-711 spectrometer·Mp's and bp's are uncorrected.

Complexes of 4. - 4·$HgCl_2$ has been reported.[1]

4·$AgClO_4$ was prepared from 4 (29 mg) in dry EtOH (5 ml) by addition of $AgClO_4$ (110 mg). A ppt formed rapidly while stirring for 10 min at r.t. It was collected by filtration. It had m.p. 255-256° (dec) (EtOH). (Found: C, 30.06; H, 3.60. $C_{10}H_{14}O_4S_2ClAg$ requires C, 29.61; H, 3.48%) IR(KBr): 1430, 1420, 1140, 1110, 1085 cm^{-1} .

$(4)_2$·$CdCl_2$ was prepared from 4 (68 mg), $CdCl_2$ (80 mg) in dry EtOH (5 ml). After standing for several days at r.t. (no ppt) acetone (4 ml) was added. After several more days the separated elongated prisms were collected and dried, m.p. 252-254°. (Found: C, 41.22; H, 5.04. $C_{20}H_{28}S_4Cl_2Cd$ requires C, 41.42; H, 4.87%). IR(KBr): 1665, 1435, 1420, 1170, 645 cm^{-1}. Its X-ray structure will be reported.[5]

4·$PdCl_2$ was prepared by stirring for 1h or a solution of 4 (77mg), K_2PdCl_4 (115mg) in aq EtOH (1:3; 4ml). The ppt was collected and dried giving yellow product, m.p. 287-290°. Trituration with dry ether gave m.p.>300° (dec). (Found: C, 32.69; H, 3.97. $C_{10}H_{14}S_2Cl_2Pd$ requires C, 31.95; H, 3.75%). IR(KBr): 1420, 1410, 1227, 1035, 900, 700 cm^{-1}. Crystals suitable for X-ray structural dteremination were obtained from a large volume of acetone after long standing. The structure will be reported.[5]

4·$HgBr_2$ was prepared by stirring for 1h of 4 and $HgBr_2$ in MeOH-EtOH (1:1), m.p. 197-198°. (Found: C, 21.38; H, 2.99; S, 11.53. $C_{10}H_{14}S_2Br_2Hg$ requires C, 21.50; H, 2.53; S, 11.47%). IR(KBr): 1445, 1230, 715 cm^{-1}. Its X-ray structure will be reported.[5]

Oxidation of 4. - a) Sulfoxides: To a solution of 4 (1.1g) in MeOH-CH_2Cl_2 (1:1; 10ml) was added at 0° one of $NaIO_4$ (2.4g) in a minimal volume of aq MeOH (1:1) with stirring. Stirring was

continued overnight at r.t. The ppt was collected by filtration. The mother liquor was evaporated to dryness and the residue was chromatographed on silica (50g) with acetone-$CHCl_3$ (1:1) using a fraction collector. The upper fraction, 542 mg (49%), m.p. 198-200° (CH_2Cl_2-hexane) was the bis-sulfoxide 6. (Found: M.W. 230.0414. $C_{10}H_{14}O_2S_2$ requires 230.0434. IR(KBr): 3040-2850, 1400, 1070, 1010 cm^{-1}. NMR($CDCl_3$): δ 5.9 (m, 2 vinylic H); 4.1-2.0 (m, 8 CH_2S and 4 allylic H). M.S. $^m/e$: M^+, 230(100); 213(56); 198(5); 167(7); 163(15); 151(21); 149(33); 137(13); 119(46); 117(43). This was followed by an intermediate fraction (150mg), consisting (NMR) of 6 (80mg) + 7 (70mg). The third fraction was the bis-sulfoxide 7, 443mg (40 %, total yield of both isomers, quant), m.p. 235-237° (CH_2Cl_2-hexane). (Found: M.W. 230.0458). IR(KBr): 3040-2800, 1650, 1440, 1070-980 cm^{-1}. NMR($CDCl_3$): δ 6.0-5.6 (m, 2 vinylic H); 3.8-1.8 (m, 8 CH_2S and 4 allylic H). M.S. $^m/e$: M^+, 230(16); 213(100); 158(21); 151(18); 149(10); 119(20); 117(24). The ratio of 6:7 is 1.2:1. Their X-ray structures have been determined.[5]

b) Bis-sulfone: A solution of m-CPBA (85%; 490mg) in $CHCl_3$ (6ml) was added dropwise with stirring at 0° to one of 4 (100mg) in $CHCl_3$ (4ml). Stirring at 0-5° was continued for 4h , then allowed to stand at r.t. for 48h. Washing with satd $NaHCO_3$ solution, drying ($MgSO_4$) and removal of solvent afforded the bis-sulfone (107mg; 82%), m.p. 292-294° (dry EtOH). (Found: C, 45.39; H, 5.32. $C_{10}H_{14}O_4S_2$ requires C, 45.78; H, 5.38%). IR(KBr): 3000, 1315, 1120 cm^{-1}. NMR (DMSO-d_6): δ 5.85 (m, 2 vinylic H); 3.40 (ABq, 8H, J=14Hz, $-CH_2SO_2$); 2.41 (m, 4 allylic H). M.S. $^m/e$: M^+, 262(67); 198(5); 197(26); 183(5); 133(41); 132(51); 131(67); 117(100).

7·$2HgCl_2$: Prepared from 7 and $HgCl_2$ in dry EtOH, standing for several days, m.p. 194-195° (dec). (Found: C, 15.58; H, 1.92; S, 8.29. $C_{10}H_{14}O_2S_2Cl_4Hg_2$ requires C, 15.53; H, 1.82; S, 8.29%). IR(KBr): 1610, 1400, 990 cm^{-1}. Its X-ray structure will be reported.[5]

Complexes of 5. - 5·$HgCl_2$: A stirred solution of 5 (207mg) in aq MeOH(1:3; 8ml) was treated with $HgCl_2$ (353mg). A ppt formed immediately. After 30 min further stirring, the ppt was removed and dried (453g; 88%), m.p. 165-170°. The pure sample had m.p. 173-174° (dry EtOH). (Found: C, 26.55; H, 3.48; S, 7.05. $C_{10}H_{14}OSCl_2Hg$ requires C, 26.47; H, 3.11; S, 7.06%). IR(KBr): 2840, 1435, 1060, 935 cm^{-1}. Its X-ray structure has been determined.[5]

5·$CdCl_2$: Prepared from 5 (100mg) and $CdCl_2$ (100mg) in isopropanol (10ml). The clear solution became turbid and a ppt formed. After 2.5h stirring at r.t. the complex was obtained (171mg; 85%), m.p. > 310°. (Found: C, 32.56; H, 3.98; S, 8.25. $C_{10}H_{14}OSCl_2Cd$ requires C, 32.87; H, 3.86; S, 8.77%). IR(KBr): 1445, 1040, 940, 700 cm^{-1}.

$(5)_3\cdot(PdCl_2)_2$: Stirring a solution of 5 (171mg) and K_2PdCl_4 (201mg) in aq MeOH (1:5; 6ml) gave a yellow ppt after 30 min, 269mg (96%). (Found: C, 39.44; H, 4.83. $C_{30}H_{42}O_3S_3Cl_4Pd_2$ requires C,

39.94; H, 4.69%). IR(KBr): 1430, 1420, 1030 cm^{-1}. Crystals for X-ray structural determination were obtained after long standing from a dilute solution in acetone. The structure will be reported.[5]

Sulfilimines. - A solution of 5 (1.46g) in MeOH (10ml) was added dropwise to one of chloramine-T·$3H_2O$ (2.5g) in aq MeOH (1:1; 32ml) with stirring. After stirring at r.t. for 3h the ppt was removed and dried, 0.66g (23%) of the sulfilimine 8. It formed long needles, m.p. 166-168° (dry EtOH). (Found: C, 57.78; H, 6.06; N, 3.75; S,18.01. $C_{17}H_{21}NO_3S_2$ requires C, 58.11 H, 6.02; N, 3.99; S, 18.25%). IR(KBr): 1270, 1130, 970 cm^{-1}. NMR($CDCl_3$): δ 7.81 (d, 2 ortho-arom H, J=8Hz); 7.26 (d, 2 meta-arom H, J=8Hz); 5.92 (br t, 2 vinylic H; J=2Hz); 3.65 (ABq, J_{AB}=10Hz, 4 CH_2O); 3.23 (ABq; J_{AB}=14Hz, 4 CH_2S); 2.58-2.25 (m, allylic H); 2.40 (s, 3 CH_3). M.S. $^m/e$: M^+, 351(52); 196(38); 181(24); 92(100).

The filtrate was concentrated under reduced pressure and cooled. The new ppt of the isomer 9 was removed, 1.84g (65%), m.p. 144-145° (dry EtOH). (Found: C, 57.95; H, 6.24; N, 3.97. $C_{17}H_{21}NO_3S_2$ requires C, 58.11; H, 6.02; N, 3.99%). IR(KBr): 1290, 1150, 965 cm^{-1}. NMR($CDCl_3$): δ 7.81 (d, 2 ortho-arom H, J=8Hz); 7.27 (d, 2 meta-arom H, J=8Hz); 5.82 (t, 2 vinylic H, J=2Hz); 3.90 (ABq, J_{AB}=9Hz, 4 CH_2O); 3.27 (ABq, J_{AB}=14Hz, 4 CH_2S); 2.41 (s, 3 CH_3); 2.15 (t, J=1Hz, 4 allylic H). M.S. $^m/e$: M^+, 351(27); 196(29); 181(55); 180(33); 81(100).

Heating of 8 or 9 respectively for 5h in an NMR tube to 160° (DMSO-d_6) caused equilibration to a mixture of the two isomers in the ratio of ca 1:1, very slightly in favor of 9. The X-ray structure of 8 will be reported.[5]

9·$3HgCl_2$: The complex was formed from its components in dry EtOH after standing at r.t. for 24h . It had m.p. 185-187°. (Found: C, 17.68; H, 2.14. $C_{17}H_{21}NO_3S_2Cl_6Hg_3$ requires C, 17.51; H, 1.82%). Its X-ray structure will be reported.[5] No analogous complex was obtained from 8 under the same conditions.

1·$HgCl_2$ has been reported.[1,5]

Oxidation of 1. - a) A solution of m-CPBA(343mg) in acetone (4ml) was added dropwise at 0° to a stirred solution of 1 (51mg) in acetone (3ml). After standing overnight the usual workup afforded the bis-sulfone (66mg), m.p. 168-169° (trit.acetone). (Found: C, 37.68; H, 4.34. $C_7H_{10}O_4S_2$ requires C, 37.82; H, 4.53%). IR(KBr): 3000, 1315, 1300, 1205, 1105 cm^{-1}. NMR(DMSO-d_6): δ 3.55 (ABq, 8 CH_2SO_2); 1.67 (s, 2 CH_2). M.S. $^m/e$: M^+-SO_2, 158(8); 79(100).

b) Oxidation as for 4 with $NaIO_4$ afforded the syn-anti-bis-sulfoxide whose X-ray structural determination was carried out.[5] It had m.p. 194-196° (acetone-hexane). IR(KBr): 2960, 2910, 1410,

1300, 1270, 1235, 1190, 1145, 1100, 1075, 1020(vs), 910, 830 cm^{-1}. NMR($CDCl_3$): δ 3.32 (ABq, 8 CH_2SO); 1.67-1.26 (m, 2 CH_2).

2·$HgCl_2$ has been reported.[1]

2·$CdCl_2$ was prepared as above for 4, m.p. > 300°. (Found: C, 25.03; H, 3.00. $C_8H_{12}S_2Cl_2Cd$ requires C, 27.02; H, 3.40%). IR(KBr): 2910, 1420, 1220, 1190 cm^{-1}. Crystals were not suitable for X-ray structural determination.

Oxidation of 2. - Oxidation of 2 (172mg) in MeOH-$CHCl_3$ (2:1; 6ml) as above with $NaIO_4$ (450mg) in water (2ml) with stirring for 2h at 0° followed by stirring overnight at r.t. and the usual workup gave a solid residue (124mg, 61%) whose NMR spectrum indicated that it consisted of at least 2 isomers. A pure isomer, presumed to be the anti-anti-bis-sulfoxide was obtained by tituration with CH_2Cl_2-dry ether. It had m.p. 241-243° (THF). IR($CHCl_3$): 2990, 1160, 1035 cm^{-1}. NMR($CDCl_3$): δ 3.35 (s, 8 CH_2SO); 2.02 (s, 4 CH_2). The mother liquor was evaporated to dryness and the residue taken up in in CH_2Cl_2-hexane. After 24h standing long fine needles were collected of a second sulfoxide, m.p. 268-270°. IR(KBr): 3500, 3400, 2980, 2930, 1660, 1420, 1400, 1095, 1040(vs), 1030 cm^{-1}. M.S. $^m/e$: M^+, 204.0241(7); 187(31); 172(11); 137(10); 93(100). The crystals were decomposed by the X-ray beam.

Bis-sulfilimine of 2 was prepared in the usual way in 66 % yield, m.p. 260-261° (dry EtOH). (Found: C, 51.54; H, 5.05. $C_{22}H_{26}O_4N_2S_4$ requires C, 51.74; H, 5.3%). IR(KBr): 1275, 1140, 1080, 970 cm^{-1}. NMR(DMSO-d_6): δ 7.53 (d, J=8Hz, 4 ortho-arom H); 7.16 (d, J=8Hz; 4 meta-arom H); 3.70-3.32 (m, 8 CH_2S); 2.60-2.50 (m, 4 CH_2); 2.42 (s, 6 CH_3). M.S. $^m/e$: M^+-NTs-NHTs, 171(93); 93(100). According to NMR this is the syn-anti-bis-sulfoxide.

3·$HgCl_2$ has been reported.[1,5]

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