

ADDITION REACTIONS OF CONDENSED AZOLE DERIVATIVES WITH DIMETHYL  
ACETYLENEDICARBOXYLATE III <sup>1)</sup>

Norio Kawahara\* and Takako Nakajima

Hokkaido Institute of Pharmaceutical Sciences, 7-1

Katsuraoka-cho, Otaru-shi, Hokkaido, 047-02, Japan

Tsuneo Itoh and Haruo Ogura

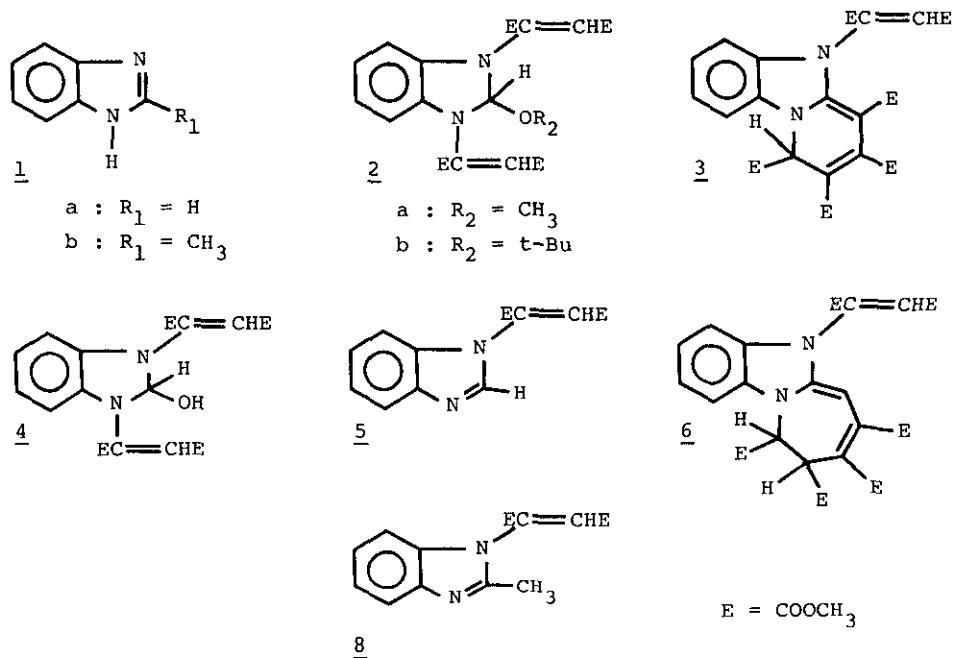
School of pharmaceutical Sciences, Kitasato University,

Minatoku, Tokyo 108, Japan

Abstract ---- Benzimidazole derivatives (1) reacted with dimethyl acetylenedicarboxylate (DMAD) in alcoholic solvents at room temperature to afford three kinds of addition products ; tricyclic compounds (3 and 6), hydration product (4) and solvent adduct (2).

Recently, we have reported that when benzoxazole derivatives were treated with dimethyl acetylenedicarboxylate (DMAD) in alcohols (MeOH, EtOH, i-PrOH and t-BuOH), some novel addition products were synthesized.<sup>1,2)</sup> In this paper, we describe the result of the addition reaction of benzimidazole derivatives with DMAD in similar reaction conditions. We could obtain a few novel addition products in t-BuOH and MeOH. Their structural assignments based on several spectral data.<sup>3)</sup>

Benzimidazole (1a, R<sub>1</sub> = H, 2.0g) was treated with DMAD (6.2ml) in t-BuOH (20ml) for 2 weeks at room temperature in the dark. A brownish crystalline solid was deposited in the reaction mixture. This solid (A) which was obtained as a mixture of four compounds, was filtered and the main product was recrystallized from MeOH 3 times to give 1,3-bis-trans-(1,2-dimethoxycarbonylvinyl)-2-methoxy-2,3-dihydro-benzimidazole (2a, R<sub>2</sub> = Me, 2.08g, mp 157-159°C) as white needles. In both <sup>1</sup>H- and <sup>13</sup>C-nmr (CDCl<sub>3</sub>) spectra of this product, only three methyl signals appeared at δ 3.02, 3.73 and 3.97 (<sup>1</sup>H-nmr), and at δ 47.85, 51.56 and 53.26 (<sup>13</sup>C-nmr) with an intensity ratio of 1 : 2 : 2. These data indicate that there are two pairs of equivalent methoxy groups in the molecule, and the resonances at δ 3.02 and



scheme 1

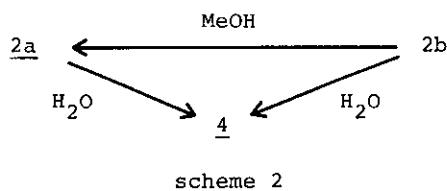
$\delta$  47.85 may be assigned to  $C_2$ -methoxy group. The original filtrate from 2a on standing at room temperature gave tetramethyl 5-trans-(1,2-dimethoxycarbonylvinyl)-9H-pyrido[1,2-a]benzimidazole-6,7,8,9-tetracarboxylate (3, 0.237g)<sup>4</sup>) as a yellow powder which recrystallized from MeOH to give pure material (mp 194-195°C). In addition to 2 and 3, four products were isolated by repeated preparative TLC (silica gel 60F<sub>254</sub> Merck 5744) from the mother liquor. The structures of 4 [oil, 0.739g,  $C_{19}H_{20}N_2O_9$ , m/e 420( $M^+$ )] and 5 [oil, 0.928g,  $C_{13}H_{12}N_2O_4$ , m/e 260( $M^+$ )] were assigned on the basis of spectral data to be a 1:2:1 molar adduct and a 1:1 molar adduct shown in scheme 1. Compound (4) contains one mole of  $H_2O$  in the molecule. Other two oily materials, however, have unsucceeded to be purified because of their too labile nature. On the other hand, the above crystalline solid (A) was purified by preparative TLC on silica gel (benzene : ethyl acetate = 3 : 2) and the main product (a pale yellow powder, 6.274g) was recrystallized from EtOAc to give pure crystalline compound (2b,  $R_2 = t-Bu$ , mp 140-141°C). The <sup>1</sup>H-nmr spectrum of 2b showed the presence of a <sup>t</sup>BuO group at  $\delta$  1.12 (9H, singlet) in the molecule. When recrystallized from MeOH, 2b was converted to 2a. Furthermore, 2b was easily changed to 4 by standing at room temperature in EtOH(EtOAc,  $CH_2Cl_2$ ) containing  $H_2O$  or stirring with silica gel in the same solvents. 2a was also converted to 4

Table 1 The some spectral data of the products

products	MS(M <sup>+</sup> )	<sup>1</sup> H and <sup>13</sup> C nmr(CDCl <sub>3</sub> ) δ(ppm)
<u>2a</u>	434	<sup>1</sup> H : 3.02(s, 3H, OCH <sub>3</sub> ), 3.73 and 3.97(each s, 6H, 2XOCH <sub>3</sub> ), 5.88(s, 2H, vinylic), 6.42(s, 1H, -CH-), 6.94(m, 4H, aromatic), <sup>13</sup> C : 47.85, 51.56 and 53.26(5XOCH <sub>3</sub> )
<u>2b</u>	476	<sup>1</sup> H : 1.12(s, 9H, t-Bu), 3.74 and 3.97(each s, 6H, 2XOCH <sub>3</sub> ), 5.84(s, 2H, vinylic), 6.46(s, 1H, -CH-), 6.80-7.00(m, 4H, aromatic)
<u>3</u>	544	<sup>1</sup> H : 3.66, 3.73, 3.77 and 3.80(each s, 3H, OCH <sub>3</sub> ), 3.90(s, 6H, 2XOCH <sub>3</sub> ), 6.20(s, 1H, vinylic), 6.50(s, 1H, -CH-), 7.20-7.50(m, 4H, aromatic), <sup>13</sup> C : 52.19, 52.53, 52.78, 53.26, 53.41 and 53.99(6XOCH <sub>3</sub> )
<u>4</u>	420	<sup>1</sup> H : 3.67, 3.69, 3.73 and 3.90(each s, 3H, OCH <sub>3</sub> ), 5.66(2H, vinylic), 6.88-6.94(m, 4H, aromatic), 7.26(s, 2H, -CH- and OH)
<u>5</u>	260	<sup>1</sup> H : 3.86 and 4.00(each s, 3H, OCH <sub>3</sub> ), 6.43(s, 1H, vinylic), 7.30-7.90(m, 4H, aromatic), 8.04(s, 1H, vinylic)
<u>6</u>	558	<sup>1</sup> H : 3.55, 3.70, 3.74, 3.78, 3.82 and 3.88(each s, 3H, OCH <sub>3</sub> ), 4.42(s, 1H, vinylic), 5.44(d, 1H, J=6Hz), 5.89(d, 1H, J=6Hz), 7.00-7.30(m, 4H, aromatic), 6.62(s, 1H)
<u>8</u>	274	<sup>1</sup> H : 2.46(s, 3H, C-CH <sub>3</sub> ), 3.52 and 3.82(each s, 3H, OCH <sub>3</sub> ), 7.00-7.40(m, 5H, aromatic and vinylic), <sup>13</sup> C : 13.69 (C-CH <sub>3</sub> ), 52.58 and 53.65(each OCH <sub>3</sub> )

slowly when stirred in the same solvents containing H<sub>2</sub>O. These data are compatible with the structure of 2b bearing a tertiary butoxy group.

When MeOH was used as the reaction solvent, only 5 (0.928g) was isolated by careful preparative TLC on silica gel (benzene : ethyl acetate = 3 : 2). Many other materials, however, were not



successful for isolation because of their too small content and/or labile nature. 2-Methylbenzimidazole (1b, R<sub>1</sub> = CH<sub>3</sub>, 2.0g) was treated with DMAD (6.2ml) in t-BuOH (20ml) for 2 weeks at room temperature in the dark. The reaction mixture was submitted to column chromatography using silica gel and the eluates were divided into five fractions, among which two compounds (6 and 7) were isolated by preparative TLC on silica gel (EtOH : CHCl<sub>3</sub> = 1 : 20) but the separation of other minor mixed products was considerably difficult even by repeated preparative TLC.

The structure of 6 (mp 189-190°C, 0.603g) was assigned from the result of the instrumental analyses. The absorption peaks at  $\delta$  5.44 (1H, d, J=6Hz) and  $\delta$  5.89 (1H, d, J=6Hz) in  $^1\text{H}$ -nmr spectrum show a typical AB quartet splitting pattern. The structure of 7 [mp 199-200°C, 0.553g, m/e 558(M<sup>+</sup>),  $^1\text{H}$ -nmr(CDCl<sub>3</sub>)  $\delta$  3.53, 3.58, 3.63, 3.69, 3.73, 3.77, 3.80 and 3.85(each singlet), 4.17(s, 1H), 5.46(d, 1H, J=6Hz), 5.94(d, 1H, J=6Hz), 7.10-7.32(m, 5H),  $^{13}\text{C}$ -nmr(CDCl<sub>3</sub>)  $\delta$  51.9, 52.4, 52.7, 53.0, 53.5 and 53.7(each OCH<sub>3</sub>)] was estimated as a mixture of the geometrical isomers of 6 since eight signals are recognized in the region of  $\delta$  3.53-3.85 in  $^1\text{H}$ -nmr spectrum. Further research is carrying out now.

When MeOH was used as the reaction solvent, four products were isolated by repeated preparative TLC on silica gel (CHCl<sub>3</sub> : ethyl acetate = 1 : 1) of the reaction mixture. These products are all oily and 8 [oil, 2.814g, m/e 274(M<sup>+</sup>), C<sub>14</sub>H<sub>14</sub>N<sub>2</sub>O<sub>4</sub>] was only purified and its structure was elucidated from spectral data to be a 1:1 molar adduct in scheme 1.

In all experiments as described above, a lot of minor products were detectable but not investigated. Although a ring-opened product was not obtained<sup>1)</sup>, a few new compounds containing solvent adducts were obtained. In the case of benzimidazole derivatives also, the formation mechanism of such adducts 2b and 4 may be assumed identical to that of benzoxazole derivatives with DMAD<sup>1)</sup>.

#### REFERENCES AND NOTES

- 1 Part II : N. Kawahara, M. Katsuyama, T. Itoh and H. Ogura, Heterocycles, 1981, 16 235.
- 2 N. Kawahara, M. Katsuyama, T. Itoh and H. Ogura, Heterocycles, 1980, 14 15.
- 3 The structure assignments of the products are based on the satisfactory elemental analyses and spectral data.
- 4 R. M. Acheson, M. W. Foxton, P. J. Abbot and K. R. Mills, J. Chem. Soc (C), 1968, 882.

Received, 6th January, 1982

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

Ishai Sataty, Michael Peled and David Ginsburg

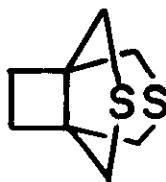
Department of Chemistry, Technion - Israel Institute of Technology, Haifa.

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.<sup>1</sup> We had available compounds 1-3<sup>2</sup> and 4<sup>3</sup> and have shown that a "Klammer" effect indeed occurs within the series (albeit 4 contains a cyclohexene ring rather than a fully reduced one).<sup>4</sup>



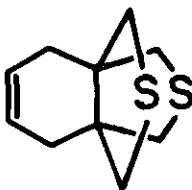
1



2



3

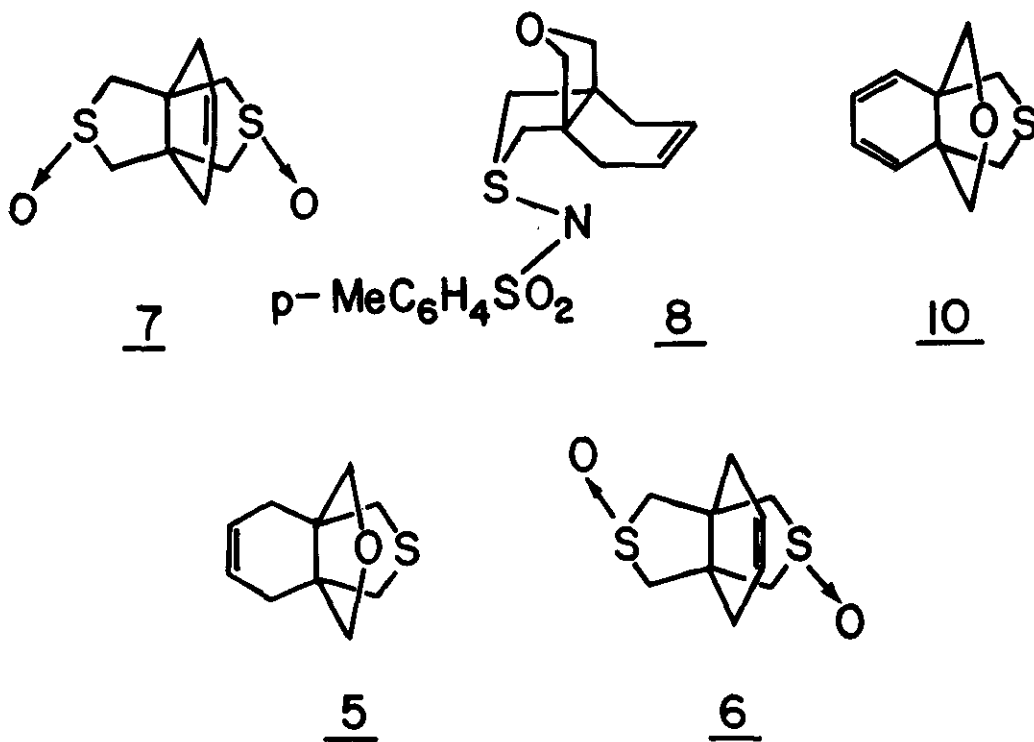


4

\* 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.<sup>5</sup>

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



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.<sup>5</sup> 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 oxathiopropelladiene 10 was treated with N-phenyltriazolinedione it reacted exclusively syn to the thioether ring, i.e. anti to the ether ring.<sup>6</sup> 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<sub>2</sub> has been reported.<sup>1</sup>

4·AgClO<sub>4</sub> was prepared from 4 (29 mg) in dry EtOH (5 ml) by addition of AgClO<sub>4</sub> (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<sub>10</sub>H<sub>14</sub>O<sub>4</sub>S<sub>2</sub>ClAg requires C, 29.61; H, 3.48%) IR(KBr): 1430, 1420, 1140, 1110, 1085 cm<sup>-1</sup>.

(4)<sub>2</sub>·CdCl<sub>2</sub> was prepared from 4 (68 mg), CdCl<sub>2</sub> (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<sub>20</sub>H<sub>28</sub>S<sub>4</sub>Cl<sub>2</sub>Cd requires C, 41.42; H, 4.87%). IR(KBr): 1665, 1435, 1420, 1170, 645 cm<sup>-1</sup>. Its X-ray structure will be reported.<sup>5</sup>

4·PdCl<sub>2</sub> was prepared by stirring for 1h or a solution of 4 (77mg), K<sub>2</sub>PdCl<sub>4</sub> (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<sub>10</sub>H<sub>14</sub>S<sub>2</sub>Cl<sub>2</sub>Pd requires C, 31.95; H, 3.75%). IR(KBr): 1420, 1410, 1227, 1035, 900, 700 cm<sup>-1</sup>. Crystals suitable for X-ray structural determination were obtained from a large volume of acetone after long standing. The structure will be reported.<sup>5</sup>

4·HgBr<sub>2</sub> was prepared by stirring for 1h of 4 and HgBr<sub>2</sub> in MeOH-EtOH (1:1), m.p. 197-198°. (Found: C, 21.38; H, 2.99; S, 11.53. C<sub>10</sub>H<sub>14</sub>S<sub>2</sub>Br<sub>2</sub>Hg requires C, 21.50; H, 2.53; S, 11.47%). IR(KBr): 1445, 1230, 715 cm<sup>-1</sup>. Its X-ray structure will be reported.<sup>5</sup>

Oxidation of 4. - a) Sulfoxides: To a solution of 4 (1.1g) in MeOH-CH<sub>2</sub>Cl<sub>2</sub> (1:1; 10ml) was added at 0° one of NaIO<sub>4</sub> (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- $\text{CHCl}_3$  (1:1) using a fraction collector. The upper fraction, 542 mg (49%), m.p. 198-200° ( $\text{CH}_2\text{Cl}_2$ -hexane) was the bis-sulfoxide 6. (Found: M.W. 230.0414.  $\text{C}_{10}\text{H}_{14}\text{O}_2\text{S}_2$  requires 230.0434. IR(KBr): 3040-2850, 1400, 1070, 1010  $\text{cm}^{-1}$ . NMR( $\text{CDCl}_3$ ):  $\delta$  5.9 (m, 2 vinylic H); 4.1-2.0 (m, 8  $\text{CH}_2\text{S}$  and 4 allylic H). M.S.  $m/e$ :  $\text{M}^+$ , 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° ( $\text{CH}_2\text{Cl}_2$ -hexane). (Found: M.W. 230.0458). IR(KBr): 3040-2800, 1650, 1440, 1070-980  $\text{cm}^{-1}$ . NMR( $\text{CDCl}_3$ ):  $\delta$  6.0-5.6 (m, 2 vinylic H); 3.8-1.8 (m, 8  $\text{CH}_2\text{S}$  and 4 allylic H). M.S.  $m/e$ :  $\text{M}^+$ , 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.<sup>5</sup>

b) Bis-sulfone: A solution of m-CPBA (85%; 490mg) in  $\text{CHCl}_3$  (6ml) was added dropwise with stirring at 0° to one of 4 (100mg) in  $\text{CHCl}_3$  (4ml). Stirring at 0-5° was continued for 4h, then allowed to stand at r.t. for 48h. Washing with satd  $\text{NaHCO}_3$  solution, drying ( $\text{MgSO}_4$ ) and removal of solvent afforded the bis-sulfone (107mg; 82%), m.p. 292-294° (dry EtOH). (Found: C, 45.39; H, 5.32.  $\text{C}_{10}\text{H}_{14}\text{O}_4\text{S}_2$  requires C, 45.78; H, 5.38%). IR(KBr): 3000, 1315, 1120  $\text{cm}^{-1}$ . NMR ( $\text{DMSO}-d_6$ ):  $\delta$  5.85 (m, 2 vinylic H); 3.40 (ABq, 8H,  $J=14\text{Hz}$ ,  $-\text{CH}_2\text{SO}_2$ ); 2.41 (m, 4 allylic H). M.S.  $m/e$ :  $\text{M}^+$ , 262(67); 198(5); 197(26); 183(5); 133(41); 132(51); 131(67); 117(100).

7- $2\text{HgCl}_2$ : Prepared from 7 and  $\text{HgCl}_2$  in dry EtOH, standing for several days, m.p. 194-195° (dec). (Found: C, 15.58; H, 1.92; S, 8.29.  $\text{C}_{10}\text{H}_{14}\text{O}_2\text{S}_2\text{Cl}_4\text{Hg}_2$  requires C, 15.53; H, 1.82; S, 8.29%). IR(KBr): 1610, 1400, 990  $\text{cm}^{-1}$ . Its X-ray structure will be reported.<sup>5</sup>

Complexes of 5. - 5- $\text{HgCl}_2$ : A stirred solution of 5 (207mg) in aq MeOH(1:3; 8ml) was treated with  $\text{HgCl}_2$  (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.  $\text{C}_{10}\text{H}_{14}\text{OSCl}_2\text{Hg}$  requires C, 26.47; H, 3.11; S, 7.06%). IR(KBr): 2840, 1435, 1060, 935  $\text{cm}^{-1}$ . Its X-ray structure has been determined.<sup>5</sup>

5- $\text{CdCl}_2$ : Prepared from 5 (100mg) and  $\text{CdCl}_2$  (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.  $\text{C}_{10}\text{H}_{14}\text{OSCl}_2\text{Cd}$  requires C, 32.87; H, 3.86; S, 8.77%). IR(KBr): 1445, 1040, 940, 700  $\text{cm}^{-1}$ .

(5)<sub>3</sub>·( $\text{PdCl}_2$ )<sub>2</sub>: Stirring a solution of 5 (171mg) and  $\text{K}_2\text{PdCl}_4$  (201mg) in aq MeOH (1:5; 6ml) gave a yellow ppt after 30 min, 269mg (96%). (Found: C, 39.44; H, 4.83.  $\text{C}_{30}\text{H}_{42}\text{O}_3\text{S}_3\text{Cl}_4\text{Pd}_2$  requires C,



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

Sulfilimines. - A solution of 5 (1.46g) in MeOH (10ml) was added dropwise to one of chloramine-T $\cdot$ 3H<sub>2</sub>O (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<sub>17</sub>H<sub>21</sub>NO<sub>3</sub>S<sub>2</sub> requires C, 58.11 H, 6.02; N, 3.99; S, 18.25%). IR(KBr): 1270, 1130, 970  $\text{cm}^{-1}$ . NMR(CDCl<sub>3</sub>):  $\delta$  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<sub>AB</sub>=10Hz, 4 CH<sub>2</sub>O); 3.23 (ABq; J<sub>AB</sub>=14Hz, 4 CH<sub>2</sub>S); 2.58-2.25 (m, allylic H); 2.40 (s, 3 CH<sub>3</sub>). M.S. <sup>m</sup>/e: M<sup>+</sup>, 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<sub>17</sub>H<sub>21</sub>NO<sub>3</sub>S<sub>2</sub> requires C, 58.11; H, 6.02; N, 3.99%). IR(KBr): 1290, 1150, 965  $\text{cm}^{-1}$ . NMR(CDCl<sub>3</sub>):  $\delta$  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<sub>AB</sub>=9Hz, 4 CH<sub>2</sub>O); 3.27 (ABq, J<sub>AB</sub>=14Hz, 4 CH<sub>2</sub>S); 2.41 (s, 3 CH<sub>3</sub>); 2.15 (t, J=1Hz, 4 allylic H). M.S. <sup>m</sup>/e: M<sup>+</sup>, 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<sub>6</sub>) 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.<sup>5</sup>

9·3HgCl<sub>2</sub>: 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<sub>17</sub>H<sub>21</sub>NO<sub>3</sub>S<sub>2</sub>Cl<sub>6</sub>Hg<sub>3</sub> requires C, 17.51; H, 1.82%). Its X-ray structure will be reported.<sup>5</sup> No analogous complex was obtained from 8 under the same conditions.

1·HgCl<sub>2</sub> has been reported.<sup>1,5</sup>

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<sub>7</sub>H<sub>10</sub>O<sub>4</sub>S<sub>2</sub> requires C, 37.82; H, 4.53%). IR(KBr): 3000, 1315, 1300, 1205, 1105  $\text{cm}^{-1}$ . NMR(DMSO-d<sub>6</sub>):  $\delta$  3.55 (ABq, 8 CH<sub>2</sub>SO<sub>2</sub>); 1.67 (s, 2 CH<sub>2</sub>). M.S. <sup>m</sup>/e: M<sup>+</sup>-SO<sub>2</sub>, 158(8); 79(100).

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

1300, 1270, 1235, 1190, 1145, 1100, 1075, 1020(vs), 910, 830  $\text{cm}^{-1}$ . NMR( $\text{CDCl}_3$ ):  $\delta$  3.32 (ABq, 8  $\text{CH}_2\text{SO}$ ); 1.67-1.26 (m, 2  $\text{CH}_2$ ).

$\underline{2} \cdot \text{HgCl}_2$  has been reported.<sup>1</sup>

$\underline{2} \cdot \text{CdCl}_2$  was prepared as above for 4, m.p.  $> 300^\circ$ . (Found: C, 25.03; H, 3.00.  $\text{C}_8\text{H}_{12}\text{S}_2\text{Cl}_2\text{Cd}$  requires C, 27.02; H, 3.40%). IR(KBr): 2910, 1420, 1220, 1190  $\text{cm}^{-1}$ . Crystals were not suitable for X-ray structural determination.

Oxidation of 2. - Oxidation of 2 (172mg) in  $\text{MeOH-CHCl}_3$  (2:1; 6ml) as above with  $\text{NaIO}_4$  (450mg) in water (2ml) with stirring for 2h at  $0^\circ$  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 titration with  $\text{CH}_2\text{Cl}_2$ -dry ether. It had m.p.  $241-243^\circ$  (THF). IR( $\text{CHCl}_3$ ): 2990, 1160, 1035  $\text{cm}^{-1}$ . NMR( $\text{CDCl}_3$ ):  $\delta$  3.35 (s, 8  $\text{CH}_2\text{SO}$ ); 2.02 (s, 4  $\text{CH}_2$ ). The mother liquor was evaporated to dryness and the residue taken up in  $\text{CH}_2\text{Cl}_2$ -hexane. After 24h standing long fine needles were collected of a second sulfoxide, m.p.  $268-270^\circ$ . IR(KBr): 3500, 3400, 2980, 2930, 1660, 1420, 1400, 1095, 1040(vs), 1030  $\text{cm}^{-1}$ . 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.  $260-261^\circ$  (dry EtOH). (Found: C, 51.54; H, 5.05.  $\text{C}_{22}\text{H}_{26}\text{O}_4\text{N}_2\text{S}_4$  requires C, 51.74; H, 5.3%). IR(KBr): 1275, 1140, 1080, 970  $\text{cm}^{-1}$ . NMR( $\text{DMSO-d}_6$ ):  $\delta$  7.53 (d,  $J=8\text{Hz}$ , 4 ortho-arom H); 7.16 (d,  $J=8\text{Hz}$ ; 4 meta-arom H); 3.70-3.32 (m, 8  $\text{CH}_2\text{S}$ ); 2.60-2.50 (m, 4  $\text{CH}_2$ ); 2.42 (s, 6  $\text{CH}_3$ ). M.S.  $m/e$ :  $M^+$ -NTs-NHTs, 171(93); 93(100). According to NMR this is the syn-anti-bis-sulfoxide.

$\underline{3} \cdot \text{HgCl}_2$  has been reported.<sup>1,5</sup>

#### REFERENCES

1. I. Sataty, M. Kapon, M. Kaftory, and D. Ginsburg, Heterocycles, 1982, 17, 159.
2. We thank Prof. Dr. K. Weinges of Heidelberg for generous samples of these compounds.
3. J. Altman, E. Babad, J. Pucknat, N. Reshef, and D. Ginsburg, Tetrahedron, 1968, 24, 975
4. Ref. 1, footnote 1.
5. M. Kapon and M. Kaftory, to be published.
6. P. Ashkenazi, J. Olikier, and D. Ginsburg, Tetrahedron, 1978, 34, 2171.

Received, 25th March, 1982