Tetrahedron Vol. 33, pp 1183 to 1188 Pergamon Press 1977 Printed in Great Britain

PROPELLANES—XXXVIII

REACTION OF TETRAENIC THIAPROPELLANES AND THEIR DERIVATIVES WITH 4-PHENYL-1,2,4-TRIAZOLINE-3,5-DIONE*

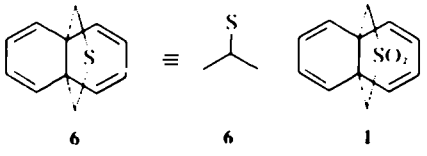
J. KALO,[a] E. VOGEL[b] and D. GINSBURG[a]†

[a]Department of Chemistry, Israel Institute of Technology, Haifa, Israel
[b]Institut fur Organische Chemie, Universität Koln, Germany

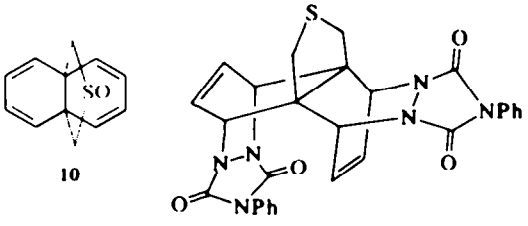
(*Received in UK 27 September 1976; Accepted for publication 16 November 1976*)

Abstract—The direction of attack of tetraenic and dienic propellanes containing thio-ether, sulfoxide and sulfone rings, by the title dienophile, has been determined. In the dienic series attack occurs only from above in all the substrates but in the tetraenic series there is exclusive attack from below in the thio-ether, mainly attack from above in the sulfone and a complex array of products is obtained from the sulfoxide.

An important set of substrates within the framework of our studies on the factors which influence the direction of attack of dienic and tetraenic propellanes[1] would be 12 - thia[4.4.3]propella - 2,4,7,9 - tetraene **6** and the sulfone **1** and sulfoxide **10** derived therefrom. It was of interest to learn whether the thio-ether **6** would behave analogously



6 **6** **1**



10

8

to the corresponding ether which is first attacked from below, then with a second mole of dienophile from above, affording the unsymmetrical *bis*-adduct **8**.[1a] We would not expect *a priori* the sulfone **1** and sulfoxide **10** to behave differently from their parent **6**. Comparison of such derivatives with their parent sulfide insofar as their PE spectra are concerned would not beget great expectations of dissimilar behavior.[2] EH calculations also predict similar rather than different behavior of these compounds.[2] One would not expect the sulfone to direct the dienophile towards attack from "above", i.e. *syn* to the sulfone in the same way as imide carbonyl groups evidently direct it to attack from their *syn* side.[1a,b] Nevertheless since sulfur is quite different than oxygen in its possibilities for hybridization, it was of interest to study this group of compounds.

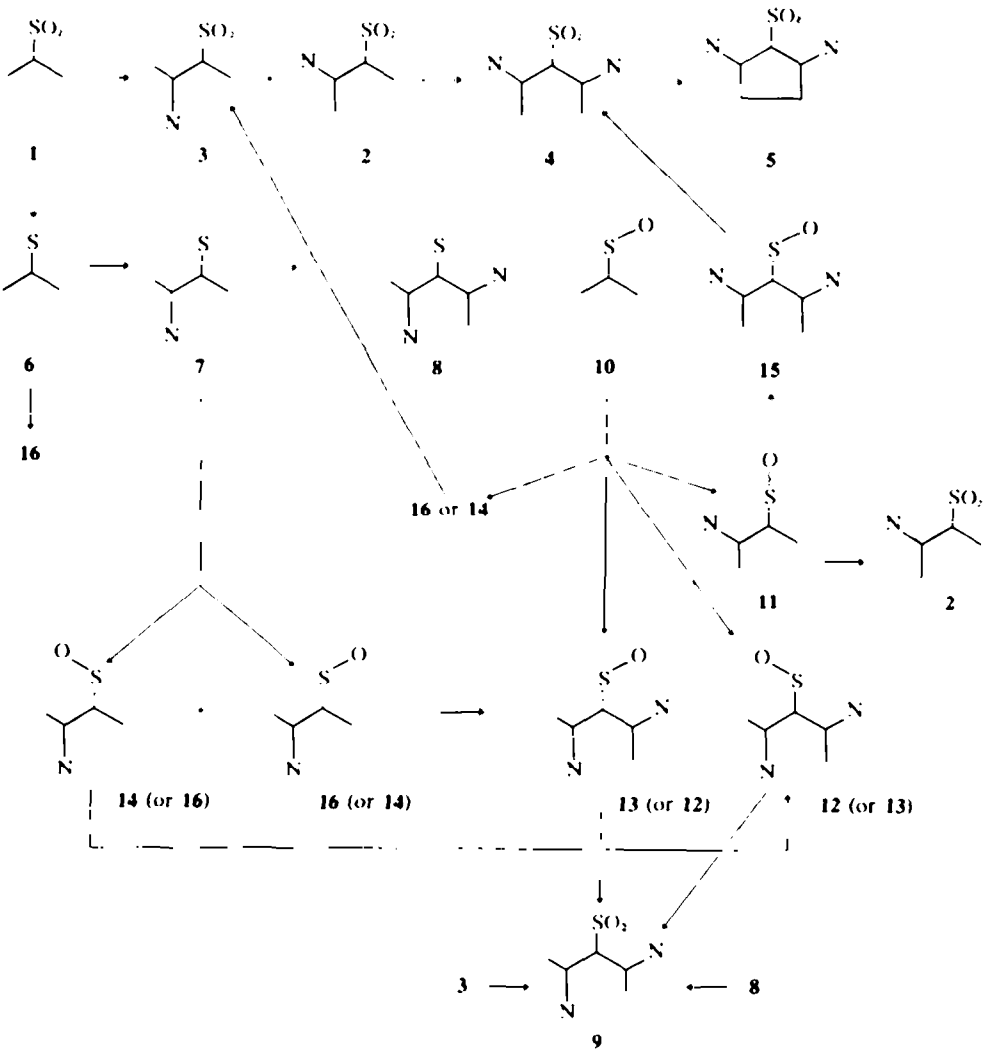
In the event, unexpected results, summarized in Scheme 1, were obtained.

The sulfone **1** affords with one equivalent of dienophile two mono-adducts **2** (90%) and **3** (5%). That **2** has the configuration shown was proved by the fact that it gives with a second equivalent of dienophile the symmetrical *bis*-adduct **4** which exhibits in its NMR spectrum a singlet for the four CH_2SO_2 protons. But even more important, we have repeated the structural proof employed in the case of the analogous *bis*-adduct of the tetraenic methylimide,[1a] and converted **4**, by irradiation, into the cage compound **5**. The yield was somewhat lower than in the case cited because some SO_2 loss accompanies the [2 + 2]photoaddition. No analogous competitive reaction can occur in the case of the methylimide.

The sulfide **6** affords with one equivalent of dienophile the mono-adduct **7**. That the configuration of **7** is correct as shown stems from its oxidation to **3**, the only possible monosulfone isomeric with **2**. And just as the second step of the Diels-Alder addition for **2** leads to attack from above to give **4**, **7** also is attacked from above to yield the unsymmetrical *bis*-adduct **8** which exhibits an AB quartet for its four CH_2S protons. The same multiplicity is found for the four CH_2SO_2 protons in its oxidation product **9**, the C_s isomer of the more symmetrical C_2, product **4**. Thus, it appears throughout Scheme 1, that here too as found earlier,[1a,b,c] the boat-shaped underpinnings of the molecule hinder approach of the second mole of dienophile from "below" as compared to the steric hindrance exerted by the CH_2S or CH_2SO_2 hydrogens. This experience will be observed once again in our discussion of the products obtained from the sulfoxide **10**. Only bridged [10] annulenes[1d] and one propellatetraene[1a] provide exceptions to this rule.

Although we have proved unequivocally the structures of the above compounds we are presently at a loss to explain wherefore the sulfone **1** behaves in a manner diametrically opposed to the behavior of the sulfide **6** and in so reminiscent a manner to the corresponding methylimide in which we have invoked secondary orbital effects to explain exclusive attack from above to give the analog of **2**.[1a] In the latter case we had support also from additional members of the methylimide family, a diene and two trienes, all of which gave a Diels-Alder adduct of the same configuration.[1b] Later we found that the unsubstituted (on nitrogen) tetraenic imide and its tetraenic anhydride precursor are also attacked ex-

*Part XXXVII, *Tetrahedron* 33, 1177 (1977).



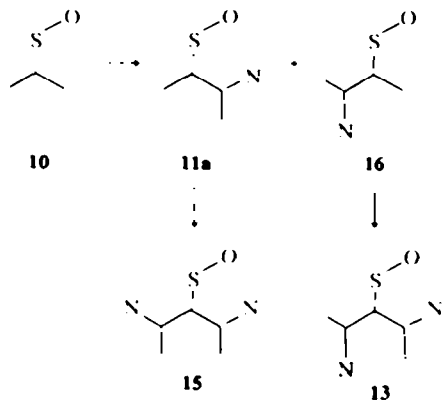
Scheme 1.

clusively from above.[1e] EH calculations are in agreement with the existence of secondary orbital effects involving the π^* orbitals (LUMO) of the CO groups of these substrates and the n combination of the lone pair orbitals (HOMO) of the doubly-bonded N atoms of the dienophile.[2] But as mentioned above we cannot invoke a similar explanation for the sulfone or sulfoxide.

Yet, experiment may be continued even whilst explanation, alack, is lacking. Thus we very much hoped that the sulfoxide might behave "logically" within our unexplained framework. Scheme 2 summarizes the behavior which might be simplistically anticipated by drawing an analogy from the behavior of **1** and **6**.

It must first be noted that the NMR spectrum of **10** indicates its unsymmetrical nature. It exhibits an AB quartet for the four CH_2SO protons. It is well known that 35–43 kcal/mole of energy are required to racemize optically active sulfoxides.[4] In the case of **10** of *meso*-type, no optical activity is possible but inversion of the sulfoxide is, in principle, possible. However, heating in an NMR tube at temperatures up to 200° for 1 hr did not cause the said ABq to collapse to a singlet. (Nor was analogous collapse noted in any other of the sulfoxides herein, under the same conditions).

Therefore let us look at the symbol of **10** in Scheme 2 as

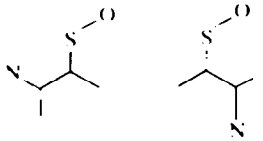


Scheme 2.

follows: The diene ring on the right has an oxygen somewhere above it. It is, to an approximation, similar to each of the diene rings in **1**. The diene ring on the left, however, is, to an approximation, similar to either of the diene rings of the sulfide **6**. How nice it would be if the ring on the right were to be attacked from above, as in the sulfone, to give **11a** and the ring on the left from below, as

in the sulfide, to give **16**. Of course, this need not occur on a 1:1 basis. We had noted that kinetically, the Diels–Alder reactions of the sulfide **6** at each stage require minutes whilst those of the sulfone **1** require hours. We should therefore not be surprised to obtain more of **16** than of **11a** and possibly **16** might even go on to react to afford a *bis*-adduct before the "sulfone side" of **10** reacted. If so the major *bis*-adduct expected would be **13** whose configuration may be correlated and proved by oxidation to the known **9**. But **11a**, if obtained, may also, in principle, react further and give **15** which may be oxidized to the already known symmetrical sulfone **4**.

If, then, we were to obtain a reaction mixture from **10** consisting of at most two mono-adducts and two *bis*-adducts and if each of the isolated mono-adducts, singly reacted further with dienophile to afford the *same* *bis*-adducts already isolated in the mixture of four products, the structures written in Scheme 2 would be reasonable, even if not proved unequivocally (note for example, that **15** may be obtained also from a compound having structure **11b** and that a fourth different mono-adduct, **14**, is also capable of existence).

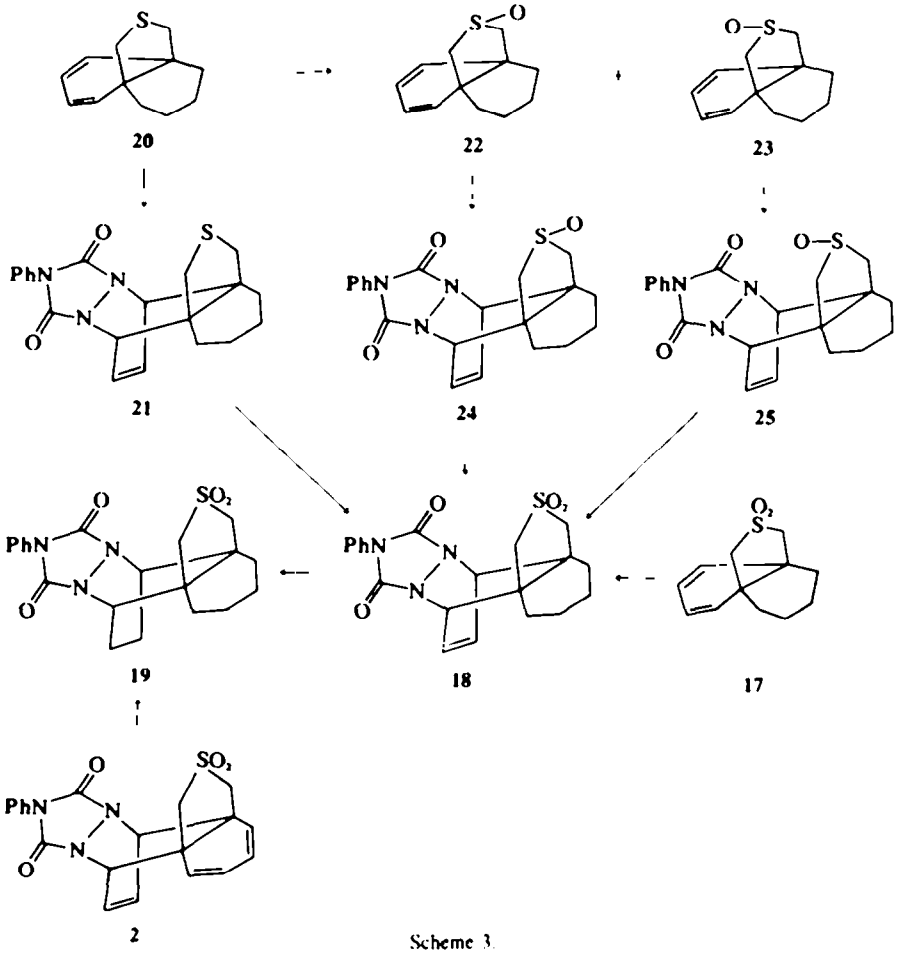


11b **14**

In the event, it was immediately clear from the NMR spectrum of the crude reaction mixture of **10** with one equivalent of dienophile that a mixture of products was obtained. This, being expected, did not lead to consternation. But the NMR spectra of the four products isolated after repeated tlc led to hope that the data summarized in Scheme 2 is indeed correct. For besides recovered starting material the four compounds isolated were eluted from the tlc plates in the order of mono-adduct, *bis*-adduct, *bis*-adduct, mono-adduct.

We must state that our hope was dashed and the contents of Scheme 2 are fiction. Scheme 2 has served as a useful vehicle in this discussion but fact is more complex than fiction and the results obtained are summarized in Scheme 1.

The relative amounts isolated of **11**, **12**, **13** and **14** (or **16**) are recorded in the Experimental. It should however, be noted from Scheme 1 that we do not know which epimeric sulfoxide **11** actually represents, **11a** or **11b**. We know that we have obtained both **12** and **13**, since each upon oxidation yields the C_s-sulfone **9**, but we do not know which epimer is which. We know that we have as the fourth component of the product mixture one of the sulfoxides of the configuration represented by **14** or **16** but again we do not know which sulfoxide epimer it is, **14** or **16**. And this despite the fact that we have in this case both epimers in hand as components of a mixture of oxidation products of the sulfide **7**. We are not prepared to assign such structural details on the basis of NMR spectra. We



Scheme 3.

have already noted that some more courageous colleagues assign configuration on the basis of NMR chemical shifts even when they have in hand only one of two possible isomers. Not being wagering men we dare not do so even when both are in hand since the odds of being correct still remain 50:50. We are hoping that it may be possible to obtain **14** or **16** as untwinned crystals so that we may learn the correct assignment of S–O epimers in the pairs **12–13**, **14–16**.

The configuration of **11** stems from its affording the *bis*-adduct **15** which was oxidized to yield the C_2, sulfone **4**. The configuration of **14** and **16** stems both from the fact that they are obtained from **7** and from the oxidation of that (**14** or **16**) obtained as a component of the product mixture from **10** to the sulfone **3**.

It should be noted that the second equivalent of dienophile *always* attacks from above, presumably for steric reasons. Steric hindrance is, relatively, less from this direction.

If the reactions summarized in Scheme 3 presented us with a surprise it is because of the way they appear in comparison with Scheme 1, not for *a priori* reasons. Here, all of the substrates were attacked by the dienophile exclusively from above.

The sulfide **20** gave the product (necessarily a mono-adduct) **21** which was oxidized to the sulfone **18**. This adduct was also obtained from the sulfone **17**. Since the adduct **2** of *proven* configuration (2→4→5 in Scheme 1) and **18** both afforded the *same* perhydro-derivative **19** upon reduction the configurations of **17** and **21** are correct as written.

Two epimeric sulfoxides **22** and **23** were obtained by periodate oxidation of **20**. These gave, respectively, the adducts **24** and **25**. The latter two compounds gave **18** upon oxidation thus proving that they are members of the *same* configurational family. But in this case we know the detailed configuration also at the sulfur atom because an X-ray structural determination showed that **24** is in full configurational detail, as represented in **24**.[7] From this follow the details at sulfur for **22**, **23** and **25**. (The X-ray structure of **24**, of course, proves the correctness also of the chemical correlations, e.g. 2→4→5; 2→19←18←17, etc.).

The above results do not necessarily prove the falseness of our thesis regarding secondary orbital overlap control of the Diels–Alder reactions under discussion (cf. preceding paper for a fuller discussion of this). It may be that it is false and that an entirely different explanation may be given for the experimental facts. We rather believe, however, that in this intricate fabric of nuances, which is, as usual, constituted of steric and electronic factors, we have not yet fathomed all of these factors sufficiently. Both the steric factors and the electronic ones of orbital overlap are through-space factors. We have not at all discussed heretofore through-bond considerations.

We continue a two-pronged attack. In Haifa we investigate, experimentally, the behavior of other substrates, both propellanes and bridged annulenes produced in Köln. In Darmstadt, Prof. R. Gleiter[8] has embarked on MINDO/3 calculations which may go beyond his EH data in helping us to understand the reasons for stereoselectivity in direction of attack in our variegated substrates.

EXPERIMENTAL

IR spectra were measured (in $CHCl_3$ unless otherwise specified) using a Perkin Elmer 257 or 237 spectrometer. NMR spectra were measured on a Varian T-60 or A-60 instrument (given in τ values) and mass spectra on the Atlas CH4 (70 eV) or a Varian MAT-711 (100 eV) mass spectrometer. M.ps are uncorrected. Organic solutions were dried over anhyd. $MgSO_4$. Solvents were removed in a rotary evaporator at water pump pressure. Preparative silica plates were 20 × 20 cm of 70 g silica gel 60 PF 254 produced by E. Merck. Degassing of solns before irradiation was carried out by a series of 4 freezing and melting operations at 10^{-3} torr. Diels–Alder reactions were conducted in CH_2Cl_2.

Mono-adduct **2**. Reaction between **1** (330 mg) in 10 ml with PTD (265 mg) in 10 ml required 1 hr before red color was discharged. After removal of solvent the crude product was triturated several times with hot MeCN affording **2** (479 mg; 80%. m.p. 279–280° (dec) accompanied by **3** (30 mg; 5%; see below). The NMR spectrum showed the presence of some unreacted **2** and **4** was also isolated in 4% yield. Compound **2**: (Found: S, 8.39. $C_{26}H_{17}N_3O_4S$ requires: S, 8.12%). IR (KBr): 2980, 2930, 1770, 1700, 1500, 1410, 1320, 1180 cm^{-1}. NMR (DMSO-d_6): 2.43 (s, 5 arom H); 3.23 (t, 2 vinylic H, J = 3 Hz); 4.19–4.34 (m, 4 dienic H); 5.00 (t, 2 C$\underline{H}$N, J = 3 Hz); CH_2SO_2 unobserved due to solvent. MS. 254 (18); 235 (100); 168 (12); 128 (15); 120 (24); 119 (5).

Bis-*adduct* **4**. Reaction between **2** (119 mg) in 50 ml and PTD (52.5 mg) in 10 ml required 48 hr stirring at room temp. Most of the product **4** precipitated (135 mg) but evaporation of solvent and trituration with $CHCl_3$ gave more **4** (27 mg; total 95%), m.p. 324–325° (dec). (Found: C, 58.74; H, 3.95; N, 14.62; S, 5.74. $C_{38}H_{22}N_4O_4S$ requires: C, 59.00; H, 3.88; N, 14.73; S, 5.62%). IR (KBr): 1780, 1730, 1505, 1410, 1325, 1130 cm^{-1}. NMR (DMSO-d_6): 2.40 (br s, 10 arom H); 3.50 (t, 4 vinylic H, J = 3 Hz); 4.75 (t, 4 C$\underline{H}$N, J = 3 Hz); 5.90 (br s, 4C$\underline{H}_2SO_2$). MS. 253 (14); 248 (9); 243 (100); 227 (88); 195 (13); 183 (24); 177 (29).

Irradiation of **4**. A soln of **4** (45 mg) in acetone (80 ml) was degassed and irradiated in a Rayonet reactor at 300 nm. The cage product **5** precipitates (24 mg), m.p. > 350°. (Found: C, 58.54; H, 4.07; N, 14.39; S, 5.74; M.W. 570.1311. $C_{38}H_{22}N_4O_4S$ requires: M.W. 570.1322). IR (KBr): 2980, 1750, 1690, 1500, 1400, 1320, 1250, 1160 cm^{-1}. NMR (DMSO-d_6 + TFA): 2.30 (s, 10 arom H); 4.90–5.10 (m, 4C$\underline{H}$N); 6.34 (br s, 4C$\underline{H}_2SO_2$); 6.64–6.80 (m, 4 cyclobutane H). MS. M^+ 570 (100); 329 (9); 279 (21); 227 (78); 214 (22); 119 (51).

Mono-adduct **7**. Immediate disappearance of red color occurred in reaction of **6** (188 mg) in 10 ml with PTD (175 mg) in 10 ml, giving **7** (89%), m.p. 177–178° (dec, benzene–hexane). (Found: C, 65.94; H, 4.63; N, 11.29; S, 8.61. $C_{26}H_{17}N_3O_2S$ requires: C, 66.17; H, 4.72; N, 11.58; S, 8.83%). IR: 2980, 2920, 1765, 1710, 1500, 1405 cm^{-1}. NMR ($CDCl_3$): 2.53 (s, 5 arom H); 3.35 (t, 2 vinylic H, J = 3 Hz); 3.70–4.40 (AA'BB', 4 dienic H); 5.17 (t; 2C$\underline{H}$N, J = 3 Hz); 6.97; 7.20 (ABq, 4C$\underline{H}_2$S, J = 12 Hz). MS. 227 (41); 135 (100); 134 (17); 119 (26).

Bis-adduct **8**. After 30 min reaction the red color disappeared when **7** (36 mg) in 2.5 ml was treated with PTD (17.5 mg) in 3 ml, giving **8** (86%), m.p. 296–298° (dec, benzene). (Found: C, 63.04; H, 4.25; N, 15.19; M.W. 538.1402. $C_{38}H_{22}N_4O_4S$ requires: C, 62.44; H, 4.11; N, 15.60%; M.W. 538.1423). IR: 1770, 1720, 1505, 1405 cm^{-1}. NMR ($CDCl_3$): 2.47 (s, 5 arom H); 2.50 (s, 5 arom H); 3.34 (t, 2 vinylic H, J = 3 Hz); 3.57 (t, 2 vinylic H, J = 3 Hz); 4.90–5.10 (m, 4C$\underline{H}$N); 6.40, 7.03 (ABq, 4C$\underline{H}_2$S, J = 12 Hz). MS. M^+ 538 (100); 361 (13); 253 (14); 227 (14); 185 (8); 135 (53); 128 (13); 119 (70); 109 (16).

Conversion of **7** *into* **3**. Oxidation of **7** (10 mg) in CH_2Cl_2 (10 ml) with *m*-chloroperbenzoic acid (*m*-CPBA) in CH_2Cl_2 (10 ml) and stirring overnight followed by decomposition with aq Na_2SO_3 (10%) and washing with aq Na_2CO_3 (10%), drying and removal of solvent gave crude **3** (11 mg). Trituration with MeOH gave pure product m.p. 162–163° (dec). (Found: 227.0687. M^+–$C_8H_5O_2S$ requires: 227.0694). IR (KBr): 2980, 2930, 1750, 1690, 1500, 1320, 1140 cm^{-1}. NMR (DMSO-d_6): 2.38 (s, 5 arom H); 2.93 (t, 2 vinylic H, J = 3 Hz); 3.57–4.34 (AA'BB', 4 dienic H); 4.90 (t, 2C$\underline{H}$N, J = 3 Hz); 6.56, 7.02 (ABq, C$\underline{H}_2$S, J = 14 Hz). MS. 228 (18); 227 (100); 168 (29); 151 (6); 133 (5); 119 (5).

The product **3** was identical by m.m.p. and spectroscopically with **3** obtained as a by-product together with **2** by reacting **1** with 1 eq PTD (see above).

Conversion of **8** *into* **9**. The oxidation was conducted as for **7** using **8** (40 mg) in 10 ml with *m*-CPBA (70 mg) in 10 ml. After workup crude **9** (45 mg) was obtained. Crystallization gave the

analytical sample, m.p. 308–310° (benzene–ether). (Found: C, 58.54; H, 3.74; N, 14.55; S, 5.58; M.W. 570.1312. $C_{28}H_{22}N_6O_4S$ requires: C, 58.94; H, 3.88; N, 14.73; S, 5.62%; M.W. 570.1321). IR: 1790, 1730, 1600, 1400, 1330, 1130 cm^{-1}. NMR ($CDCl_3$): 2.50 (br s, 10 arom H); 3.17 (t, 2 vinylic H, J = 3 Hz); 3.50 (t, 2 vinylic H, J = 3 Hz); 4.67–5.00 (m, 4CHN); 6.00, 6.66 (ABq, 4CH_2S, J = 14 Hz). MS. M$^+$ 570 (5); 227 (57); 177 (9); 120 (10); 119 (100).

Reaction of **3** *with PTD.* After 15 min the color disappeared in the reaction of **3** (7 mg) in 2 ml with PTD (3.2 mg) in 1 ml and **9** was obtained, identical by m.m.p. and spectroscopically with the sample described above.

12 - *Thia*[4.4.3]*propella* - 2,4,7,9 - *tetraene* - 12 - *oxide* **10**. To a soln of **6** (184 mg) in MeOH (5 ml) was added dropwise with stirring at 0° a soln of sodium periodate (214 mg) in aq MeOH (1:1, 6 ml). Stirring was continued overnight, at room temp. The salt formed and solvent were removed and the residue taken up in $CHCl_3$, clarified by filtration and the solvent removed. The crude product (200 mg) was crystallized, m.p. 82–83° (ether–hexane). (Found: C, 70.27; H, 5.74; S, 15.82; M.W. 204.0604. $C_{12}H_{12}OS$ requires: C, 70.65; H, 5.93; S, 15.72%; M.W. 204.0609). IR: 2940, 1400, 1070, 1015 cm^{-1}. NMR ($CDCl_3$): 3.73–4.60 (m, 8 dienic H); 6.45, 6.88 (ABq, 4CH_2SO, J = 14 Hz). MS. M$^+$ 204 (27); 155 (18); 153 (12); 142 (40); 141 (100).

Reaction of **10** *with PTD.* The red color was discharged after 20 min reaction of **10** (117 mg) in 5 ml with PTD (1 eq, 110 mg) in 5 ml. Removal of solvent gave a mixture (as obvious from NMR spectrum). After using 2 silica plates (acetone (1)–hexane (1), **10** (18 mg) was recovered and the mixture (122 mg) was again subjected to separation on 4 silica plates, 5 runs on each with acetone (1)–hexane (1). Four compounds were isolated (italicized in the text):

First component, Mono-adduct **11**. 19 mg (18%), m.p. 250–252° (dec, benzene–ether). (Found M$^+$–C_4H_4SO (retro-D.A.) 227.0682; requires: 227.0694). IR: 1790, 1735, 1415, 1090, 1020 cm^{-1}. NMR ($CDCl_3$): 2.53 (s, 5 arom H); 3.40 (t, 2 vinylic H, J = 3 Hz); 3.90–4.50 (AA'BB', 4 dienic H); 5.30 (t, 2CHN, J = 3 Hz); 6.22, 6.88 (ABq, 4CH_2SO, J = 14 Hz). MS. 228 (18); 227 (100); 149 (5); 119 (27).

Oxidation of **11** (8 mg) in CH_2Cl_2 (5 ml) with *m*-CPBA (15 mg) in CH_2Cl_2 (5 ml) gave in the usual way crude product, m.p. 278–279° ($CHCl_3$–hexane), m.m.p. with authentic **2**, 278–279° and identical with **2** spectroscopically.

Conversion of **11** *into* bis-*adduct* **15**. The red color disappeared after 4 hr reaction of **11** (7 mg) in 2 ml with PTD (3.5 mg) in 1 ml, affording **15**, m.p. 314–316° (dec, $CHCl_3$–hexane). (Found: M$^+$–$C_{16}H_{11}N_3O_3S$ (retro-D.A.), 227.0686; requires: 227.0694). IR: 1790, 1735, 1500, 1410, 1030 cm^{-1}. NMR ($CDCl_3$): 2.57 (s, 10 arom H); 3.80 (t, 4 vinylic H, J = 3 Hz); 5.03–5.34 (m, 4CHN); 6.07 (s, 4CH_2SO). MS. 227 (33); 177 (19); 134 (16); 119 (100).

Oxidation of **15** (5 mg) in CH_2Cl_2 (5 ml) by *m*-CPBA (5 mg) in CH_2Cl_2 (5 ml) as above gave **4**, m.p. 323–325° (dec), m.m.p. with authentic **4**, 324–325° and identical spectroscopically.

Second component, bis-adduct **12**. 28 mg (27%), m.p. 215–216° (benzene–ether). (Found: 227.0709. M$^+$–$C_{16}H_{11}N_3O_3S$ (retro-D.A.) requires: 217.0695). IR: 1790, 1735, 1510, 1410, 1060, 1030 cm^{-1}. NMR ($CDCl_3$): 2.47 (s, 5 arom H); 2.53 (s, 5 arom H); 3.30 (t, 2 vinylic H, J = 3 Hz); 3.53 (t, 2 vinylic H, J = 3 Hz); 4.97 (t, 2CHN, J = 3 Hz); 5.14 (t, 2CHN, J = 3 Hz); 6.36 (br s, 4CH_2SO). MS. 227 (20); 183 (40); 152 (75); 145 (20); 133 (55); 119 (40); 112 (50); 104 (100).

Oxidation of **12** (8 mg) as above with *m*-CPBA (15 mg) in CH_2Cl_2 as above gave **9** (10 mg), m.p. 307–309° (dec, benzene–ether), m.m.p. with authentic **9**, 308–310° and identical spectroscopically.

Third component, bis-adduct **13**: 40 mg (38%), m.p. 221–223° (dec, benzene–ether). (Found: M.W. 554.1430. $C_{28}H_{22}N_6O_4S$ requires: 554.1376). IR: 1790, 1740, 1410, 1030 cm^{-1}. NMR ($CDCl_3$): 2.50 (s, 10 arom H); 3.23 (t, 2 vinylic H, J = 3 Hz), 3.63 (t, 2 vinylic H, J = 3 Hz); 4.90–5.17 (m, 4CHN); 6.08, 7.22 (ABq, 4CH_2SO, J = 14 Hz). MS. M$^+$ 554 (14); 227 (56); 209 (32); 207 (100); 152 (40).

Oxidation of **13** (8 mg) with *m*-CPBA (15 mg) in CH_2Cl_2 as above gave **9** (8 mg), m.p. 309–310° (dec, benzene–ether), m.m.p. with authentic **9**, 308–310° and identical spectroscopically.

Fourth component, mono-adduct **14**. 18 mg (17%), m.p. 161–162° (dec, $CHCl_3$–hexane). (Found: M$^+$–C_4H_4OS (retro-D.A.), 227.0682; required: 227.0694). IR: 1780, 1720, 1510, 1410, 1090, 1020 cm^{-1}. NMR ($CDCl_3$): 2.53 (s, 5 arom H); 3.30 (t, 2 vinylic H, J = 3 Hz); 3.67–4.30 (AA'BB', 4 dienic H); 5.13 (t, 2CHN, J = 3 Hz); 6.67, 7.00 (ABq, 4CH_2SO, J = 14 Hz). MS. 227 (98); 152 (98); 136 (6); 134 (24); 119 (70); 105 (20); 104 (100).

Oxidation of **14** (5 mg) with *m*-CPBA (15 mg) in CH_2Cl_2 as above gave **3** (6 mg), m.p. 160–162° (dec), mixed with authentic **3**, 160–163°, identical spectroscopically with **3**.

Conversion of **14** *into* bis-*adduct* **12**. The red color disappeared after 4 hr reaction of **14** (7 mg) in 2 ml with PTD (3.5 mg) in 1 ml. The product had m.p. 215–216° and was identical with authentic **12** by m.m.p. and spectroscopically.

Oxidation of **7** *to both configurationally epimeric sulfoxides.* To a soln of **7** (55 mg) in CH_2Cl_2 (3 ml) was added dropwise with stirring at room temp. a soln of sodium periodate (33 mg) in aq MeOH (1:1; 3 ml). MeOH (3 ml) was added to obtain a homogeneous soln and the whole was stirred overnight. After the usual workup the crude product (63 mg) was chromatographed using 3 silica plates, 3 runs each with hexane (3)–acetone (1). Two isomers were isolated, **14** (20 mg) identical by mixed m.p. and spectroscopically with **14** described above, and **16** (25 mg), m.p. 155–157° (dec, CH_2Cl_2–hexane).

Compound **16**: (Found: M$^+$–C_4H_4OS (retro-D.A.), 227.0682; required 227.0694). IR (KBr): 3000, 1760, 1710, 1500, 1410, 1060 cm^{-1}. NMR ($CDCl_3$): 2.57 (s, 5 arom H), 3.20 (t, 2 vinylic H, J = 3 Hz); 3.50–4.53 (AA'BB', 4 dienic H); 5.13 (t, 2CHN, J = 3 Hz); 6.53, 7.24 (ABq, 4CH_2SO, J = 12 Hz). MS. 228 (12); 227 (95); 152 (80); 134 (26); 119 (88); 105 (20); 104 (100).

Conversion of **16** *into bis-adduct* **13**. The red color disappeared after 10 min reaction of **16** (9.5 mg) in 3 ml with PTD (4.5 mg) in 2 ml, affording product (10 mg) identical by m.m.p. and spectroscopically with **13** described above.

Adduct **18**. The red color was discharged after 3 hr reaction of **17**[7] (112 mg) in 5 ml with PTD (87.5 mg) in 5 ml afforded crude **18** (180 mg). Trituration with $CHCl_3$ gave the analytical sample, m.p. 311–312° (dec, 320–321°) (Found: C, 60.24; H, 5.39; N, 10.39; M.W. 399.1291. $C_{20}H_{21}N_3O_4S$ requires: C, 60.20; H, 5.31; N, 10.53%; M.S. 399.1252). IR (KBr): 2940, 2880, 1780, 1700, 1500, 1410, 1320, 1140 cm^{-1}. NMR (DMSO-d_6): 2.30 (s, 5 arom H); 3.17 (t, 2 vinylic H, J = 3 Hz); 5.14 (t, 2CHN, J = 3 Hz); 6.12, 6.57 (ABq, 4CH_2SO_2, J = 16 Hz); 8.00–8.60 (m, CH_2). MS. M$^+$ 399 (20); 228 (14); 227 (100); 145 (8).

Perhydro-derivative **19**. (a) A suspension of **2** (29 mg) in EtOAc (150 ml) with PtO_2 (5 mg) was shaken with H_2 at 40 psi during 2 hr. The catalyst and solvent were removed from the now transparent soln and the crude residue (22 mg) was purified by chromatography on basic alumina (grade I) using $CHCl_3$ (1)–hexane (4). The analytical sample of **19** had m.p. 272–273° (dec, benzene–hexane). (Found: C, 59.52; H, 5.68; N, 10.15; S, 8.08; M.W. 401.1436. $C_{20}H_{23}N_3O_4S$ requires: C, 59.90; H, 5.78; N, 10.48; S, 8.00%; M.W. 401.1409). IR: 2960, 1770, 1710, 1510, 1320, 1130 cm^{-1}. NMR ($CDCl_3$): 2.50 (s, 5 arom H); 5.94 (s, 2CHN); 6.20, 6.77 (ABq, 4CH_2SO_2, J = 15 Hz); 7.60–8.34 (m, 12CH_2). MS. M$^+$ 401 (26); 228 (100); 227 (21); 120 (6).

(b) Reduction of **18** as for **2** gave **19**, m.p. 272–274° (dec), m.m.p. with **19** prepared from **2**, 272–273°. The two specimens were also identical spectroscopically.

Adduct **21**. The red color disappeared after 3 hr reaction between **20** (83 mg) in 2 ml with PTD (68 mg) in 2 ml, affording crude **21** (120 mg) purified on basic alumina (Grade I) using $CHCl_3$ (3)–hexane (7), m.p. 214–215° (benzene–hexane). (Found: M.W. 367.1374. $C_{20}H_{21}N_3O_3S$ requires: 367.1355). IR (KBr): 2940, 2880, 1770, 1700, 1500, 1415 cm^{-1}. NMR ($CDCl_3$): 2.50 (s, 5 arom H); 3.43 (t, 2 vinylic H, J = 3 Hz); 5.30–5.70 (m, 2CHN); 6.50, 7.17 (ABq, 4CH_2S, J = 12 Hz); 8.00–8.80 (m, 8CH_2). MS. M$^+$ 367 (35); 228 (17); 227 (100); 183 (6); 133 (10); 119 (9).

Oxidation of **20** *to mixture of sulfoxides.* Oxidation of **20** (200 mg) in CH_2Cl_2 (1 ml)–MeOH (3 ml) as above with $NaIO_4$ (235 mg) in aq MeOH (6 ml) with added MeOH (5 ml) overnight gave a mixture of **22** and **23**. Separation was accomplished on 2 silica plates, 3 runs, acetone (1)–hexane (3).

Compound **23**: (90 mg), m.p. 89–90° (hexane). (Found: M.W. 208.0947. $C_{12}H_{16}OS$ requires: 208.0922). IR: 2940, 2860, 1070, 1010 cm^{-1}. NMR ($CDCl_3$): 3.80–4.38 (AA'BB', 4 dienic H); 6.41,

7.20 (ABq, $4CH_2SO$, J = 14 Hz); 8.60 (s, $8CH_2$). MS. M^+ 208 (50); 160 (10); 145 (100); 133 (34); 131 (40).

Compound **22**: (80 mg), remained an oil. (Found: M.W. 208.0908). IR: 2980, 2920, 1060, 1010 cm^{-1}. NMR ($CDCl_3$): 3.90–4.53 (AA'BB', 4 dienic H); 6.69, 7.01 (ABq, $4CH_2SO$, J = 14 Hz); 8.15–8.70 (m, $8CH_2$). MS. M^+ 208 (8); 192 (17); 145 (100); 131 (44).

Adduct **24**. The red color disappeared after 3 hr reaction of **22** (50 mg) in 2 ml with PTD (45 mg) in 2 ml. The crude product on trituration with MeOH gave the analytical sample, m.p. 278–279° (dec). (Found: M.W. 383.1319. $C_{20}H_{21}N_3O_3S$ requires: 383.1303). IR: 2960, 1780, 1720, 1410, 1080, 1020 cm^{-1}. NMR ($CDCl_3$): 2.47 (s, 5 arom H); 3.47 (t, 2 vinylic H, J ≈ 3 Hz); 5.47 (t, 2CHN, J = 3 Hz); 6.29, 6.99 (ABq, $4CH_2SO$, J = 14 Hz); 8.00–8.80 (m, $8CH_2$). MS. M^+ 383 (29), 366 (10); 228 (13); 227 (100); 145 (5).

Adduct **25**. The red color disappeared after 6 hr reaction of **23** (20 mg) in 2 ml with PTD (18 mg) in 2 ml. Trituration of product **25** with benzene gave the analytical sample (32 mg), m.p. 298–299° (dec). (Found: C, 62.69; H, 5.58; N, 10.86; S, 8.23. $C_{20}H_{21}N_3O_3S$ requires: C, 62.72; H, 5.53; N, 10.95; S, 8.37%). IR: 2950, 2880, 1780, 1720, 1410, 1080, 1030 cm^{-1}. NMR ($CDCl_3$): 2.43 (s, 5 arom H); 3.30 (t, 2 vinylic H, J = 3 Hz); 5.30 (t, 2CHN, J = 3 Hz); 6.29, 6.65 (ABq, $4CH_2SO$, J = 14 Hz); 8.30–8.80 (m, $8CH_2$). MS. 208 (31); 192 (10); 145 (100); 144 (10); 131 (45); 128 (12).

Configurational correlation of **21**, **24**, **25**. (a) Oxidation of **21** (45 mg) by *m*-CPBA (100 mg) in CH_2Cl_2 gave as above the sulfone **18** (47 mg) after workup and trituration with $CHCl_3$, m.p. 312–313° (dec). M.m.p. with authentic **18** described above 312–313° (dec). The samples were also spectroscopically identical.

(b) Oxidation of **24** by *m*-CPBA (100 mg) similarly gave, after trituration with MeOH, pure **18**, m.p. 311–312° (dec), m.m.p. with above 312–313° (dec), identical spectroscopically.

(c) Oxidation of **25** (30 mg) by *m*-CPBA (60 mg) also gave, as above, using MeOH **18**, m.p. 312–313° (dec), identical by m.m.p. (312–313°, dec) and spectroscopically.

Acknowledgement—We are grateful to Herr Heinrich Fischer for preparing sufficient quantities of certain starting materials used in this work.[5]

REFERENCES

[1a]M. Korat, D. Tatarsky and D. Ginsburg, *Tetrahedron* **28**, 2315 (1972); [1b]C. Amith and D. Ginsburg, *Ibid.* **30**, 3415 (1974); [1c]J. Kalo, J. M. Photis, L. A. Paquette, E. Vogel and D. Ginsburg, *Ibid.* **32**, 1013 (1976); [1d]P. Ashkenazi, E. Vogel and D. Ginsburg, *Ibid.* **33**, 1169 (1977); [1e]J. Kalo, E. Vogel and D. Ginsburg, *Ibid.* **33**, 1177 (1977); [1f]P. Ashkenazi, J. Oliker and D. Ginsburg, unpublished results.

[2]Prof. R. Gleiter, private communication.

[3]Z. Bernstein and D. Ginsburg, *Heterocycles* in press.

[4]J. B. Lambert, *Topics in Stereochemistry* (Edited by N. L. Allinger and E. L. Eliel) Vol. 6, p. 89. Wiley-Interscience, New York (1971).

[5]H. Fischer, Staatsexamensarbeit, Universität Köln (1975).

[6]L. A. Paquette, R. E. Wingard, Jr., J. C. Philips, G. L. Thompson, L. K. Read and J. Clardy, *J. Am. Chem. Soc.* **93**, 4508 (1971).

[7]M. Kaftori, private communication.