The Unusual Reaction of Tetrachlorothiophene Dioxide with an Adduct of 5,6-Bismethylenenorbornene and Hexachloronorbornadiene

Edward C. Gravett, Judith A. K. Howard,*† Kenneth Mackenzie,* Liu Shi-Xiong‡ and Peter B. Karadakov‡
School of Chemistry, The University, Bristol BS8 1TS, UK

Hexachloronorbornadiene forms a 1 : 1 adduct **3** with 5,6-bismethylenenorbornene, which, on reaction with 1,2,3,4-tetrachlorothiophene dioxide, yields by loss of SO_2, cycloreversion and further cycloaddition two compounds shown by mass, ^{13}C NMR and ^1H NMR spectroscopy and a single-crystal X-ray structure determination to be the isomeric products of a rare type of *specific* diene-capture by perchlorothiophene dioxide; a rational explanation for this and other examples is proposed, and a further example of norbornene sp^2 C pyramidalisation is disclosed.

In connection with our interest in polycyclic compounds having face-proximate π-systems for their synthetic[1] and mechanistic relevance[2] we have investigated the reaction of hexachloronorbornadiene **1** with 5,6-bismethylenenorbornene, **2**. Diene **1** is an efficient electron-poor dienophile, exothermic reaction with cyclopentadiene at ambient pressure giving stereospecifically an *endo–endo* adduct, isodrin, **5**.[3] These observations cogently exemplify orbital symmetry theory for [4 + 2]π thermal cycloaddition, favourable transition-state secondary non-bonding orbital interactions[4] being expected to facilitate stereospecific formation of adduct **5**. Additionally, *exo*-π-face selectivity usually observed in diene capture by norbornenes and norbornadienes without bridge substituents, and believed[5] to be significantly due to sp^2 C pyramidalisation[5,6] at the dienophilic site, is precluded here by the steric restraint imposed by the CCl_2 bridge in **1**. Diene **1** is therefore expected to be *endo* specific at C-5–C-6 in its reaction with bismethylenenorbornene, **2**, whilst ample experimental and theoretical precedent exists[6] for the selective capture of moderately reactive electron-poor dienophiles at the *endo* face of the 1,3-diene element in **2**. Two stereoisomers, **3** and **4** can thus in principle arise when dienophile **1** is exposed to diene **2**, molecular mechanics computations indicating little difference in strain-energy (E_s) (223.3 and 226.7 kJ mol^{-1}, respectively) or in ΔH_f (79.03 and 82.47 kJ mol^{-1}) for the two isomers. In fact, when components **1** (0.05 mol) and **2** (0.075 mol) were heated with benzene (5 ml, sealed tube, 165 ± 5 °C, 24 h), the viscous brown product was taken up in dichloromethane, the coloured by-product was precipitated with petroleum, and the product solution was evaporated, a *ca.* 90% yield of a viscous clear, non-crystallising oil was obtained, having ^1H and ^{13}C NMR signals and mass spectra consistent with a single pure monoadduct, either **3** or **4**.

The small difference in E_s and ΔH_f calculated for isomers **3** and **4** almost certainly arises from the conformational mobility permitted by the C-3, C-10 methylene groups but the transition state requirements for their formation must be very different, that for formation of **4** being disadvantaged by severe steric repulsion occasioned by C-2–C-3 vinylic chlorine

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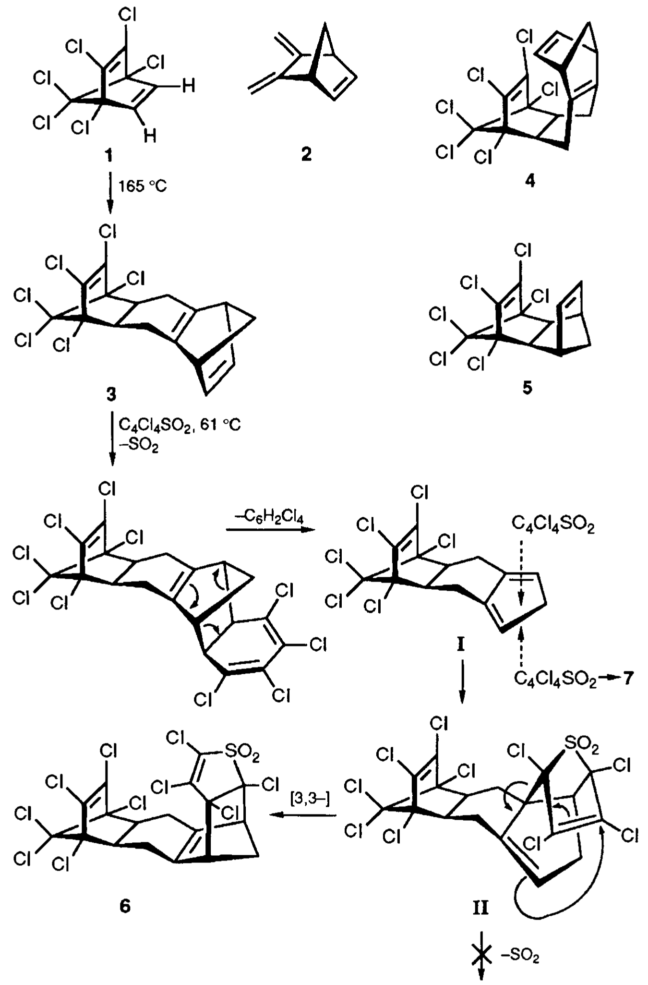
† *Present address*: Department of Chemistry, University of Durham, Science Laboratories, South Road, Durham DH1 3LE, UK.

‡ L. S.-X. is on leave from Department of Chemistry, Futzhou University, Futzhou, Fujan 350002, People's Republic of China, and P. B. K. from Institute of Organic Chemistry, Bulgarian Academy of Sciences, Sofia 1040, Bulgaria.



Scheme 1 A substantial lowering in π-energy is expected for **6** owing to the vinyl sulphone element. (For relevant CNDO calculations see P. Caramella, E. Albini, T. Bandeira, A. C. Coda, P. Grünanger and F. M. Albini, *Tetrahedron*, 1983, **39**, 689.) Adduct **II** can therefore be regarded as the likely kinetic product in alternative direct pathways involving [4 + 2]π cycloaddition between **1** and 'TCTD' as is supported by the MNDOC calculations for **6** and **II**. (MNDOC: W. Thiel, *J. Am. Chem. Soc.*, 1981, **103**, 1413; 1420. Starting geometries for MNDOC obtained by MM2 computation.)

in **1** as C-2 and C-3 of diene **2** come into close proximity. The available evidence therefore indicates **3**§ to be the most likely structure of the *single* adduct isolated.¶

In preliminary experiments with adduct **3**, tetracyclone adduction gave 1,2,3,4-tetraphenylbenzene and a compound having *m/z* 744 (with the correct Cl_6 isotopic ion-cluster), 26 less than expected for tetracyclone cycloaddition with concomitant cheletropic CO extrusion.[7] The isolation of tetraphenylbenzene suggests an addition–decarbonylation–cycloreversion sequence[8] followed by further tetracyclone addition and CO extrusion. However, the high molecular mass of this compound prompted us to use thiophene dioxide derivatives in a similar cyloaddition in order to vitiate spectroscopic difficulties, and to probe the scope of this unexpected result.

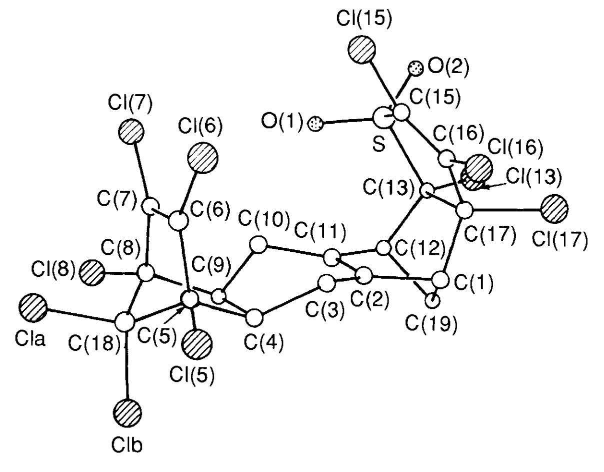


Fig. 1 Computer-generated representation of the X-ray crystal structure of **6**. The planes defined by C(1)C(2)C(11)C(12) and C(2)C(3)C(10)C(11) deviate 4.8° in the *endo* direction; C(2) and C(11) are pyramidalised.

Thiophene 1,1-dioxide derivatives exhibit pronounced enophilic and trienophilic reactivity in [4 + 2] and [4 + 6]π thermal cycloadditions[9] (in remarkable contrast to thiophenes,[10] which show little propensity for enophilic behaviour.[11] The synthetically most widely utilised thiophene dioxide is 2,3,4,5-tetrachlorothiophene 1,1-dioxide (TCTD).[12] Exemplifying TCTD reactivity, during its preparation a product derived from a Diels–Alder dimer is often isolated (1.1%) but TCTD is inefficient in its ability for self-annelation compared to certain 2,3,4,5-substituted cyclopentadienones.[7] More significantly, TCTD reacts slowly with ethylene at ambient temperature and pressure whilst mixtures of products rapidly result when TCTD is exposed to, *e.g.* cyclopentadiene, which however exhibits mainly dienophilic properties (*cf.* ref. 12*a*).

When compound **3** (1.5 mmol) was exposed to TCTD (1.1 mmol, chromatographically pure) in boiling $CHCl_3$ (20 ml) for 24 h, followed by removal of $CHCl_3$ and flash-chromatography of the product, only 1,2,3,4-tetrachlorobenzene[8] and two new compounds were isolated: **6** (44%, m.p. 203.5–204.5 °C, decomp.) and **7** (45%, m.p. 199.5–200.5 °C, decomp.). Compounds **6** and **7** were each characterised by ^1H NMR, ^{13}C NMR, and mass spectrometry and combustion analysis as decachlorotrienes of composition $C_{18}H_{10}Cl_{10}SO_2$,|| and the very close correspondence of their spectroscopic properties provides compelling evidence for their relationship as stereoisomers.

Recourse to single-crystal X-ray structure analysis showed that **6** has the molecular structure illustrated (Fig. 1).** The

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§ **3**: ^1H NMR (400 MHz), δ: 1.94 and 2.08 (each dt, H-16,16′), 2.04 and 2.55 (each m, H-3,3′, 10,10′), 3.14 (m, H-4,9), 3.22 (quint., H-1,2) and 6.69 ('t', H-13,14), all signals having the correct relative intensity; ^{13}C NMR, δ: 143.8 (C-2,11), 142.0 (C-13,14), 130.5 (C-6,7), 102.3 (C-15), 83.2 (C-5,8), 71.3 (C-16), 52.9 (C-1,2), 43.8 (C-4,9) and 22.1 (C-3,10); *m/z*: 414 (M^+), 379 ($M^+ - Cl$) and 343 ($M^+ - HCl_2$); M, calc.: 413.9070; found: *m/z* 413.9103.

¶ The single-crystal X-ray structure of the tetracyclone adduct of this compound is being investigated.

|| *Spectroscopic correlations*; data for **6** with data for **7** in square brackets; ^1H NMR (400 MHz) δ 1.67 (m), 2.18 (m), 2.64 (overlap. ms) [2.28 (m), 2.20 (m), 2.75 (m)] (H-3, 3′, −10, 10′); 2.22, 2.58 [2.50, 2.61] (each dt, H-19, 19′), 3.07 (m) [3.01, 3.16 (each m)] (H-4, -9); 3.32, 3.42 [3.28, 3.37] (each m, H-1, 12), all signals having the correct relative intensity; ^{13}C NMR (100 MHz), δ 142.7, 141.5, 140.5, 132.8 [141.5, 140.9, 140.5, 130.6] (C-2, 11, 15, 16); 131.7, 131.5 [131.4, 131.3] (C-6, 7); 102.4, 90.4 [102.5, 90.9] (C-18, 13); 82.3, 82.1, 81.1 [82.3, 82.2, 81.4] (C-5, 8, 17); 61.9, 51.9 [61.5, 61.2, 51.7] (C-1, 12, 19); 46.2, 45.7 [44.9, 44.5] (C-4, 9); 23.8, 23.1 [22.4, 22.1] (C-3, 10); *m/z* 642 (M^+), 576, 541, 388 ($M^+ - C_4Cl_4SO_2$), for **6** and **7**, all ions having the correct chlorine isotope abundance ratios.

** *Crystal data* for **6**: $C_{18}H_{10}Cl_{10}O_2S$, $M = 644.8$, triclinic, space group $P\bar{1}$, $a = 8.253(4)$, $b = 10.977(4)$, $c = 13.885$ Å, $\alpha = 71.51(4)$, $\beta = 81.76(4)$, $\gamma = 86.98(4)°$; $V = 1181(1)$ Å^3; $Z = 2$, $D_c = 1.814$ mg mm^{-3}; μ(Mo-Kα) = 12.92 cm^{-1}; $F(000) = 640$; λ(Mo-Kα) = 0.71069 Å; R (R_w) 0.0459 (0.0667) [3000 data, $F > 5.0\sigma(F)$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

appearance of this compound and its stereoisomer **7** but no other annelation products find analogy in the reactions of 1,2-bismethylenecyclohexane and thiophene 1,1-dioxide[9a] and 2,3-dimethylbuta-1,3-diene with TCTD;[12a] in most cases, exposure of compounds having a 1,3-diene element to thiophene dioxides results in mixtures of products resulting from thiophene dioxides apparently exhibiting diene and dienophilic behaviour. The very high diene reactivity of thiophene dioxides, their propensity to deliver the kinetic adduct and the occasional isolation (*e.g.* at 50 °C) of the primary SO_2-bridged adduct[12a] suggests that the primary step in the reaction with 1,3-diene compounds may be 'normal' dienophile-capture by, *e.g.* TCTD, followed by fast Cope rearrangement. Relevant analogy is found in the apparent dienophilic reactivity of tetraphenylcyclopentadienone towards 1-methoxybuta-1,3-diene,[13] also reasoned to be a cycloaddition–Cope rearrangement sequence.[14] Further experiments are clearly needed to confirm the proposed [3.3] sigmatropic shift mechanism which is, however, likely to be favoured by the constrained adduct framework geometry and also by heavy substitution with electronegative groups.[15] Preliminary results from MNDOC calculation yield ΔH_f 1243 and 1272 kJ mol^{-1} for compound **6** and the intermediate **II** respectively, consistent with **II** as kinetic product.

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References

1 K. Mackenzie, *J. Chem. Soc.*, 1965, 4646 (see also refs. 12*e* and 12*f*).

2 K. B. Astin, A. V. Fletcher, A. A. Frew, K. Mackenzie, A. S. Miller, K. W. Muir and N. M. Ratcliff, *J. Chem. Soc., Perkin Trans. 2*, 1982, 111; K. Mackenzie, *J. Chem. Soc.*, 1962, 457.

3 S. B. Soloway, A. M. Damiana, J. W. Sims, H. Bluestone and R. E. Lidov, *J. Am. Chem. Soc.*, 1960, **82**, 5377.

4 R. B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry*, Verlag Chemie, Weinheim, 1970; I. Fleming, *Frontier Orbitals and Organic Chemical Reactions*, Wiley, 1978.

5 R. Huisgen, P. H. J. Ooms, M. Mingin and N. L. Allinger, *J. Am. Chem. Soc.*, 1980, **102**, 3951, and references cited.

6 L. A. Paquette, H. Künzer, K. E. Green, O. de Lucchi, G. Licini, L. Pasquato and G. Valle, *J. Am. Chem. Soc.*, 1986, **108**, 3453 and references cited; L. A. Paquette, A. G. Schaefer and J. Blount, *J. Am. Chem. Soc.*, 1983, **105**, 3642.

7 M. A. Ogliaruso, M. G. Romanelli and E. I. Becker, *Chem. Rev.*, 1965, **65**, 261, and references cited.

8 *Cf.* K. Mackenzie, *J. Chem. Soc.*, 1960, 473, for relevant examples of the reaction of *norbornadiene* with a variety of cyclopentadienones or synthetic equivalents.

9 (*a*) J. L. Melles, *Recl. Trav. Chim. Pays-Bas*, 1952, **71**, 869; (*b*) W. J. Baily and E. W. Cummins, *J. Am. Chem. Soc.*, 1954, **76**, 1932; (*c*) H. Bluestone, R. Bimber, R. Berky and Z. Mandel, *J. Org. Chem.*, 1961, **26**, 346; (*d*) S. E. Reiter, L. C. Dunn and K. N. Houk, *J. Am. Chem. Soc.*, 1977, **99**, 4199; (*e*) J. Nakayama, S. Yamaoka, T. Nakanishi and M. Hosino, *J. Am. Chem. Soc.*, 1988, **110**, 6598.

10 For theoretical rationale, see P. W. Lert and C. Trindle, *J. Am. Chem. Soc.*, 1971, **93**, 6392.

11 For rare examples of dienophile capture by thiophenes see S. Rajappa in *Comprehensive Heterocyclic Chemistry*, ed. C. W. Bird and G. W. H. Cheeseman, vol. 4, ch. 3.14, Pergamon, Oxford, 1984. Thiophene derivatives show greater reactivity in *intramolecular* reaction with dienophilic sites: see G. Himbert, H. J. Schlindwein and G. Mass, *J. Chem. Soc., Chem. Commun.*, 1990, 405.

12 (*a*) M. S. Raasch, *J. Org. Chem.*, 1980, **45**, 856, 867; (*b*) P. R. Spurr and D. P. G. Hamon, *J. Am. Chem. Soc.*, 1983, **105**, 4734; K. Kanematsu, K. Harano and H. Dantsuji, *Heterocycles*, 1981, **16**, 1145; (*c*) K. Beck and S. Hünig, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 187; (*d*) W.-D. Fessner, G. Sedelmeier, P. R. Spurr, G. Rihs and H. Prinzbach, *J. Am. Chem. Soc.*, 1987, **109**, 4626; (*e*) K. Mackenzie, G. Proctor and D. J. Woodnutt, *Tetrahedron*, 1987, **43**, 5981; (*f*) J. A. K. Howard, K. Mackenzie, R. E. Johnson and K. B. Astin, *Tetrahedron Lett.*, 1989, **30**, 5005; (*g*) D. Hilvert, K. W. Hill, K. D. Nared and M.-T. M. Auditor, *J. Am. Chem. Soc.*, 1989, **111**, 9261.

13 H. von Euler, H. Haselquist, G. Hanshoff and A. Glaser, *Chem. Ber.*, 1953, **86**, 969.

14 D. M. Bratby, J. C. Chadwick, G. I. Fray and R. G. Saxton, *Tetrahedron*, 1977, **33**, 1527.

15 For similar thermal and Lewis acid catalysed Cope-type rearrangements, see P. Yates and P. Eaton, *Tetrahedron*, 1961, **12**, 13; R. C. Cookson, J. Hudec and R. O. Williams, *Tetrahedron Lett.*, 1960, 29. In the present instance SO_2 present in the reaction mixture could function as a Lewis acid.