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Sequential Cycloaddition-Cycloreversion-Cycloaddition-Cope Rearrangement with an Annelated Norbornadiene and Electrophilic Dienes. Unusual $[\pi^2_s + \pi^2_a + \sigma^2_a]$ Transformation of a Pentacyclo-[11.4.0.1^{7,10}.0^{4,13}.0^{6,11}]octadeca-3,8,14,17-tetraene.[1]

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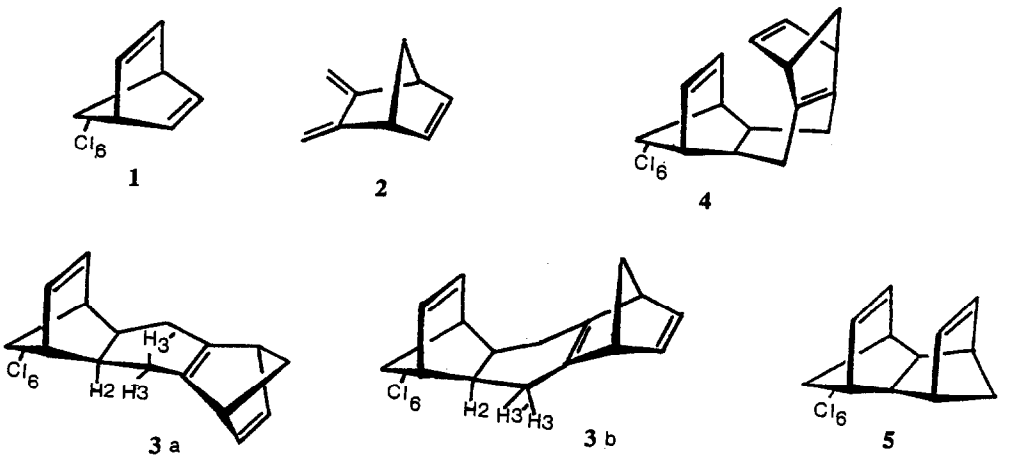
Abstract : Hexachloronorbornadiene efficiently forms a 1:1 adduct **3** with 5,6-bismethylenenorbornene. Adduct **3** on reaction with 1,2,3,4-tetrachlorothiophene dioxide (TCTD) under mild conditions gives an SO_2 bridged adduct, which loses SO_2, the product cycloreverting to give 1,2,3,4-tetrachlorobenzene and an annelated cyclopentadiene **8**; **8** reacts further with TCTD to give, in 1:1 ratio, two compounds (**14** and **15**) shown by mass, ^{13}C and ^1H NMR spectroscopy and single crystal X-ray structure determination to be the stereoisomeric products of a rare type of *specific diene* capture by TCTD. Evidence is presented that this result (and analogous examples) is best understood in terms of "normal" [4+2]π cycloadditions to **8** as dienophile towards electron-deficient TCTD, followed by rapid Cope rearrangement of the SO_2-bridged intermediate adducts to give the observed products. At low temperatures adduct **3** behaves as expected towards electron-deficient diene tetracyclone ; the [4+2]π cycloadduct decarbonylates on mild thermolysis, concomitant cycloreversion also giving diene **8**. At much higher temperatures in the presence of excess tetracyclone, diene **8** likewise behaves as dienophile; the carbonyl-bridged major cycloadduct decarbonylates to give an intermediate which undergoes an unusual thermally-allowed $[\pi^2_s + \pi^2_a + \sigma^2_a]$ 1,3-shift/cycloaddition, delivering a symmetrical cage-like structure **24**, as indicated by mass and ^{13}C and ^1H NMR spectroscopy.

Introduction:

In connection with our interest in polycyclic compounds having face-proximate π–systems for their synthetic and mechanistic relevance,[2,3] we have investigated the thermal [4+2]π cycloaddition of hexachloro-norbornadiene **1** with bismethylenenorbornene **2**, in the expectation that either of two cycloadducts **3** and **4** or both might be accessible (Scheme 1). This expectation arises from the fact that the diene **1** is an efficient electron-poor dienophile, exothermic reaction with cyclopentadiene at ambient pressure giving stereo-specifically an *endo-endo* adduct, isodrin **5**.[4] Such ready formation of adduct **5** cogently exemplifies orbital symmetry theory for a thermal [4+2]π cycloaddition, favourable transition-state secondary (non-bonding) orbital interactions[5] being expected to facilitate stereospecific *endo-endo* addition. The *exo*-π-face selectivity usually observed in diene (and 1,3-dipole) capture by dienophilic norbornenes and norbornadienes without bridge substituents and believed[6] to be significantly due to sp^2C *exo*- pyramidalisation[6,7a] at the dienophilic site, is precluded here by the very effective steric shielding of the *exo*- π-face 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**.

There is also ample experimental evidence for the selective capture of moderately reactive electron poor dienophiles at the *endo*- face of the 1,3-diene element in **2**, with appropriate theoretical rationalisation.[7] Two stereoisomers **3** and **4** can then be expected in principle when dienophile **1** is exposed to diene **2**, particularly as MM computations indicate little difference in strain energies (E_S) which are 287.4 and 280.2 kJmol^{-1} for **3** and **4** respectively.[8]



E_S = 287.4kJmol^{-1} E_S = 272.3kJmol^{-1}

Scheme 1

Isolation and Characterisation of Adduct 3.

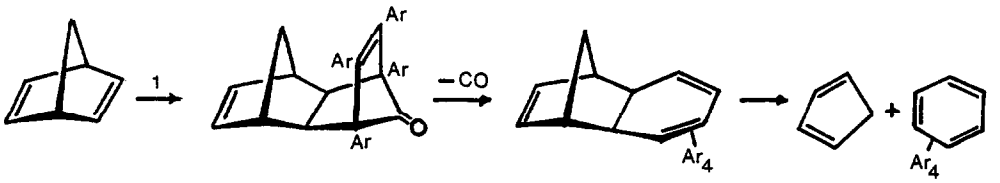
In fact when components **1** (0.05mol) and **2** (0.075mol) are heated with benzene (5ml, sealed tube, 165±5°C, 24hr) and the viscous brown oily product taken up in dichloromethane, a coloured by-product precipitated by dilution with petroleum and the product solution evaporated, a *ca.* 90% yield of a viscous, clear non-crystallising oil is obtained. This product has ^{1}H, ^{13}C NMR and mass spectra consistent with a single mono-adduct, either **3** or **4**. Although the difference in E_S calculated for the two isomers is quite small and almost certainly arises from the conformational mobility permitted by the C-3 and C-10 methylene groups in the central unbridged cyclohexene ring, the transition-states for their formation must be very different. The transition-state for formation of **4** is clearly disadvantaged by severe steric repulsion between C-2, C-3 vinylic chlorine atoms in **1** as C-2, C-3 of the etheno bridge in **2** come into close proximity, and on these grounds **3** is the most likely structure for the mono-adduct; this assignment is at least consistent with further MM computational and ^{1}H NMR spectroscopic evidence.

The adduct **3** can be envisaged to have two conformations which result from the flipping of the cyclohexene ring, depicted as **3a** and **3b**. These two conformations have strain energies E_S of 287.4 and 272.3 kJmol^{-1} respectively, a sufficiently large difference as to suggest that **3b** will strongly predominate at equilibrium. This expectation is borne out by a detailed analysis of the (400MHz) ^{1}H NMR spectrum of a carefully purified sample of the adduct, supported by COSY and simulation experiments. The NMR analysis is facilitated by the division of the twelve protons into two non-interacting sets of six spins, insulated from each other by the central ring quaternary sp^{2}C atoms. The features of the norbornadiene element are very satisfactorily reproduced when the relevant coupling constants (measured directly and from ^{13}C satellites) and the relevant signal frequencies are inserted into a simulation programme.[9] More importantly however, for the remaining six proton signals, spin coupling analysis of the two ring junction and four cyclohexene methylene

group nuclei yields conformationally significant couplings of *ca.* 8.9Hz and 0Hz between H-2 and H-3, H-3' (≡ H-11 and H-10, H-10'). Measured from minimised MM calculated structures, the relevant dihedral angles are H-2/H-3' = 155° and H-2/H-3 = 35° for **3a** and 84° and 35° respectively for conformer **3b**. The Karplus[10] calculated coupling constants $^3J_{H\text{-}2/H\text{-}3'}$ and $^3J_{H\text{-}2/H\text{-}3}$ are 10.6 and 7.2 Hz respectively for structure **3a** but 1.0 and 7.2 Hz respectively for conformer **3b**. Obviously the calculated data for **3b** correlates best with the experimental data for adduct **3**.

Chemical Properties of Adduct 3.

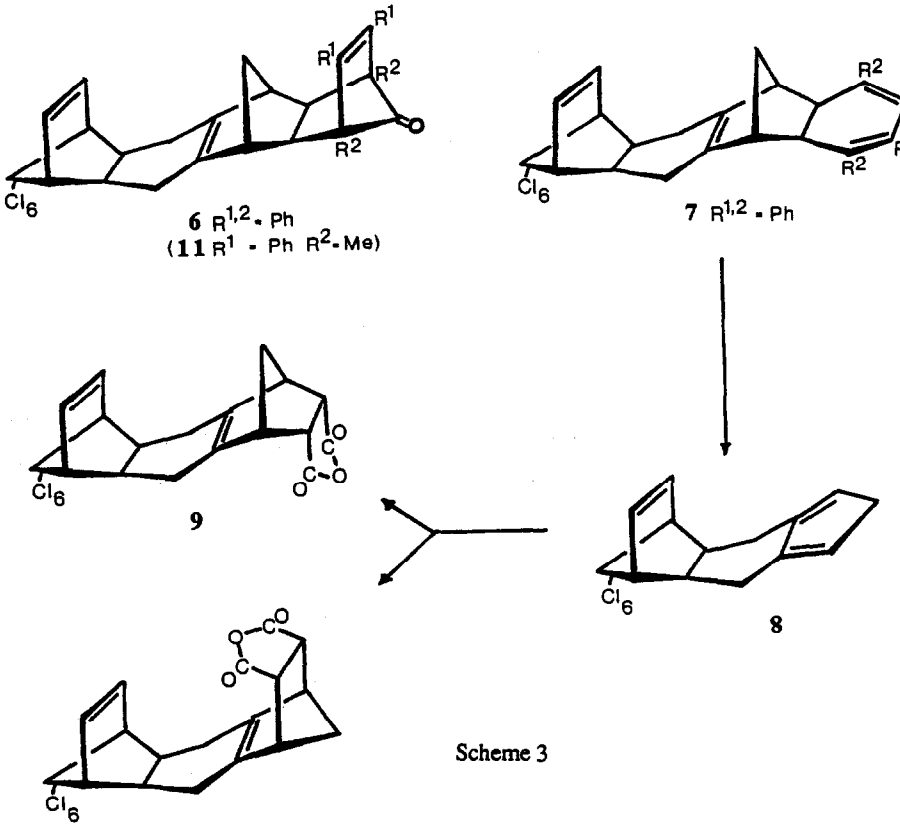
It is known that norbornadiene exhibits high reactivity in inverse electron demand thermal [4+2]π cycloaddition with e.g. tetra-arylated cyclopentadienones, the adducts readily losing CO by cheletropic extrusion on mild thermolysis,[11] giving products which themselves fragment by rapid cycloreversion to cyclopentadiene and a tetra-arylated benzene[12] (Scheme 2). (In this reaction sequence norbornadiene behaves as an acetylene equivalent[13]).



Scheme 2

It appeared of interest to examine whether the ring fused norbornadiene **3** would also manifest similar reactivity and adduct fragmentation, yielding an annelated cyclopentadiene **8** as a potentially useful synthetic reagent. Accordingly exposure of triene **3** to an excess of tetracyclone in boiling dichloromethane gives a carbonyl-bridge mono adduct **6** whose mass spectrum shows no molecular ion, but fragment ions with m/z 382 (corresponding to 1,2,3,4-tetraphenylbenzene) and more interestingly an ion with m/z 388 with the correct $^{35}Cl/^{37}Cl$ isotopic ion-cluster corresponding to the cycloreversion product triene **8** (Scheme 3). Thermochemical analogy invites trapping experiments with electron deficient dienophiles to intercept cyclopentadiene derivative **8**; but heating adduct **6** in carbon tetrachloride (77°C) with phenylvinyl sulphoxide or phenylvinyl sulphone, or especially with highly reactive N-phenyltriazolindione[14] delivers tetraphenylbenzene and unreacted dienophile, but no product identifiable as an adduct of **8**. Clearly cycloreversion occurs, but **8** escapes capture by these dienophiles under these conditions. Perhaps for N-phenyltriazolindione (which is reported to react with cyclopentadiene instantaneously at -78°C[14]) the steric requirements for formation of the *endo*- transition-state is foiled by the bulky N-phenyl group. However failure to react with the sulphoxide and sulphone suggests that **8** is not especially reactive as a diene. However when adduct **6** is heated with an excess of maleic anhydride under similar conditions besides tetraphenylbenzene two isomeric adducts are formed in 4:1 ratio whose NMR spectroscopic parameters allows their identification as the *anti-endo* and *syn-endo* adducts **9** and **10**. Very similar results are obtained in the thermal decomposition of the analogous dimethyldiphenylcyclopentadieneone adduct **11** of **3**, thermolysis in the presence of maleic anhydride giving besides dimethyl-1,2-terphenyl, a similar mixture of adducts **9** and **10**. However if dienophile **3** is heated with tetracyclone in excess at higher temperatures (≈ 136°C) tetraphenylbenzene is certainly formed, together with as main product a tetraphenylated compound having m/z 744 (with the correct Cl_6 isotopic ion cluster for $C_{42}H_{30}Cl_6$) apparently formed by cycloaddition of **8** with tetracyclone and loss of CO, but the molecular symmetry of the compound, as reflected in the ^1H and ^{13}C NMR parameters is inconsistent with any obvious simple reaction pathways which might be envisaged for its formation, (see below). The high molecular mass of the compound, and inability to obtain crystals suitable for X-ray crystallographic analysis prompted an

investigation of the reaction of dienophile 3 with tetrachlorothiophene-1,1-dioxide in the expectation that an analogous decachloro- compound would furnish good quality crystals for X-ray analysis.

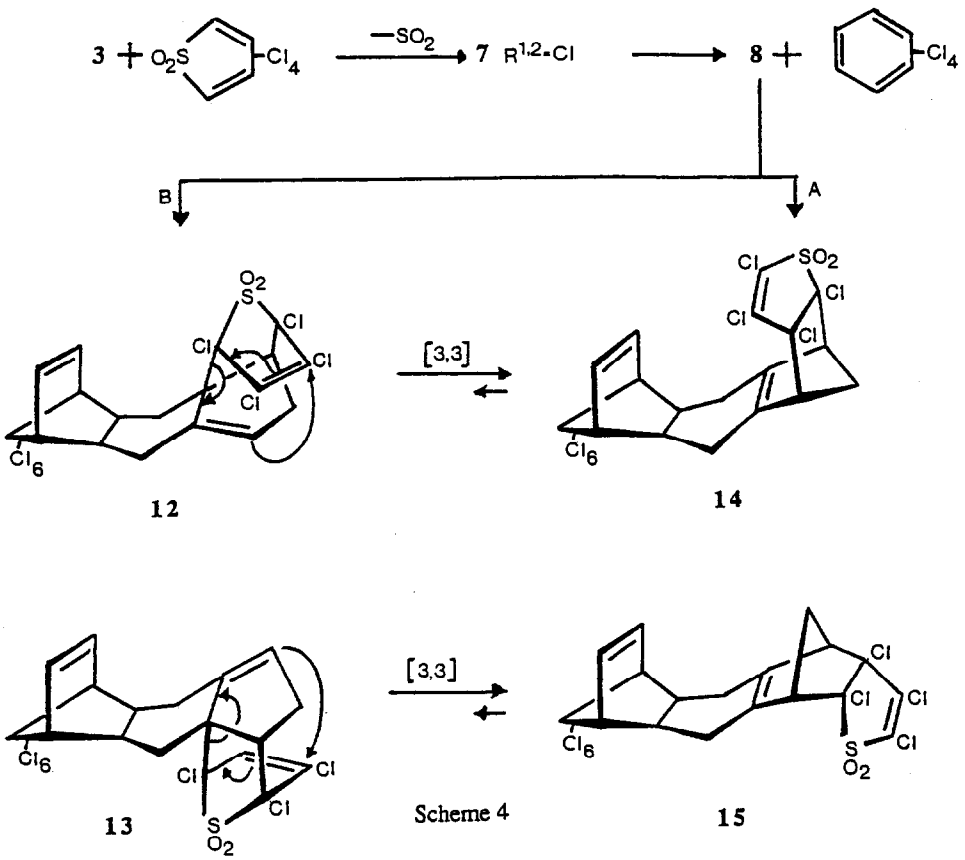


Scheme 3

Thermal [4+2]π Cycloaddition of Dienophile 3 with Tetrachlorothiophenedioxide ("TCTD").

Thiophene-1,1-dioxide derivatives exhibit pronounced enophilic and trienophilic reactivity in [4+2]- and [4+6]π thermal cycloadditions,[15] (in remarkable contrast to thiophenes[16] which show little propensity for enophilic behaviour[17]). The synthetically most widely utilised thiophene dioxide is 2,3,4,5-tetrachlorothiophene-1,1-dioxide, a strongly electron deficient diene.[18] Exemplifying TCTD reactivity, during its preparation a product derived from its Diels-Alder dimer is often isolated (≈1%), but the compound is inefficient in its ability for self-annelation compared to e.g. 2,3,4,5-tetrachlorocyclopentadieneone which rapidly forms a non-dissociating dimer in solution at 25°C.[11] The reduced propensity of TCTD for self addition suggests in fact that the chlorovinyl sulphone elements present have rather poor dienophilic reactivity, but the enophilic power of TCTD is strikingly revealed by its observable reaction with ethene at ambient pressure and temperature.[18a] Exposure of cyclopentadiene to TCTD on the other hand gives mixtures of products mainly containing the adduct from dienophile capture by enophilic TCTD, but also a significant amount of product is isolated which appears to derive from the addition of cyclopentadiene to TCTD acting as dienophile. The SO_2- bridged adducts formed from dienophile capture by TCTD often extrude SO_2 spontaneously, but the primary adduct is occasionally isolated.[18a,b] The extremely high enophilic reactivity of TCTD and the expected ease of removal of SO_2 from its adducts also provides impetus for investigating the products of its reaction with dienophile 3.

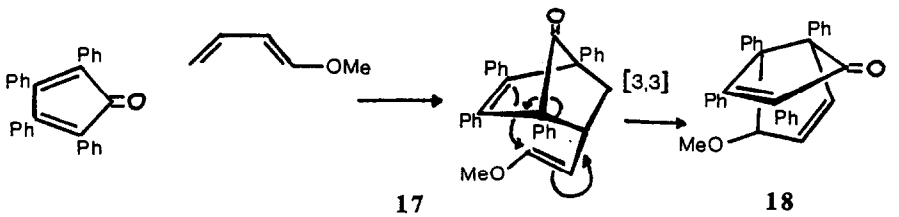
When compound **3** (1.5mmol) is exposed to TCTD (1.1mmol) in boiling chloroform (20ml), followed by solvent removal and flash chromatography of the products, only 1,2,3,4-tetrachlorobenzene and two new compounds **14** and **15** are isolated (in 1:1 ratio). The same two new compounds are also slowly formed when the reaction is conducted at room-temperature. Characterisation by $^{1}H/^{13}C$ NMR , mass spectrometry and combustion analysis shows that **14** and **15** are closely related isomers of composition $C_{18}H_{10}Cl_{10}SO_2$ and the very close correspondence of their spectroscopic properties (especially ^{13}C NMR parameters) provides compelling evidence for their relationship as stereoisomers. The elemental composition suggests the sequence (Scheme 4, path B) **3** + TCTD → adduct, - SO_2, - $C_6H_2Cl_4$ → **8** followed by **8** reacting as diene with TCTD as dienophile. Compound **14** in particular affords good quality crystals suitable for X-ray crystal structure analysis, revealing the molecular features shown in Fig. 1 seemingly consistent with the above reaction sequence. The appearance of compound **14** and stereoisomer **15** and no other annelation products finds a parallel in the reaction of 1,2-bismethylenecyclohexane with thiophene-1,1-dioxide[15a] and of 2,3-dimethylbutadiene with TCTD.[18a]



Scheme 4

It is not immediately clear however why diene **8** captures TCTD as dienophile to deliver equal amounts of adducts **14** and **15**, whereas the almost certainly less sterically demanding dienophile, maleic anhydride is stereoselective in its reaction with diene **8** giving a 4:1 ratio of *anti-endo* and *syn-endo* adducts **9** and **10**. The anomaly is particularly striking given the perceived low reactivity of diene **8** towards e.g. phenylvinyl sulphone and to N-phenyl triazolinedione (but where there could be a steric component). The very high reactivity of

thiophene-1,1-dioxides towards dienophiles, and the occasional isolation of the initial SO_2- bridged adduct[18a,b] suggests that the primary step in the reaction with 1,3-dienes is normal *endo*- dienophile capture by TCTD followed by fast Cope rearrangement of the initial, kinetic adduct to give a more stable (thermodynamic product) isomer, seemingly derived by dienophile behaviour of e.g. TCTD, (Scheme 4, path A). Relevant analogy is found in the apparent dienophile reactivity of tetracyclone towards 1-methoxybuta-1,3-diene,[19] also reasoned to be in reality capture of methoxybutadiene (π-rich dienophile) by the electrophilic diene tetracyclone, giving one stable stereoisomer of the expected carbonyl-bridge adduct **16**. The other, major product, **17**, has stereoelectronic features compatible with fast Cope rearrangement into the main product observed,**18** (Scheme 5).[20] Other examples are known of halogenated carbonyl-bridge compounds having appropriate stereochemistry undergoing relatively fast Cope [3,3] sigmatropy, especially when catalysed by Lewis acids.[21] Theoretical reasoning also points to e.g. **12** being the kinetic and **14** being the potential thermodynamic product of reaction of diene **8** with TCTD. For example a substantial lowering of π-energy is expected for **14** compared to **12** owing to the vinyl sulphone element,[22] introduced by rearrangement and perhaps contributing to the driving force. MNDOC[23] calculations for example yield ΔH_f values of 1243 kJmol^{-1} for the vinyl sulphone compound **14** and 1272 kJmol^{-1} for the proposed intermediate **12**, consistent with **12** as kinetic product.



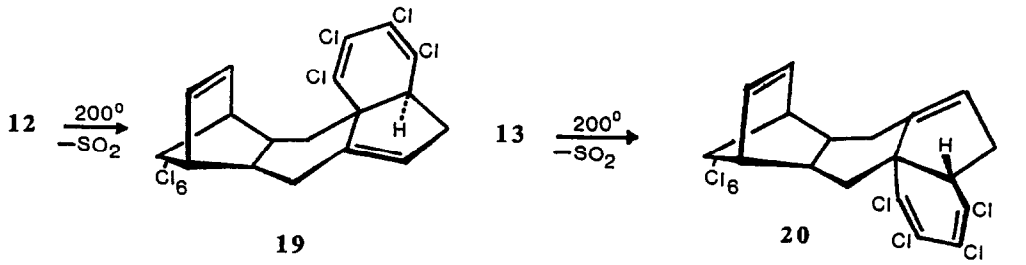
17 **18**

(**16** =exo-adduct)

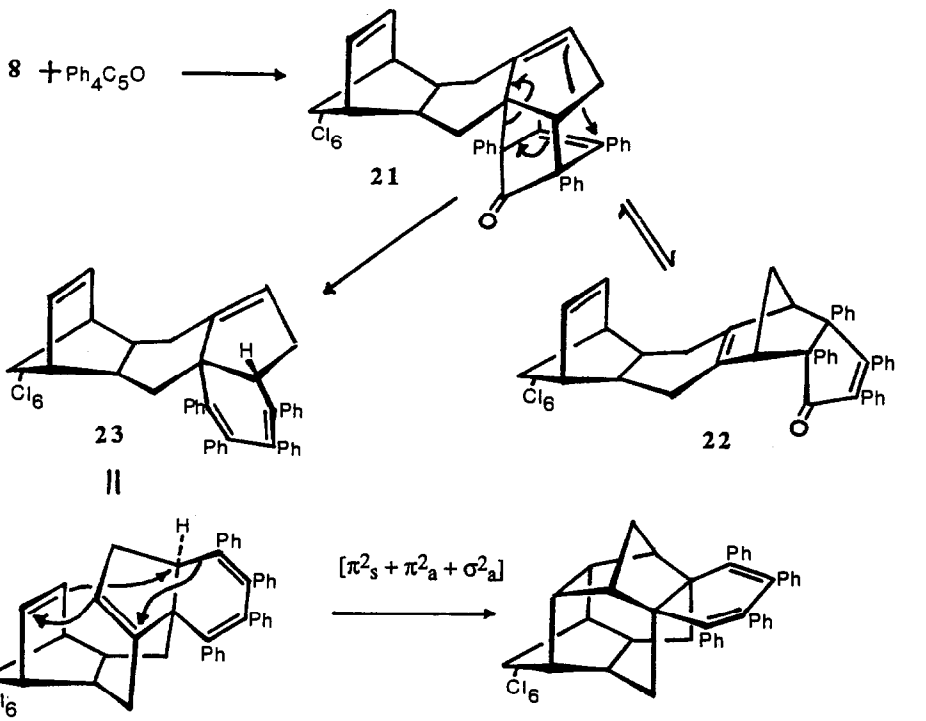
Scheme 5

The Cope rearrangement is often observed to be reversible.[21] Conditions under which the putative Cope rearrangement products **14** and **15** might come into equilibrium with their sigmatropic isomers **12** and **13** were therefore sought under higher temperature regimes. If formed, SO_2- bridged compounds **12** and **13** are expected to lose SO_2 rapidly and irreversibly at temperatures ≈ 200°C. Accordingly, heating solutions of **14** and **15** (in 1,2-dichlorobenzene, 210±5°C, 18hr), solvent removal and chromatography of the products gives respectively 95% and 97% of the respective pentacyclotetraenes **19** and **20** (Scheme 6), by the expected Cope sigmatropy delivering **12** and **13** which, as anticipated, irreversibly lose SO_2.[18b] Whilst this is not a definitive proof that **12** and **13** are initial metastable kinetic adducts in the reaction of intermediate diene **8** with TCTD, it is undeniable proof that **12,14** and **13,15** are connected by a Cope rearrangement reaction co-ordinate.

The stage is now reached when the higher temperature reaction of dienophile **3** with excess tetracyclone may be rationalised. In the first sequence of reactions diene **8** is delivered as described above (Scheme 3). Further addition ensues to give initially an adduct **21**, which whilst potentially in equilibrium with Cope rearrangement product **22** analogous with **14**, can also eject CO, delivering the pentacyclotetraene **23** analogous with **20**. The observed (major identifiable) product has ^1H and ^{13}C NMR parameters consistent with the symmetric cage structure **24** whose formation from **23** represents an orbital symmetry allowed thermal [π^2_s + π^2_a + σ^2_a] pericyclic reaction[5] of unusual type, (Scheme 6). Such a scheme does imply that diene **8** is stereoselective for *anti-endo* cycloaddition with tetracyclone, but is consistent with the steric requirement for *syn-endo* addition of this diene which is expected to result in more severe non-bonded interactions in the transition-state than for addition of TCTD. In the light of these findings the thermal properties of tetraenes **19** and **20** command attention and this is in hand.



3 + Ph_4C_5O −CO → 7 → 8 (Scheme 3)



Scheme 6

EXPERIMENTAL.

General Procedures.

NMR spectra were run on JEOL GX270, GX400 or Alpha500 spectrometers as solutions in $CDCl_3$ with TMS as internal standard. Chemical shifts are given in δ values as ppm downfield from TMS, ^{13}C spectra were referenced to the resonant frequency of the deuteriated solvent. ^{1}H NMR data is presented in the format: chemical shift [integral, multiplicity, coupling constants in Hz (if readily measurable), assignment]. ^{13}C NMR data is presented in the format: chemical shift [sign in 135° DEPT spectrum, assignment]. In most cases 2D COSY, CHSHF or JRES spectra were used to unambiguously assign the NMR spectra. E. I. mass spectra were obtained with probe samples using an AEI-GEC MS902 spectrometer with VG micromass facilities; all ion clusters showed the correct chlorine isotope abundance ratios in appropriate cases, data are presented in the format mass (assignment, % abundance). All melting points are uncorrected. Preparative TLC was carried out using Merk type PF-254,366 silica gel spread to a thickness of 0.8mm and visualised under a short wave UV lamp. Flash column chromatography was carried out using Merk type 60 silica gel, and dry flash chromatography with Merk type "H" silica gel. All solvents for chromatography were redistilled before use; petrol refers to the 40-60° b.p. fraction.

Preparations.

1,12,13,14,15,15-Hexachloropentacyclo[10.2.1.1^{5,8}.0^{2,11}.0^{4,9}]hexadeca-2(11),6,13-triene 3.

In a typical preparation, hexachloronorbornadiene **1** (15.10g, 0.05mol), bismethylenenorbornene[24] **2** (8.90g, 0.075 moles), and benzene (5ml) were sealed in a glass tube which was heated in a Carius furnace at 165±5°C for 24 hours. The viscous brown oil thus obtained was purified by dissolving in the minimum of DCM, followed by addition of *ca.* 150ml of petrol. The resulting precipitate (mainly polymeric material) was filtered off and the solvent removed *in vacuo* to yield a viscous golden oil, which was pure enough, by NMR, for reaction purposes. A small sample was purified by prep. TLC using 30%DCM/petrol as eluent, the resulting colourless oil was reluctant to crystallise. An overall yield for (155) of *ca.* 90% was indicated. (Accurate mass measurement, found: 413.910; $C_{16}H_{12}Cl_6$ requires 413.907); δ_H(400MHz) 1.94 (1H, d-t, J 5.8 and 1.7, 16-H), 2.04 (2H, m, 3,10-H), 2.08 (1H, d-t, J 5.8 and 1.7, 16'-H), 2.55 (2H, br. d, J 16.5, 3',10'-H), 3.14 (2H, m, 2,11-H), 3.22 (2H, m, 5,8-H) and 6.69 (2H, t, 6,7-H); δ_C(100MHz) 22.1 (-, 3,10-C), 43.8 (+, 2,11-C), 52.9 (+, 5,8-C), 71.3 (-, 16-C), 83.2 (0, 1,12-C), 102.3 (0, 15-C), 130.5 (0, 13,14-C), 142.0 (+, 6,7-C) and 143.8 (0, 4,9-C); *m/z* 414 (M^+, 67%), 379 (M^+-Cl, 100) and 343 (M^+-HCl_2, 16).

1,16,17,18,19,19-Hexachloro-7,8,9,10,-tetraphenylheptacyclo[14.2.1.1^{5,12}.1^{7,10}.0^{2,15}0^{4,13}0^{6,11}]heneicosa-4(13),8,17-triene-20-one 6.

A solution of **3** (3.48g, 8.4mmol) and tetracyclone (1.23g, 3.2mmol) in DCM (20ml) was heated under reflux for *ca.* 2 weeks, fresh DCM being added to replace any that evaporated. The solvent was removed *in vacuo* with minimal heating to give *ca.* 5g of purple foaming solid. Dry flash chromatography using a large funnel and increasing polarity solvent from neat petrol to neat DCM gave *ca.* 1.5g of purple solid which was mainly the adduct (176) contaminated with tetracyclone. Prep. TLC of this solid using 16 plates and 5 elutions with 30%DCM/petrol separated out the adduct (1.24g, 1.5mmol, 47% - yield not corrected for unreacted tetracyclone), m.p. 190-192°C dec (from DCM). (Found: C, 62.59; H, 3.81. $C_{45}H_{32}Cl_6O{\cdot}CH_2Cl_2$ requires C, 62.33; H, 3.87%); δ_H(400MHz) 1.56 (1H, d, J 9.2, 21-H), 2.37 (2H, m, 3,14-H), 2.57 (1H, d, J 9.2, 21'-H), 2.59 (2H, m, 3',14'-H), 2.67 (2H, s, 6,11-H), 3.22 (2H, br. s, 5,12-H), 3.23 (2H, m, 2,15-H), 6.83 (4H, m, Ar-H), 6.98 (6H, m, Ar-H), 7.20 (2H, m, Ar-H), 7.26 (4H, m, Ar-H) and 7.34 (4H, m, Ar-H); δ_C(100MHz) 19.8 (-, 3,14-C), 39.8 (-, 20-C), 43.3 (+, 2,15-C), 47.2 (+, 6,11-C), 49.5 (+, 5,12-C), 65.7 (0, 7,10-C), 83.1 (0, 1,16-C), 102.2 (0, 19-C), 126.9, 127.1, 127.6, 128.0, 129.2, 129.5 (+,+,+,+,+,+, Ar-C), 130.8 (0, 17,18-C), 134.6, 136.0 (0,0, Ar-C), 139.9, 142.3 (0,0, 4,13,8,9-C) and 196.8 (0, 19-C); *m/z* 388 (M^+-$C_{31}H_{22}O$, 10%) and 382 (M^+-$C_{15}H_{10}Cl_6O$, 100).

Preparation of *anti-* and *syn-* 1,12,13,14,15,15-hexachloropentacyclo[10.2.1.1^{5,8}.0^{2,11}.0^{4,9}]hexadeca-4(9),13-diene-6,7-dicarboxylic anhydride, 9 and 10.

A solution of the tetracyclone adduct **6** (84mg, 0.1mmol) and maleic anhydride (25mg, 0.25mmol) in carbon tetrachloride (5ml) was heated under reflux for 48 hours. The solvent was removed *in vacuo* to give 110mg of solid which by NMR was a 1: 1.2: 1: 0.2 mixture of maleic anhydride : tetraphenylbenzene : major product isomer **9** : minor product isomer **10**. Data for the major *anti-* isomer **9** (data for the minor *syn-* isomer in parentheses); δ_H(400MHz; $CDCl_3$) 1.54 (1.54) (1H, d, J 8.9, 16-H), 1.94 (1.70) (1H, d, J 8.9, 16'-H), 2.16 (1.75) (2H, m, 3,10-H), 2.48 (2.65) (2H, m, 3',10'-H), 3.18 (3.12) (2H, m, 2,11-H), 3.28 (3.35) (2H, m, 5,8-H) and 3.60 (3.60) (2H, m, 6,7-H); δ_C(100MHz; $CDCl_3$) 20.8 (22.0) (-, 3,10-C), 48.3 (44.7) (+, 2,11-C), 48.0 (47.8) (+, 6,7-C), 50.3 (50.3) (+, 5,8-C), 52.4 (52.4) (-, 16-C), 82.7 (82.5) (0, 1,12-C), 102.2 (102.2) (0, 15-C), 130.5 (132.1) (0, 4,9-C), 137.6 (138.1) (0, 13,14-C) and 171.2 (171.0) (0, C=O). *m/z* 486 (M^+, 50%), 458 (M^+-CO, 48) and 415 (M^+-HCl_2, 100).

Isolation of 1,12,13,17,18,18-hexachloro-5,6,7,8-tetraphenyl-heptacyclo[10.5.1.0^{2,4}.0^{4,9}.0^{4,16}.0^{9,14}0^{13,17}]. octadeca-5,7-diene 24.

A solution of **3** (0.50g, 1.2mmol) and tetracyclone (0.45g, 1.2mmol) in bromobenzene was heated under reflux for 48 hours. The solvent was removed with gentle heating under a N_2 blow down to yield *ca.* 0.95g of purple solid. This solid mixture was resolved by flash column chromatography, using 30%DCM/petrol as eluent, to give; unreacted **3** (0.3g, 0.7mmol), tetraphenylbenzene (0.2g, 0.5mmol), the cage structure **24** (0.15g, 0.2mmol, 40%) and several smaller fractions which consisted mainly of unreacted tetracyclone and other unidentifiable products. The cage compound **24** had m.p. 250-260°C (dec), (Found: C, 67.25; H, 4.15. $C_{42}H_{30}Cl_6$ requires C, 67.49; H, 4.05%); δ_H(400MHz; $CDCl_3$) 1.93 (2H, br.d, J 15.1, 3,10-H), 2.10 (2H, br.d, J 15.1, 3',10'-H), 2.26 (1H, d, J 6.2, 15-H), 2.94 (2H, m, 1,12-H), 3.02 (2H, m, 2,11-H), 3.07 (1H, d, J 6.2, 15'-H) and 6.5→7.1 (20H, m, Ar-H); δ_C(100MHz; $CDCl_3$) 24.3 (-, 3,10-C), 36.4 (-, 15-C), 39.5 (+, 2,11-C), 45.9 (0, 4,9-C), 59.8 (+, 1,12-C), 75.3 (0, 13,17-C), 84.6 (0, 1,12-C), 101.0 (0, 18-C), 125.0, 126.4, 126.5, 130.0, 130.3, 131.3 (+,+,+,+,+,+, Ar-C), 136.9, 137.7 (0,0, Ar-C) and 138.6, 139.8 (0,0, 5,8,6,7-C); *m/z* 744 (M^+, 17%), 709 (M^+-Cl, 5), 420 (M^+-$C_9H_6Cl_6$, 4) and 272 (M^+-$C_{37}H_{30}$, 100).

Preparation of Adducts 14 and 15.

The triene **3** (0.61g, 1.5mmol), and chromatographically pure TCTD (0.31g, 1.1mmol) were dissolved in 20ml of chloroform. The solution was heated under reflux for 24 hours. The solvent was removed *in vacuo* and the resulting mixture of isomers purified and resolved by flash column chromatography using 30%DCM/petrol as elution solvent, giving **14** (0.15g, 0.24mmole, 44% based on TCTD) and **15** (0.16g, 0.25mmole, 45% based on TCTD). The other fractions consisted mainly of unreacted **3** and 1,2,3,4-tetrachlorobenzene. The yield calculations assume that 2 equivalents of TCTD are needed to form 1 equivalent of each adduct.

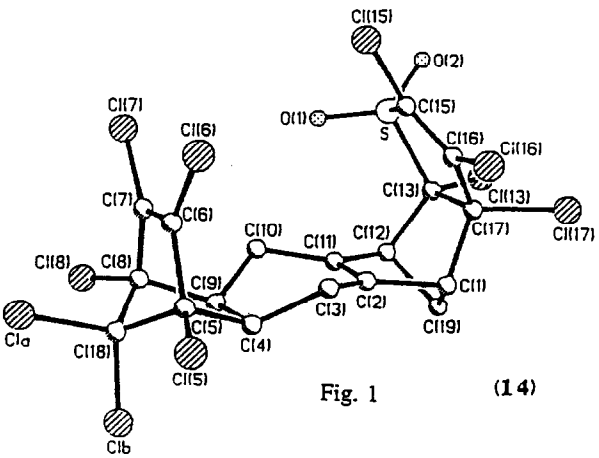


Fig. 1 (14)

[Vinylic carbons C-2 and C-11 are pyramidalised in the *endo*-direction by 4.8°]¶

Data for *endo-syn-endo* 5,6,7,8,13,15,16,17,18,18-decachloro-14-thiahexacyclo[10.5.1.1^{5,8}.0^{2,4}.0^{4,9}.0^{13,17}]. nonadeca-2(11),6,15-triene-14,14-dioxide 14.

m.p. 203.5-204.5°C (dec), (Found: C, 33.46; H, 1.55.$C_{18}H_{10}Cl_6SO_2$ requires C, 33.52; H, 1.56%); δ_H(400MHz; $CDCl_3$) 1.67 (1H, m, 3-H), 2.18 (1H, m, 10-H), 2.22 (1H, d-t, J 10.1 and 1.6, 19-H), 2.58 (1H, d-t, J 10.1 and 1.6, 19'-H), 2.64 (2H, m, 3',10'-H), 3.07 (2H, m, 4,9-H), 3.32 (1H, m, 1-H) and 3.42 (1H, m, 12-H); δ_C(100MHz; $CDCl_3$) 23.1, 23.8 (-,-, 3,10-C), 45.7, 46.2 (+,+, 4,9-C), 51.9 (-, 19-C), 61.9 (+, 1,2-C), 81.1, 82.1, 82.3 (0,0,0, 5,8,17-C), 90.4 (0, 13-C), 102.4 (0, 18-C), 131.5, 131.7 (0,0, 6,7-C), 132.8 (0, 16-C), 140.5 (0, 15-C) and 141.5, 142.7 (0,0, 2,11-C); *m/z* 642 (M^+, 4%), 576 (M^+-SO_2, 66), 541 (M^+-SO_2Cl, 100) and 388 (M^+-$C_4Cl_4SO_2$, 45).

Data for *endo-anti-endo* 5,6,7,8,13,15,16,17,18,18-decachloro-14-thiahexacyclo[10.5.1.1^{5,8}.0^{2,4}.0^{4,9}.0^{13,17}]. nonadeca-2(11),6,15-triene-14,14-dioxide 15.

m.p. 199.5-200.5°C (dec), (Found: C, 33.62; H, 1.56. $C_{18}H_{10}Cl_6SO_2$ requires C, 33.52; H, 1.56%); δ_H(400MHz; $CDCl_3$) 2.20 (1H, m, 10-H), 2.28 (2H, m, 3,3'-H), 2.50 (1H, d-t, J 10.0 and 1.7, 19-H), 2.61 (1H, d-t, J 10.0 and 1.5, 19'-H), 2.75 (1h, m, 10'-H), 3.01 (1H, d-d-d, J 9.8, 7.1 and 5.9, 4-H), 3.16 (1H, d-d-d, J 9.8, 8.8 and 4.6, 9-H), 3.28 (1H, m, 1-H) and 3.37 (1H, m, 12-H); δ_C(100MHz; $CDCl_3$) 22.1, 22.4 (-,-, 3,10-C), 44.5, 44.9 (+,+, 4,9-C), 51.7 (-, 19-C), 61.2, 61.5 (+,+, 1,2-C), 81.4, 82.2, 82.3 (0,0,0, 5,8,17-C), 90.9 (0, 13-C), 102.5 (0, 18-C), 130.6 (0, 16-C), 131.3, 131.4 (0,0, 6,7-C), 140.5 (0, 15-C) and 140.9, 141.5 (0,0, 2,11-C); *m/z* 642 (M^+, 15%), 576 (M^+-SO_2, 73), 541 (M^+-SO_2Cl, 100) and 388 (M^+-$C_4Cl_4SO_2$, 90).

Isolation of *endo-syn* 7,8,9,10,14,15,16,17,18,18-decachloropentacyclo[11.4.0.1^{7,10}.0^{4,13}.0^{6,11}]octadeca-3,8,14,17-tetraene 19.

A solution of **14** (14mg, .022mmol) in *o*-dichlorobenzene (1ml) was sealed in a Young's tube which was then heated in a Wood's metal bath at 210±5°C for 18 hours. The solvent was distilled off *in vacuo* and the resulting solid was purified by prep. TLC using 30%DCM/petrol as eluent to yield **19** (12mg, 0.021mmol, 95%), m.p. 204-206°C (Accurate mass measurement found: 575.771. $C_{18}H_{10}Cl_{10}$ requires 575.767); δ_H(500MHz; $CDCl_3$) 1.60 (1H, m, 12-H), 2.09 (1H, m, 12'-H), 2.20 (1H, m, 5'-H), 2.53 (1H, m, 2'-H), 2.77 (4H, overlapping multiplets (by 2D JRES spectrum signals are centered at 2.74, 2.75, 2.77 and 2.78), 6,11,2,5-H), 2.98 (1H, d-d, J 7.3 and 9.8, 1-H) and 5.83 (1H, m, 3-H); δ_C(100MHz; $CDCl_3$) 25.9 (-, 2-C), 26.8 (-, 5-C), 37.0 (-, 12-C), 42.3 (+, 11-C), 49.4 (+, 6-C), 53.8 (0, 13-C), 53.9 (+, 1-C), 81.7, 82.5 (0,0, 7,10-C), 102.6 (0, 18-C), 123.2, 124.4 (0,0, 14,17-C), 127.8 (+, 3-C), 130.9, 131.3, 132.4, 132.7 (0,0,0,0, 8,9,15,16-C) and 144.4 (0, 4-C); *m/z* 576 (M^+, 95%), 541 (M^+-Cl, 100), 505 (M^+-HCl_2, 15), 469 (M^+-H_2Cl_3, 15), 433 (M^+-H_3Cl_4, 12) and 397 (M^+-H_4Cl_5, 7).

Isolation of *endo-anti* 7,8,9,10,14,15,16,17,18,18-decachloropentacyclo[11.4.0.1^{7,10}.0^{4,13}.0^{6,11}]octadeca-3,8,14,17-tetraene 20.

A solution of **15** (37mg, .057mmol) in *o*-dichlorobenzene (1ml) was sealed in a Young's tube which was then heated in a Wood's metal bath at 210±5°C for 18 hours. The solvent was distilled off *in vacuo* and the resulting solid was purified by prep. TLC using 30%DCM/petrol as eluent to yield **20** (32mg, 0.055mmol, 97%), m.p. 240-242°C (Accurate mass measurement, found: 575.769. $C_{18}H_{10}Cl_{10}$ requires 575.767); δ_H(500MHz; $CDCl_3$) 0.86 (1H, t, J 13.4 and 12.9, 12-H), 2.14 (1H, m, 5'-H), 2.43 (1H, d-d, J 12.9 and 6.0, 12'-H), 2.47 (1H, m, 2-H), 2.64 (1H, m, 2'-H), 2.77 (1H, d-d, J 10.0 and 7.1, 1-H), 3.04 (1H, m, 5-H), 3.16 (1H, d-d-d, J 13.4, 9.8 and 6.0, 11-H), 3.43 (1H, d-d-d, J 10.7, 9.8 and 8.6, 6-H) and 5.77 (1H, m, 3-H); δ_C(100MHz; $CDCl_3$) 22.5 (-, 2-C), 33.5 (-, 12-C), 35.5 (-, 5-C), 44.0 (+, 6-C), 44.7 (+, 11-C), 53.6 (0, 13-C), 57.6 (+, 1-C), 82.4, 82.7 (0,0, 7,10-C), 103.1 (0, 18-C), 123.0, 126.0 (0,0, 14,17-C), 127.2 (+, 3-C), 130.5, 131.8, 131.9, 132.0 (0,0,0,0, 8,9,15,16-C) and 140.8 (0, 4-C); *m/z* 576 (M^+, 100%), 541 (M^+-Cl, 85), 505 (M^+-HCl_2, 18), 469 (M^+-H_2Cl_3, 17), 433 (M^+-H_3Cl_4, 12) and 397 (M^+-H_4Cl_5, 6).

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§ Striking examples of the π-bond protective effect of the CCl_2 group in hexahalogenated norbornenes are found in (1) the unreactivity of the ClC=CCl element towards $KMnO_4$; when the bridge chlorines of e.g. dihydoaldrin derivatives are removed by zinc, oxidation proceeds rapidly to give an α-diketone by loss of 2HCl (S. B. Soloway, Private Communication); and in (2) the survival of the vinyl ether group in annelated 1,2,4,7,7-pentachloro-3-ethoxy norbornenes in the presence of warm conc. sulphuric acid (*c.f.* ref. 2).

¶ Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.