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THE 7,8-EPOXY-2,3,5,6-TETRAKIS(METHYLENE) BICYCLO[2.2.2]OCTANE; SYNTHESIS AND DIELS–ALDER REACTIVITY†

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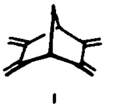
Abstract—The preparation of 7,8-epoxy-2,3,5,6-tetrakis(methylene)bicyclo[2.2.2]octane (5) is described. Evidence for transannular interaction between the homoconjugated *s-cis*-butadiene functions in **5** is found in the UV absorption spectrum. The Diels–Alder addition of **5** to tetracyanoethylene (TCE) is *syn*-regioselective and leads to the monoadducts **16**:**17** (85:15). The dienes **16**,**17** are less reactive than **5** toward TCE. *anti*-regioselectivity (leading to *exo*-2, *endo*-3-bis(chloromethyl)-5,6-bis(methylene)-*syn*-7,8-epoxybicyclo[2.2.2]octanes)(**25**) is observed in the double elimination of HCl from the *syn*-7,8-epoxy-*exo*-2,*endo*-3,*exo*-5,*endo*-6-tetrakis(chloromethyl)bicyclo[2.2.2]octane (**11**), precursor of **5**. The structures of the regioisomers **16**, **17** were confirmed spectroscopically and chemically. Elimination of HCl from the chloromethyl groups in **26** (TCE adduct of **25**) and HCN from the TCE adducts **16**, **17** and **26** can be induced by CsF in DMF.

The 2,3,5,6-tetrakis(methylene)bicyclo[2.2.n]alkanes **1**–**4** have been prepared for the first time in our laboratory.[1-3] Homo- and hyperconjugative interactions[4] between the two homoconjugated *s-cis*-butadiene chromophores occur as shown by UV absorption spectroscopy[1-3] and by photoelectron spectroscopy.[5] The tetraenes **1**–**4** have interesting chemical properties; for instance, the first equivalent of a strong dienophile such as tetracyanoethylene (TCE) adds more rapidly than the second equivalent,[6] thus allowing isolation of the corresponding monoadduct in good yield.[7,8] Stereoselectivity of the Diels–Alder additions has also been observed in some cases.[8] Tetrahapto- and bis(tetrahapto) transition metal complexes of **2**–**4** have been prepared;[9] they are thought to become useful intermediate, as the tetraenes **1**–**4**, in the synthesis of polyfunctionalised, polycyclic systems. We report here the preparation of 7,8-epoxy-2,3,5,6-tetrakis(methylene)bicyclo[2.2.2]octane (**5**) and present some of its spectroscopic and chemical properties. In particular we shall show that the cyclo-additions of the first equivalent of a strong dienophile such as TCE is regioselective due to the epoxide ring.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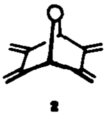
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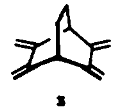
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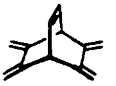
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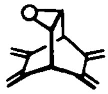
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RESULTS AND DISCUSSIONS

The *exo*-2,3,5,6-tetrakis(ethoxycarbonyl)bicyclo[2.2.2]oct-7-ene (**7**) was obtained (EtOH/toluene, para-toluenesulfonic acid, reflux) from the corresponding bis-anhydride **6** (95%). The all-*exo* tetraester **7** was isomerized into an equilibrated mixture of the more stable stereoisomers containing 80%. of the all-*trans* isomer **8**.[10] Without purification, this mixture was reduced with LAH in THF (reflux, 2 days) and yielded a mixture of tetrols from which 75% (based on **7**) of the pure isomer **9** could be isolated in a crystalline form. Treatment with $SOCl_2$ in dry pyridine (80%, 2 hr) furnished the corresponding tetrakis(chloromethyl)-bicyclo[2.2.2]oct-2-ene **10**. Epoxidation with metachloroperbenzoic acid in AcOEt afforded the epoxide **11**. This reaction required relatively drastic conditions (80°, 3 days, high conc), probably because of steric hindrance due to the two *exo*-chloromethyl groups in **10**. Quadruple elimination of HCl was achieved by heating **10** in THF in the presence of 10 equivalents of tbutOK (45°, 3 days) and yielded the epoxy-tetraene **5** (74%). The tetrachloride **10** can also be used to prepare the pentaene **4**, or after catalytic hydrogenation (4 atm, acetone, 10% Pd/C) of the endocyclic double bond, the tetraene **3** by treatment with excesses of tbutOK in THF.

The structures of **5**, **7**–**11** were deduced from their mode of formation, by their elemental analysis and by their spectroscopic characteristics (see experimental part). As was found for the tetraenes **1**–**4**, **5** showed an important transannular interaction between the two homoconjugated *s-cis*-butadiene chromophores. This was revealed by the UV absorption spectrum and by comparison of it with that of *exo*-2,3-epoxy-5,6-bis(methylene)bicyclo[2.2.2]octane **13**.[11] The V←N transition band of the diene chromophore in **5** is split into two bands of similar intensity which have a similar separation to the equivalent bands in **13** (Fig. 1). The λ_{max} of **5** show very small blue-shifts of 4 nm compared to those of **3**.[3] About the same hypsochromic shift is observed on comparing the UV absorption spectra of the

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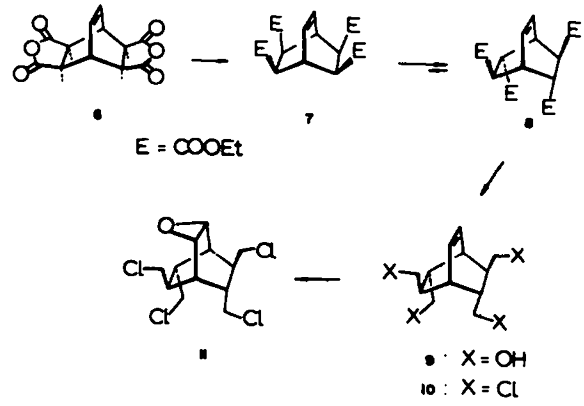
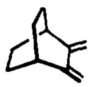
† "Interaction between non-conjugated chromophores", Part 10. Part 9, see Ref. 23. This work has been reported to the meeting of the "Société Suisse de chimie", in Bern (Oct. 1978).

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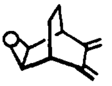
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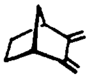
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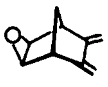
λmax: 252 nm (isooctane) 248 248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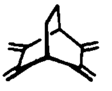
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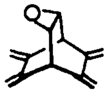
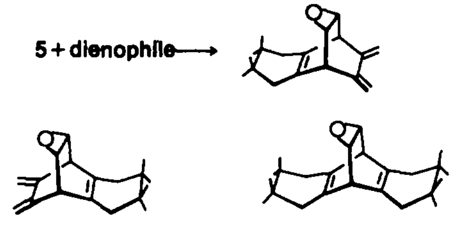
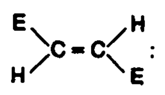

5

239 252;231 248;228

5 + dienophile ⟶



TCE:	16	17	18
E−C≡C−E:	19	20	21
 :	22	23	24

E = COOCH$_3$

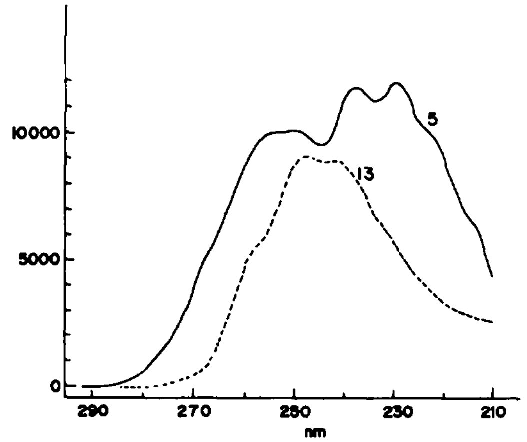
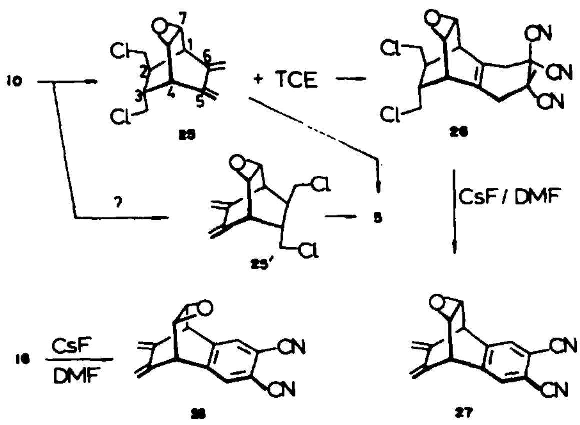


Fig. 1. UV absorption spectra in isooctane of the tetraene 5(——) and of the epoxy-diene 13 (---).

epoxy-diene 13 with that of the parent-diene 12.[12] A somewhat larger shift (~11 nm) was observed on comparing the UV absorption spectrum of *exo*-2,3-epoxy-5,6-bis(methylene)norbornane (15) with that of 2,3-bis(methylene)norbornane (14).[13] Although the norbornane skeleton is known to be more favorable than the bicyclo[2.2.2]octane skeleton for homoconjugative interactions,[14] the very small differences observed here (and in other cases, cf[15]) might also be due to Franck-Condon effects.

In the presence of two equivalents of TCE, 5 furnished the bis-adduct 18 quantitatively. However, when the tetraene 5 was mixed with one equivalent of TCE in benzene, a 85:15 mixture of the monoadducts 16, 17 was formed. None of the bis-adduct 18 could be detected in these conditions ($<2\%$, tlc, NMR), thus indicating an important reactivity decrease of the dienes16, 17 toward TCE compared with that of 5. The product ratio 16/17 was not affected by the change of solvent(acetone, MeCN, EtOH, CH_2Cl_2, $CHCl_3$) or by adding 0.02 equivalent of $ZnCl_2$. Contrastingly, no significant regioselectivity ($50\pm6/50\mp6$) was observed in the cycloadditions of 5 with dimethylacethylenedicarboxylate (DAD) and dimethylfumarate yielding the corresponding mixtures of monoadducts 19, 20 and, respectively, 22, 23. The structures of the regioisomers 16, 17 were indicated by their ^1H- and ^{13}C-NMR spectra and with the help of LIS reagents[16] (complexation of the epoxide appeared to be favored over that of the cyano groups. They were confirmed chemically in the following way.

When treated with 3 equiv of tbutOK in THF (50°, 12 hr) the tetrachloride 11 (10% in THF) eliminated selectively 2 moles of HCl from the chloromethyl groups *anti* to the epoxide ring and yielded the diene 25 (65%, after purification on a SiO_2 column) together with some tetraene 5 (12%). The structure of 25 was deduced from its spectral characteristics and with the help of $Yb(dpm)_3$ induced shifts[16] of the ^{13}C NMR spectrum (see Experimental). Gas phase chromatography showed no detectable amount of the corresponding syn isomer 25'. The

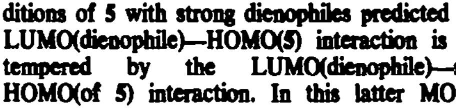


elimination of HCl from 25 yielding 5 occured 20–40 times more slowly than the eliminations yielding 25 from 10. Therefore, if 25′ were generated, it had a good chance to yield 5 readily. The high selectivity observed in the reaction 10→25+25′ can be attributed to steric hinderance due to the oxirane ring, inhibiting the approach of the base on the *syn*-*exo* side of 10. This assumes that *endo* attack by the base is unlikely. Another interpretation could be to invoke an enhanced acidity of the C–H hydrogens *anti* to the epoxide ring, due to the long range effect of the electrophilic character of this function (see below).[17]

The diene 25 added one equivalent of TCE and yielded the adduct 26. All our attempts (tbutOK in THF or DMSO, KOH in EtOH) to eliminate HCl from 26 lead to polymerisation, except when using the "naked" fluoride anion as a base.[18] Heating 26 in DMF (110°, 15 hr) in the presence of a 8–10 fold excess of CsF yielded the diene 27 (CsF was found to work better than KF + 18-crown-6 ether). Under these conditions the double elimination of HCl from the chloromethyl groups and the double elimination of HCN from the TCE residue were competitive. Aromatization of the adducts 16, 17 occurred also under similar conditions (4 fold excess of CsF, 100°, 15 hr) yielding a mixture of 28, 27 whose spectral data showed that 28 was the major product whereas 27 was the minor compound. The same treatment repeated with the pure adduct 16 yielded only the diene 28, thus confirming the structures of the regioisomers 16, 17.

The regioselectivity of the TCE addition to the tetraene 5 can be attributed to several factors. On one hand one can invoke a pre-equilibrium with the formation of a charge-transfer complex implying the nonbonding n(0) electrons of the oxirane and directing the attacking dienophile onto the *syn*-*exo* side of 5. The higher electron affinity of TCE compared with that of dimethylacetylenedicarboxylate and dimethylfumarate could explain the varying regioselectivities of the cycloadditions of these dienophiles to 5. On the other hand, one could invoke a long-range effect of the epoxide ring on the two diene functions, making the *anti*-diene less reactive than the *syn*-diene toward TCE*. We have explored the latter hypothesis with MO calculations.

According to the perturbation MO theory[19] and to a first approximation,[20] the shape and energy of the frontier MO's of the dienes should enable us to predict their relative Diels–Alder reactivity toward a given dienophile. In our case, one predicts that the cycloaddition of a strong (electron poor) dienophile such as TCE in the *syn*-*exo* or *syn*-*endo* face of 5 will be favored because the p_π coefficient of the highest occupied MO (HOMO) are larger (Fig. 2) at the carbons of the *syn*-diene (carbons C-2,2′,3,3′) than at the carbons of the *anti*-diene (C-5,5′,6,6′). This might arise from the stabilizing LUMO (epoxide)—HOMO (diene) homoconjugative interaction that is expected to be larger for the *anti*-diene than for the *syn*-diene because of a more favorable overlap between these MO's in the former case than the latter (see Fig. 3). The LUMO(epoxide)—HOMO(diene) homoconjugation could be responsible, in part at least, of the rate retardation effect exerted by an homoconjugated *exo*-epoxide function on the Diels–Alder additions of 2,3-bis(methylene)norbornanes:[22,23]



k^{I}_{TCE}: (1.0)	1/178	1/4	1/5	at 20°, toluene[22,23]
k^{I}_{DAD}: (1.0)	1/16	1/1.6		at 25°, CCl_4[22]

The above interpretation may well prove to be too naive. Indeed the *syn*-regioselectivity of the cycloadditions of 5 with strong dienophiles predicted from the LUMO(dienophile)—HOMO(5) interaction is certainly tempered by the LUMO(dienophile)—subjacent HOMO(of 5) interaction. In this latter MO, the p_π eigenvectors are larger at the carbons of the *anti*-diene than at the carbons of the *syn*-diene (Fig. 2). According to our hypothesis, the epoxide ring should also have a differential effect on the charged distribution between the two dienes in 5. In fact, the calculations showed very small differences between the charges at the olefinic carbon *syn* and *anti*. Moreover, contradicting effects were calculated depending upon the method used (EHT,[24] MINDO/3[25] and MNDO[26]). From these studies, it appeared that the differential effect of the epoxide ring on the ground state properties of the *syn* and *anti* dienes in 5 is a very small one. This does not exclude, however, a more important differential effect on the polarized configurations[27] of the transition states of the cycloadditions of 5 and on the transition states of the Elcb or E2 eliminations[28] of HCl from the chloromethyl groups in 10 yielding selectively the diene 25. More experimental

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*Preliminary results with methylvinylketone, methyl acrylate, acrylonitrile and maleic anhydride have shown these dienophiles to add to 5 with similar *syn*-regioselectivities.

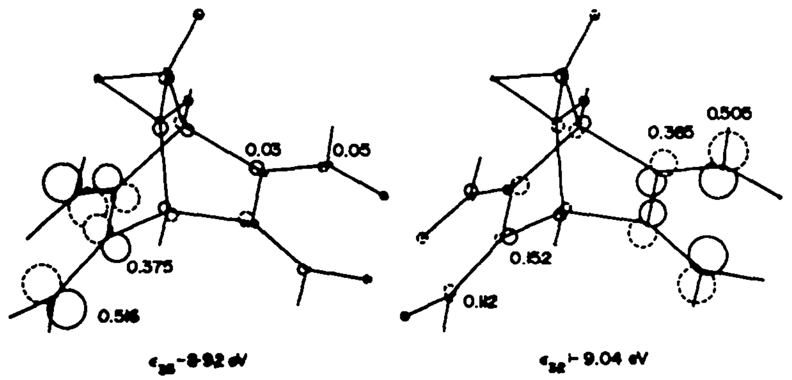

Fig. 2. HOMO's of 5 by the MINDO/3[25] method (minimized geometry). Similar HOMO's were calculated with the MNDO method.[26] The p_π coefficients are reported (MO drawing program, cf.[29]).

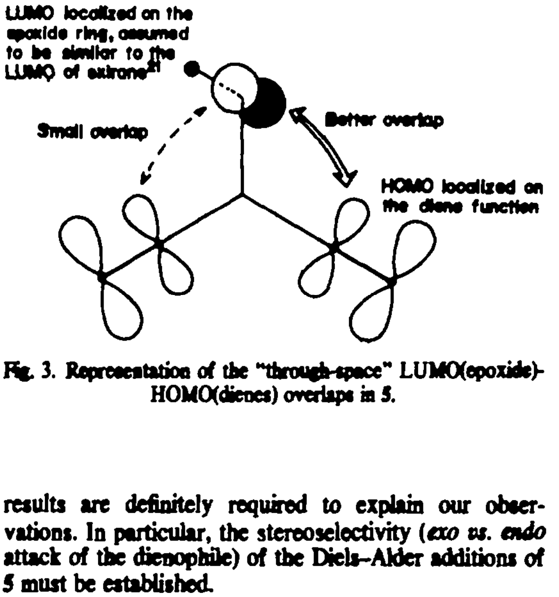

Fig. 3. Representation of the "through-space" LUMO(epoxide)-HOMO(dienes) overlaps in 5.

results are definitely required to explain our observations. In particular, the stereoselectivity (*exo vs. endo* attack of the dienophile) of the Diels–Alder additions of 5 must be established.

EXPERIMENTAL

M.p.s are not corrected, *Tottoli* apparatus; IR spectra ($\tilde{\nu}$[cm^{-1}], *Beckmann* IR-20A spectrometer; UV spectra, *Carl Zeiss* RPQ 20A/C or *Pye Unicam* SP 8–100 instruments (λ_{max}[nm](ε)); Mass spectra (MS(EI)) at 70 eV, CEC 21–490 *Bell–Howell* spectrometer (*m/e* [amu](% base peak)); MS in chemical ionization mode (CH$_4$, 1 Torr), GC–MS system HP 5980 A, *Hewlett Packard*; ^{1}H NMR spectra, *Bruker* WP 80 CW spectrometer: δ[ppm](multiplicity, apparent coupling constant *J*[Hz], number of protons, attribution [Eu(dpm)$_3$ relative induced shift]), *s*, singlet; *br*, broad; *d*, doublet; *t*, triplet; *qa*, quartet; *m*, multiplet; δ_{TMS} = 0.0 ppm; ^{13}C NMR spectra *Bruker* WP 60 spectrometer (15.08 MHz, spectrum width: 3750 Hz, 4096 points, FT mode): δ[ppm](multiplicity, apparent $^1J_{CH}$coupling constants [±2 Hz], tentative attribution [Yb(dpm)$_3$ relative induced shift]); elementary analysis, by the "Microlabor" of the University of Geneva (Dr. K. Eder). Abbreviations: *i.v.* = *in vacuo*, RT = room temperature, anhyd = anhydrous, sh = shoulder.

exo-2,3,5,6-*Tetrakis*(*ethoxycarbonyl*)*bicyclo*[2.2.2]*oct-7-ene* (7). 250 g (1 mole) bicyclo[2.2.2]oct-7-ene-*exo*-2,3,5,6-tetracarboxylic-2,3,5,6-dianhydride (*Aldrich*), 2.5 g *p*-toluenesulfonic acid, 1.5 l. EtOH and 0.75 l. toluene were heated under vigorous reflux in a 5 l. reactor fitted with a Soxlet extractor containing 60 g of molecular sieves (3–4 Å). The molecular sieves were renewed every 12 hr. After 3 days, the mixture was evaporated to dryness and dissolved in CH$_2$Cl$_2$ (900 ml), then washed successively with sat NaHCO$_3$ aq (1×, 300 ml) and with water (3×, 300 ml). After drying (Na$_2$SO$_4$) the solvent was evaporated *i.v.* and dried *i.v.* over P$_4$O$_{10}$, yield: 380 g(95%), white powder, m.p. 120–121° (EtOH); IR(KBr): 3000, 1780, 1380; ^{1}H NMR(CDCl$_3$): 6.42(m, 2H), 4.09(q, 7, 8H), 3.32(m, 2H), 3.05(m, 4H), 1.22(t, 7, 12H); MS(EI): 396(33), 352(22), 351(100), 323(25), 277(64), 250(35), 231(19), 208(29), 204(32), 177(51), 149(21), 131(32) (Found: C, 60.57; H, 7.21. Calc. for C$_{20}$H$_{28}$O$_8$(396.44): C, 60.59; H, 7.12%).

(±)-exo - 2, endo - 3,exo - 5,endo - 6 - *Tetrakis*(*ethoxycarbonyl*)*bicyclo* - [2.2.2] *oct* - 7 - *ene* (8). 40 g of 7 and 20 g anhyd K$_2$CO$_3$ heated under reflux in 300 ml abs EtOH for 30 hr. After cooling the K$_2$CO$_3$ was filtered off and the EtOH evacuated *i.v.* The residue was dried *i.v.* over P$_4$O$_{10}$ and paraffin, yield: 40 g(100%), oil containing 80% of 8 (v p c on a 50 m capillary column C-SD/SE 30, 220°, ret. time: 30'). IR(film): 2990, 1735, 1460, 1370, 1190; ^{1}H NMR(CDCl$_3$):): 6.4(t, 2H), 4.2(m, 8H), 3.5(m,2H), 3.1(m, 4H), 1.3(m, 12H); MS(EI): 396(0.8), 351(9.5), 350(15), 322(6), 277(12), 276(20), 177(32), 176(8), 175(20), 15(100), 150(33), 149(22).

(±)-exo - 2,endo - 3,exo - 5,endo - 6 - *Tetrakis*(*hydroxymethyl*) *bicyclo*[2.2.2] *oct* - 7 - *ene* (9). Under N$_2$, 350 ml sat soln of LAH in abs THF was added dropwise to a stirred suspension of 50 g (0.126 mol) crude 8 in 400 ml abs THF. After heating under reflux for 2 days, and then cooling to 0°, 40 ml of a sat soln of Na$_2$SO$_4$ in H$_2$O was added portionwise. After again heating to the b.p. it was filtered rapidly on SiO$_2$ (50 g). The SiO$_2$ + salts were extracted with hot EtOH (2×, 400 ml, 2 hr. heating under reflux and hot filtration). The extract was evaporated and the residue crystallised from EtOH at −15°, yield: 21.4 g (75%), colourless crystals, m.p. 155–156°; IR(KBr): 3350, 2900, 2860, 1450, 1380, 1350, 1305, 1120; UV(EtOH), end absorption ε_{210} = 120; ^{1}H NMR(D$_2$O): 6.2(m 2H), 4.6(s, OH), 3.6(m, 2H), 3.4(br.s, 2H), 3.2(br.s, 2H), 3.13 (br.s, 2H), 2.54(m, 2H), 1.41(m, 2H), 1.06(m, 2H); MS(CI): 229(14), 227(8), 212(12), 211(55), 209(19), 195(12), 194(89), 192(13), 181(11), 177(10), 175(100), 145(87); (Found: C, 63.14, H, 8.84. Calc. for C$_{12}$H$_{20}$O$_4$(228.29): C, 63.13; H. 8.83%.)

(±)-exo - 2,endo - 3,exo - 5,endo - 6 - *Tetrakis*(*chloromethyl*)-*bicyclo*[2.2.2] - *oct* - 7 - *ene* (10). *Anhyd pyridine* (5 g, 0.062 mol) was added under N$_2$ and vigorous stirring to freshly distilled SOCl$_2$ (9.3 g 0.078 mol). Then pure 9 (4.7 g, 0.02 mol) was added portionwise. After heating to 80° SOCl$_2$ (12.8 g, 0.108 mol) was added and heating was continued at 80° for 2 hr. After cooling to 0°, cold CH$_2$Cl$_2$ (120 ml) was added and excess SOCl$_2$ hydrolysed by adding 25 ml water. The mixture was extracted with CH$_2$Cl$_2$ (3×, 30 ml) and the organic phases washed with sat NaHCO$_3$ aq (2×, 70 ml), then with 3N HCl (3×, 40 ml) and finally dried (MgSO$_4$). Active charcoal (0.5 g) was added with stirring for 2 min. After filtration, the soln was evaporated to dryness and the residue recrystallised from CHCl$_3$: pentane yielding 5 g (80%), colourless crystals, m.p. 112°–113°; IR(KBr): 3010, 2980, 2960, 2910, 1450, 1440, 1375, 1330, 1305, 1290, 1160, 1100, 1020, 940, 915, 850, 785, 720, 700, 690. UV(EtOH): end absorption ε_{210} < 100; ^{1}H NMR (CDCl$_3$): 6.4(m, 2H), 3.2-3,9(m, 8H), 3.0(m, 2H), 1.3-1.9(m, 4H); MS(EI): 306(0.4), 304(2), 300(3.3), 255(0.8), 253(2.3), 251(2.4), 180(7), 178(41), 176(63), 129(17), 127(50), 91(100). (Found: C, 47.83; H, 5.40. Calc. for $C_{12}H_{16}Cl_4$(302.07): C, 47.71; H, 5.33%.)

(±)-syn-7,8-*Epoxy*-exo-2,endo-3,exo-5,endo-6-*tetrakis* (*chloromethyl*)-*bicyclo*[2.2.2] *octane* (11). *m*-Chloroperbenzoic acid (24 g, 0.15 mol) was added portionwise to 10 (6 g; 0.02 mol) in 120 ml EtOAc and heated to 80° for 3 days. After cooling to 0°, 10% K_2CO_3 aq (250 ml) was added slowly. The soln was evaporated to dryness and extracted (3 ×, 60 ml) with CH_2Cl_2. The extracts were washed with 10% K_2CO_3 aq (3 ×, 60 ml) and dried ($MgSO_4$). Active charcoal (0.5 g) was added and the soln heated under reflux for 2 min. After filtration the soln was evaporated to dryness and recrystallised from $CHCl_3$: pentane, yielding 5.7 g (90%), colourless crystals, m.p. 125–126°. IR(KBr): 3040, 2960, 2900, 2870, 1445, 1170, 1150, 905, 850, 780; UV(EtOH): end absorption, $\varepsilon_{210} < 100$. ^1H NMR($CDCl_3$): 3.2-3.9(m, 10H), 2.7(m, 2H), 1.2-2.3(m,4H); ^{13}C NMR($CDCl_3$): 52.08(d, 184, C-7[100]), 50.20(d, 184, C-8[98.2]), 47.16(t, 148, *exo*-2-CH_2Cl[12.5]), 46.5(t, 148, *exo*-5-CH_2Cl[23.8]), 45.16(t, 148, *endo*-6-CH_2Cl[13.1]), 45.16 (t, 148, *endo*-3-CH_2Cl[11.5]), 42.12(d, 138, C-2[21.8]), 40.06(d, 136, C-6[32.9]), 39.27(d, 128, C-5[32.7]), 39.27(d, 128, C-3[20.8]), 32.77(d, 139, C-1[39.6]), 32.65(d, 139, C-4[36.0])(cf. here-below the ^{13}C NMR characteristics for 25); MS(EI): 322(2), 320(6), 318(14), 316(11), 285(11), 283(29), 281(33), 271(14), 269(39), 267(41), 253(10), 251(10), 249(11), 247(29), 245(43), 219(16), 217(27), 215(10), 213(8), 145(49), 144(11), 143(100), 141(22), 139(22). (Found: C, 45.54; H, 5.23. Calc. for $C_{12}H_{16}OCl_4$(318.07): C, 45.31; H, 5.07%.)

7,8-Epoxy-2,3,5,6-tetrakis(*methylene*)*bicyclo*[2.2.2]*octane* (5). t-butOK (*Fluka*) (16.2 g; 0.144 mol) was added portionwise to a stirred mixture of 5 g (0.015 mol) epoxide 11 in 50 ml anhyd THF. The mixture was heated to 60° for 3 days. After pouring on ice (80 g) the mixture was extracted with pentane (3 ×, 80 ml). The organic extract was washed with water (3 ×, 50 ml), dried ($MgSO_4$) and evaporated *i.v.* to dryness. The residue was recrystallised from pentane at −20°, yield: 2 g(74%), colourless crystals, m.p. 85–85.5°. IR($CHCl_3$): 3100, 3000, 2960, 1650, 1620, 1440, 1400, 1260, 1185, 1095, 1020, 990, 945, 930; UV(iso-octane): 266(sh., 5800), 255(10200), 251(10200), 238(11800), 230(11900); UV(EtOH 95%): 266(sh., 6200), 255(10900), 249(10900), 237(12400), 229(12750). ^1H NMR($CDCl_3$): 5.35(s, 2H), 5.25(s,2H), 4.9(s,2H), 4.75(s,2H), 3.3(m, 4H); MS(EI): 172(54, 157(11), 144(17), 143(27), 141(29), 130(8), 129(68), 128(100), 127(34), 115(43), 91(21), 77(11), 65(9), 63(10), 51(13), 39(10). (Found C. 83.85; H, 7.13. Calc. for $C_{12}H_{12}O$(172.23): C, 83.68; H, 7.02%.)

TCE monoadducts of the tetrane 5 (16, 17). A mixture of 344 mg (2 mol) of 5, 20 ml anhyd benzene and 256 mg (2 mol) TCE (*Fluka*) was stirred at RT for 2 hr and evaporated to dryness, yield: 600 mg (100%) of a 85:15 mixture of the *syn* and *anti* adducts 16, and, 17 respectively. Crystallisation of this mixture from acetone:ether (5:1) yielded 400 mg(67%) of pure 16, colourless crystals, m.p. 235–237° (dec). IR(KBr): 3000, 2980, 2260, 1810, 1715, 1645, 1630, 1440, 1235, 1180, 1075, 1010; UV(dioxane): 253(sh, 6100), 237(10500), 224(sh, 9250); UV(EtOH 95%): 252(sh., 6000), 235(9900), 224(sh., 9500). ^1H NMR(acetone-d_6): 5.5(s, 2H), 5.1(s, 2H), 3.6(m, 2H), 3.5(br.s, 4H), 3.4(m, 2H); MS(EI): 300(13), 273(14), 272(51), 271(38), 230(11), 207(11), 206(18), 205(30), 193(21), 192(18), 191(16), 190(16), 180(21), 179(25), 178(27), 144(68), 129(83), 128(100), 115(100). (Found: C, 71.92; H, 4.00. Calc. for $C_{18}H_{12}ON_4$(300.33): C, 71.99; H, 4.03%). The minor adduct 17 was isolated from the mother-liquor of the above crystallisation of 16 by hplc (*Siemens S* 111) on a SiO_2 column(25 cm, ∅ = 1/8in, LiChrosorbSi 60, 80 atm., $CHCl_3$), yield: 50 mg (8%), colourless crystals, m.p.: 215–217°(dec). IR(KBr): 2980, 2940, 2860, 2260, 1715, 1630, 1440, 1370, 1265, 1190, 840; UV(dioxane): 242(sh., 7800), 231(9700), 225(9900); UV(EtOH 95%): 241(sh., 8200), 231(9800), 225(10000); ^1H NMR(acetone-d_6): 5.0(s, 2H), 4.8(s,2H), 3.5–4.0(m, 8H); MS(EI): 300(3), 273(9), 272(30), 271(20), 230(9), 207(12), 206(19), 205(32), 192(21), 191(15), 190(19), 189(18), 180(24), 179(19), 178(29), 177(18), 152(26), 144(67), 129(97), 128(100), 127(47), 115(90). (Found: C, 72.11; H, 4.10. Calc. for $C_{18}H_{12}ON_4$(300.32): C 71.99, H 4.02%.) The following relative Eu(dpm)$_3$ induced shifts [LIS] were recorded for the δ_H of the olefinic protons of a 85:15 mixture of 16: 17 (2 mg) in $CDCl_3$(0.5 ml) 16 5.00 (s, H(E)[0.03]); 5.38(s, H(Z)[0.03]); 17 4.85(s, H(E)[0.29]); 5.33(s, H(Z)[0.37]).

TCE bis-adduct of the tetraene 5 (18). A mixture of 172 mg (1 mmol) of 5, 10 ml anhyd benzene and 256 mg (2 mmol) TCE was stirred at RT for 12 hr. After evaporation to dryness, the crude adduct was recrystallised from acetone/pentane, yield: 400 mg (94%), white powder, m.p. 218–219° (dec). IR(KBr): 3010, 2980, 2970, 2860, 2260, 1620, 1440, 1370, 1230, 1180, 920, 840; UV(EtOH 95%): end absorption $\varepsilon_{210} = 4000$; ^1H NMR(acetone-d_6): 4.0(m, 2H), 3.5–3.8(m, 10H); MS(EI): 428(15), 399(100), 373(27), 371(22), 363(15), 361(14). (Found: C, 67.15; H, 2.89. Calc. for $C_{24}H_{12}0N_8$(428.41): C, 67.28; H, 2.82%.)

(±)-exo-2,endo-3-*bis*(*chloromethyl*)-5,6-*bis*(*methylene*)-syn-*7,8-epoxybicyclo*[2.2.2]*octane* (25). Under N_2 t-butOK (3.2 g, 29 mmol) was added portionwise to a stirred mixture of 3 g (9.4 mmol) of 10 in 30 ml anhyd THF. The mixture was stirred at 50° for 12 hr. After pouring into ice(80 g) the mixture was extracted with pentane (3 ×, 100 ml). After evacuation of the solvent *i.v.*, the residue was purified on a SiO_2 column (hexane: CH_2Cl_2 1:1). First fraction: 5, 0.2 g (12%);; second fraction: 25, 1.5 g (65%), m.p. 40–41°. IR(CH_2Cl_2): 3090, 3030, 2960, 2900, 1810, 1645, 1620, 1485, 1440, 1410, 1315, 1305, 1205, 1150, 930; UV(EtOH 95%): 254(sh., 6000), 245(9000), 241(sh., 8800); UV(dioxane): 256(sh., 6000), 246(9100), 242(sh., 8900); ^1H NMR($CDCl_3$): 5.5(s, 1H), 5.4(s, 1H), 5.0(s, 1H), 4.9(s, 1H), 3.8(d, 2H), 3.5–2.9(m, 6H), 2.1(m, 1H), 1.4(m, 1H); ^{13}C NMR($CDCl_3$): 143.27(s, C-5[21.8]), 139.93(s, C-6[21.3]), 110.73(t, 158, $H_2C = C(6)$[12.0]), 107.81(t, 158, $H_2C = C(5)$[12.5]), 52.69(d, 184, C-7[98.4]), 51.96(d, 182, C-8[100]), 46.55(d, 135, C-3[32.7]), 46.37(t, 150, *exo*-2-$ClCH_2$[23.4]), 46.07(t, 150, *endo*-3-$ClCH_2$[13.2]), 41.88(d, 136, C-1[37.6]), 41.52(d, 137, C-4[38.8]), 40.73(d, 136, C-2[32.6]). The attributions were based on the assumption that the lanthanide chelate coordinates preferentially the epoxide and has an "average" position that deviates from the "apparent" symmetry plane of the bicyclo-[2.2.2]octane skeleton toward C-3(carbon bearing the *endo*-$ClCH_2$ substituent). One cannot exclude a competitive coordination with the *exo*-2-$ClCH_2$ group. In that hypothesis, our assignments might have to be interchanged between the pairs C-2/C-3, C-5/C-6, C-5′/C-6′ and C-7/C-8. Nevertheless, we think that there is no ambiguity about the assignment of the *syn*-7,8-epoxy function (*cf* ^{13}C NMR data of 11). MS(E1): 246(1.6), 244(9), 242(13), 211(14), 209(5), 197(4), 195(11), 169(13), 167(21), 145(32), 91(100). (Found: C, 58.88; H, 5.68. Calc. for $C_{12}H_{14}0Cl_2$(245.15): C, 58.79; H, 5.75%.)

TCE adduct of the epoxy-diene 25 (26). A mixture of 25 (245 mg, 1 mmol) and TCE (128 mg, 1 mmol) in 15 ml anhyd benzene was stirred at RT for 5 hr. After evaporation of the solvent *i.v.*, the residue was recrystallised from acetone:ether, yield: 360 mg(96%), colourless crystals, m.p. 229.5–230°. IR(KBr): 3070, 3030, 2990, 2960, 2940, 2920, 2260, 1625, 1445, 1430, 1415, 1340, 1280, 1270, 1250, 1240, 1230, 1215, 985, 945, 910, 895, 845, 830, 790, 730, 710, 670; UV(EtOH): end absorption $\varepsilon_{210} = 2200$; ^1H NMR(acetone-d_6): 3.9(d, 2H), 3.7–3.1(m, 10H), 2.2(m, 1H), 1.3(m, 1H); MS(EI): 376(0.8), 374(5), 372(7), 339(3), 337(7), 325(4), 323(10), 319(7), 287(95), 279(24), 273(23), 272(29), 271(19), 259(100), 244(86) (Found: C, 58.00; H, 3.95. Calc. for $C_{18}H_{14}ON_4Cl_2$(373.24): C, 57.92; H, 3.78%.)

anti-*7,8-Epoxy-5,6-bis*(*methylene*)-(*1,2-dicyanobenzo*)[*4,5-b*]-*bicyclo*-[2.2.2]*octane* (27). Under N_2 and stirring, 26 (500 mg, 1.3 mol) and anhyd CsF (2.5 g, 16.5 mmol) in 70 ml anhyd DMF were heated to 110° for 15 hr. After evacuation of the solvent *i.v.* the residue was extracted with 50 ml acetone. The soln was concentrated *i.v.* purified by elution on a SiO_2 column (CH_2Cl_2: hexane: THF 5:5:1) yield: 65 mg(20%), colourless powder, m.p. 250–255° (dec). IR(KBr): 3040, 2920, 2240, 1620, 1605, 1480, 1400, 1340, 1240, 1200, 915, 845, 830; UV(dioxane): 252(17000), 227(48000); UV(EtOH 95%); 253(15000), 227(42000); MS(EI): 246(45), 245(23), 231(60), 218(48), 217(98), 216(71), 215(51), 203(71), 202(23), 191(43), 190(100); ^1H NMR(acetone-d_6): 8.0(s, 2H), 5.4(s, 2H), 5.0(s, 2H), 4.5(m, 2H), 3.7(m, 2H). (Found: C, 77.95; H, 4.07. Calc. for $C_{16}H_{10}ON_2$(246.27): C, 78.03; H, 4.09%.)

syn-*7,8-Epoxy-5,6-bis*(*methylene*)-(*1,2-dicyanobenzo*)[4,5-b]-*bicyclo*[2.2.2]*octane* (28). Under N_2 and stirring the pure adduct

16 (500 mg, 1.66 mmol) and anhyd CsF(1 g, 6.6 mmol) in 85 ml anhyd DMF were heated to 100° for 15 hr. After evacuation of the solvent *i.v.* (10^{-1} Torr) the residue was extracted with 30 ml acetone. The soln was concentrated and purified by elution on a column (50 cm, ∅ 4 cm) of SiO_2 (CH_2Cl_2: hexane: THF 5:5:1), yield: 95 mg(23%), white powder, m.p. 209–210° (dec). IR(KBr): 3050, 2990, 2970, 2920, 2240, 1625, 1485, 1400, 1340, 1250, 1185, 1055, 970, 920, 905, 840; UV(dioxane): 243(sh, 22000), 223(48000); UV(EtOH 95%); 247(16000), 223(44000); ^1H NMR(acetone-d_6): 7.9(s, 2H), 5.7(s, 2H), 5.3(s, 2H), 4.5(m, 2H), 3.7(m, 2H): MS(EI): 246(38), 245(23), 231(69), 218(49), 217(97), 216(77), 215(62), 203(64), 202(23), 191(35), 190(100) (Found: C, 78.15; H, 4.14. Calc. for $C_{16}H_{10}ON$ (246.27): C, 78.03; H, 4.09%.)

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