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Intramolecular 2H Group-Transfer (Dyotropic Rearrangements) in Alicyclic and Heterocyclic Bridged-Ring Systems [1]

K. Mackenzie, G. Proctor and D.J. Woodnutt
School of Chemistry, The University, Bristol BS8 1TS, U.K.

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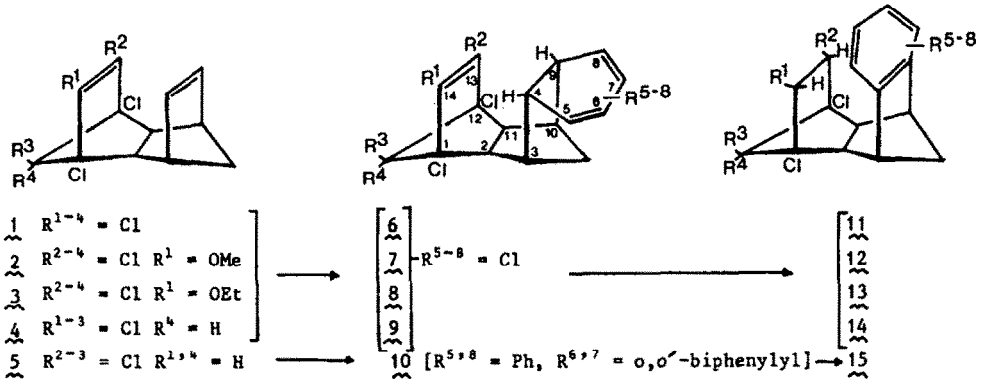
Summary: Examples of alicyclic frameworks containing a cyclohexa-1,3-diene ring as 2H donor held proximate to a variously-substituted acceptor Π-bond are compared for their reactivity in thermal 2H group-transfer reactions. Kinetic analysis reveals marked effects on rearrangement-rate as the acceptor Π-bond substituents are varied. Attempted synthesis of exact structural analogues of these compounds but with a 2,3-diazacyclohexadiene component replacing the cyclohexa-diene element [by (4 + 2)Π cycloadditions of 3,6-diaryl-1,2:4,5-tetrazines to dienophiles of the isodrin type] usually gives instead products of concomitant 2H group-transfer. These results are compared with the similar but generally slower 2H group-transfer rearrangement of pentacyclic 2-pyrazoline derivatives having relevant critical stereochemical features which result from 1,3-diarylnitrilimine (4 + 2)Π adductions with dipolarophiles of the isodrin type. Alkoxy and chlorine substitution of the acceptor Π-bond is rate-retarding for 2H group-transfer in both the alicyclic and heterocyclic representative systems examined, indicating truly pericyclic behaviour.

Since the stereospecific intramolecular group-transfer[2] of two hydrogen atoms in a non-catalysed thermal rearrangement was first clearly recognised[3,4] (viz 6 - 10 → 11 - 15 Scheme 1) there have been very few reports of other examples[5] of this theoretically interesting[2,6] and sometimes useful[7] dyotropic[8] process. (Intermolecular examples of 2H group-transfer are better known[9]). Those examples which we have previously disclosed are all essentially irreversible



Scheme 1

exothermic reactions in which saturation of the acceptor Π-bond and demonstrable[3] energy release accompanying aromatisation of the (substituted) 1,3-cyclohexadiene element indubitably provides substantial driving force. More recently, thermoneutral and reversible 2H group-transfer re-arrangements in oxygen-bridged systems having critical stereochemical features common to those of compounds 6 - 10 have been described by Vogel et.al., with approximate kinetic parameters[5].

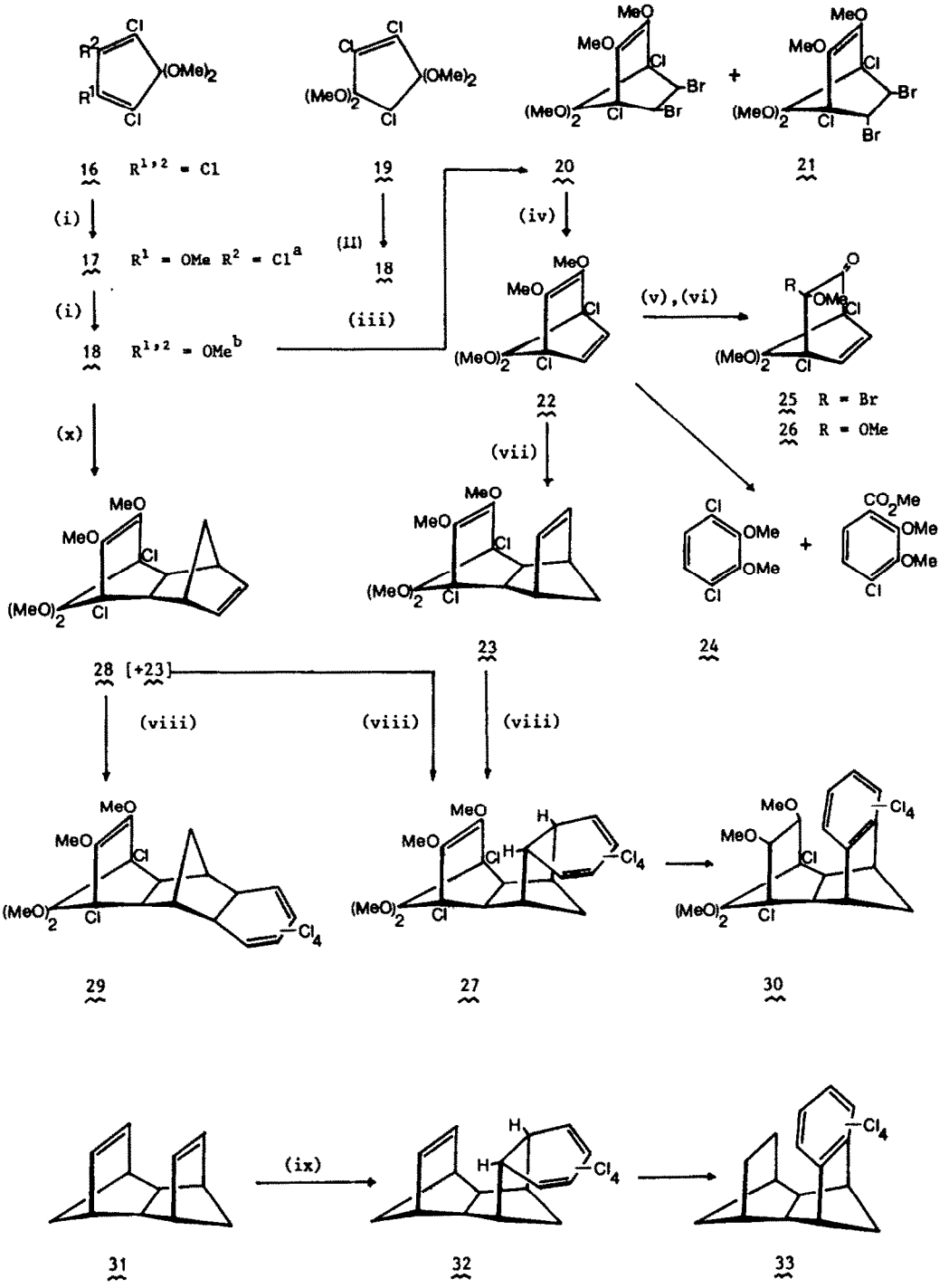
It is clear from our earlier work that the rearrangements of trienes 7 and 8 into their aromatic isomers 12 and 13 occur at similar but noticeably retarded rates compared to the analogous transformation, 6 → 11; the latter rearrangement occurs even at 20-25°, whereas trienes 7 and 8 are stable at this temperature. Models of these compounds indicate that the hydrogen nuclear displacements during their transfer must be quite small, and the thermal isomerisation can alternatively be described as a "Π-switching" process[6]. The slower rearrangements of 7 and 8 can then perhaps be qualitatively understood in terms of the greater and less symmetrical electronic

perturbation in the conjugated ClC = COEt function compared to the dichloroethene element in triene 6. This and other relevant considerations prompted us to investigate the effect on 2H group-transfer rate of replacing both vinylic chlorines at the receptor site with either alkoxy groups, or with hydrogen to provide a more fundamental basis for comparison, and in addition to probe the effects of replacing the cyclohexa-1,3-diene donor elements in e.g. 6 and 8 with five- and six-membered heterocyclic groups to further define the scope and limitations for 2H group-transfer within a closely related group of structures. Part A of the following describes the expedient synthesis of trienes 27 and 32 (Scheme 2) as suitable model compounds for kinetic comparisons with trienes 6 and 8, and in Part B we describe the synthesis, properties and rearrangements of relevant heterocyclic analogues of these systems (previously unknown types), and make kinetic comparisons.

Part A. Synthesis and Rearrangement of Trienes 27 and 32: Strategy for making isodrin analogues 1 - 3 is based on the (exothermic) endo-endo cycloaddition of polyhalogenated norborna-dienes with cyclopentadiene;[10] but whilst 2-alkoxypentachloronorbornadienes are readily accessible from 1,2,3,4,7,7-hexachloronorbornadiene and hence the cyclopentadiene adducts 2 and 3,[10] two vinylic chlorines cannot be so readily substituted by alkoxy groups using the earlier methodology (KOH-ROH- DMSO). However, whilst it is well known that 7-norborna-2,5-dienone acetals are thermally unstable,[11] significant amounts of their endo-endo cyclopentadiene adducts can be formed under appropriate conditions,[12] and the same compounds sometimes accompany the major exo-endo cycloadducts in thermal addition of halogenated cyclopentadienone acetals with norbornadiene[13]. These alternative pathways to pentacyclic triene 27 employed here are illustrated in Scheme 2, starting from tetra-chloro-cyclopentadienone acetal 16.

Some points of incidental interest arise in connexion with the chemistry depicted in Scheme 2. Dimethoxydiene acetal 18 (a rarely utilized synthon) has previously been obtained but in poorish yields concomitant with decomposition from methoxy trichlorodienone acetal 17 by prolonged exposure to KOH-MeOH mixtures (∿68°), the product containing the methanol adduct of diene 17, cyclopentendione bis-acetal 19[14]; we find that diene 18 is advantageously prepared from trimethoxytrichlorodiene 17 by treatment with KOH-MeOH-DMSO mixtures at 25° with little decomposition, but also accompanied by chromatographically separable bis-acetal 19 (18 : 19 ∿ 1:1). [The reagent-limited conversion of dienone-acetal 16 into trimethoxytrichloro compound 17 is similarly accomplished (>98% conversion) and its structure as the 2,5,5-trimethoxy compound and not the 1,5,5-isomer as earlier claimed[14] follows from the structures of derivatives of its thermal cycloadducts[15], its spectroscopic and chemical properties[16] and other independent evidence[17]] Dienone-acetal 18 is also formed from trichlorocyclopentendione bis-acetal 19 in strongly basic media (^{t}BuOK-DMSO); the derived anion evidently eliminates $\bar{O}Me$ which substitutes vinylic chlorine in situ giving 18 (60% conversion).

Cycloaddition of diene 18 with cis/trans dibromo-ethylene mixtures is stereoselective for cis-alkene, as expected, - but surprisingly slow for a comparitively electron-rich diene compared to the similar reaction with diene 16 (e.g. at ∿ 100°[11]), perhaps due to steric retardation; little reaction occurs below 170-180°. Efficient debromination of cis-endo dibromo-adduct 20 to give virtually pure norbornadienone acetal 22 is achieved in high yield only under specific conditions (Zn-HOAc-Et_2O ∿ 0°), prolonged exposure to zinc causing decomposition (presumably by Lewis acid co-ordination - and in this connexion $Yb(fod)_3$ reagent fails to catalyse[18] cycloaddition of norbornadienone acetal 22 with cyclopentadiene at 20°). As a potentially interesting synthon, norbornadienone acetal 22 is room-temperature stable in solution for several days, but at 40° ($CDCl_3$) decomposes with $\tau\frac{1}{2}$ ca. 3h; it reacts very rapidly with $C_5H_5\overset{+}{N}HBr_3^-/CH_2Cl_2$ (1 mol) giving the reactive α-bromo ether 25 (>90%) which is easily solvolysed under neutral conditions in alcohols giving high yields of e.g. norborn-5-ene-2,3,7-trione bis-acetal derivative 26.



Scheme 2

Reagents and Notes: (i) KOH-MeOH-DMSO, 20° (ii) $KOBu^t$- DMSO, 20° (iii) cis+trans BrCH=CHBr, 170-180°, sealed tube (iv) Zn-HOAc-Et_2O, 0° (v) $C_5H_5NHBr_3$-CH_2Cl_2, 20° (vi) MeOH-$CaCO_3$, 68° (vii) cyclopentadiene, 125-135°, sealed tube (viii) tetrachlorothiophenedioxide, heptane, 98° (ix) $C_4Cl_4SO_2$, 36° (x) norbornadiene. (a) Characterised as the norbornadiene adduct; (b) characterised by vinylene carbonate adduction.

Heating norbornadienone acetal 22 with cyclopentadiene (pressure, 120-130°) gives only very poor yields of the required cycloadduct 23, (6%), bridge extrusion giving 3,6-dichlorocatechol dimethyl ether 24 as the major product. Nevertheless, adduct 23 affords the target pentacyclic triene 27 by inverse electronic demand[19] adduction with highly reactive tetrachlorothiophene dioxide[20] ("TCTD") and concomitant SO_2 bridge elimination; the endo-endo-exo pentacyclic triene 27 obtained is identical to that derived by a similar TCTD - cycloaddition with isomer 23-enriched fractions from the stereoisomeric mixture of adducts (23,28) resulting from adduction of diene 18 with norbornadiene. The latter cycloaddition is both remarkably retarded and much less stereoselective than for the similar addition of diene 16[13,21] a clear manifestation of the comparitively electron-rich character of diene 18 compared to its analogue 16 in an inverse-demand cycloaddition.[19]

Thermal Rearrangement of Triene 27, Kinetic Comparison with its Analogues 6 and 8, and the Elusive Character of Triene 32:

Triene 27 is less mobile in 2H group-transfer isomerisation into aromatic compound 30 than analogues 7 and 8; for example, heating crystals of triene 27 *in vacuo* with δ_H monitoring gives $\tau_{\frac{1}{2}} \sim 11.5$h at 130.2 ± 0.1°, somewhat larger than estimated for trienes 7 and 8, inviting more precise kinetic comparison of the family of trienes 6, 7, 8 and 27. The rearrangements of 6, 7 and 8 are unaffected by air and catalysts[3], and monitoring of thermostatted decalin solutions of trienes 6, 8 and 27 at the relevant principal λ_{max} (near 300 nm, where the products are nearly transparent[22]) gives data affording excellent linear first-order rate plots from which the data-pairs in Table 1 are obtained, computation[23] giving the activation parameters in Table 2*.

Table 1

Unimolecular Rate Constants for Isomerisations

6:	Temp. (°C):	79.8°	82.2°	84.8°	87.7°	90.0°	95.0°	96.0°
	k_1, s^{-1} x 10^5	3.85	4.85	6.26	8.46	10.6	16.6	18.4
8*:	Temp. (°C):	99.8°	105.5°	107.0°	109.8°	115.0°	115.2°	120.0°
	k_1, s^{-1} x 10^5:	1.68	2.87	3.46	4.59	7.32	7.72	11.3
27:	Temp. (°C):	110.4°	114.3°	119.5°	120.1°	124.9°	127.5°	130.3°
	k_1, s^{-1} x 10^5	1.72	2.48	4.01	4.31	6.59	8.34	10.6
42:	Temp. (°C):	185.7°	190.1°	196.0°	201.3°	205.2°		
	k_1, s^{-1} x 10^5:	3.38	4.75	7.40	10.8	13.99		
43:	Temp.(°C):	185.7°	191.7°	196.7°	202.1°	207.6°		
	k_1, s^{-1} x 10^5	5.28	8.39	12.3	18.7	27.9		
44:	Temp.(°C):	185.7°	193.0°	196.7°	199.5°	207.6°		
	k_1, s^{-1} x 10^5:	2.34	3.94	5.15	6.28	11.04		
53:	Temp. (°C):	165.2°	175.9°	177.1°	185.7°	190.7°		
	k_1, s^{-1} x 10^5:	7.47	16.8	18.5	34.7	48.3		
55:	Temp. (°C):	165.2°	170.1°	177.1°	185.7°	190.7°		
	k_1, s^{-1} x 10^5:	6.65	9.72	16.2	31.1	43.2		

*Similar data apply to compound 7; k_1 (7): k_1 (8) is 1.17 at 120°

Table 2

Eyring Activation Parameters for Isomerisations

	$\Delta E_a^{(a)}$	$\Delta H^{\#(a)}$	$\Delta S^{\#(b)}$	$\Delta G^{\#(a)}$	log A
6:	25.07 ± 0.17	24.48 ± 0.17	-9.76 ± 0.09	27.39	11.09 ± 0.10
8:	27.69 ± 0.35	27.08 ± 0.35	-8.22 ± 0.14	29.53	11.43 ± 0.20
27:	28.20 ± 0.11	27.61 ± 0.10	-8.88 ± 0.05	30.25	11.29 ± 0.06
42:	31.88 ± 0.27	31.29 ± 0.26	-11.55 ± 0.14	34.73	10.70 ± 0.13
43:	33.44 ± 0.16	32.85 ± 0.16	-7.29 ± 0.05	35.02	11.63 ± 0.08
44:	31.11 ± 0.17	30.52 ± 0.16	-14.00 ± 0.11	34.69	10.17 ± 0.08
53:	29.72 ± 0.18	29.12 ± 0.18	-11.68 ± 0.10	32.61	10.67 ± 0.09
55:	29.81 ± 0.24	29.22 ± 0.23	-11.69 ± 0.13	32.71	10.67 ± 0.12

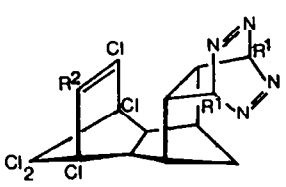
(a) kcal. mol^{-1} (b) cal. mol^{-1} $^oK^{-1}$ converted from data expressed in kJ, J.

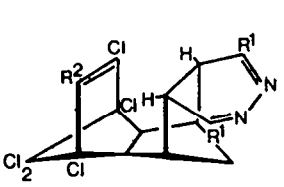
The data in Table 2 consistently show a small but significant negative activation entropy term $\Delta S^{\dagger}$ in the 2H transfer/Π-switching rearrangement of trienes 6, 8 and 27; this may be interpreted as due to transition state stiffening as the relevant cyclohexadiene allylic sp^3 carbons rehydridise during rearrangement with concomitant aromatisation. This effect is absent in the example discussed by Vogel et.al., who record a small positive entropy term for what is effectively an intramolecular variant of the ethane + ethene ⇌ ethene + ethane transformation. The rate differential k_1 (6)/k_1(8) is at least an order of magnitude near 96° but the effect of an additional methoxy group at the 2H receptor Π-bond is seen to be less marked [k_1(8)/k_1(27) = 2.67 near 110°]; thus it appeared that strongly conjugating methoxyl groups disfavour 2H group-transfer compared to chlorine atoms. In a reaction proceeding via biradical or zwitterionic intermediates, both types of substituent would be expected to be stabilising and rate-enhancing, and arguably the relatively small effects observed here are due to differential stabilisation of an intermediate as MeO groups are replaced by Cl atoms; Π-bond unsubstituted triene 32 is therefore a cogently relevant target for synthesis and comparison. Attempted synthesis of triene 32 by exposure of hexadechloroisodrin 31 to TCTD results in rapid addition and SO_2 extrusion at 25-35°, but here concurrent Π-switching occurs and the isolated product is the known[3] isomer 33! At 36° and 0.36 M in each component, δ_H monitoring of the reaction of 31 with TCTD shows second-order kinetics with a half-completion time of ∿ 720s and 75% vinyl proton signal (5.26) attenuation after ca. 0.5h giving k_2 as roughly 4×10^{-3} $(mol/lit)^{-1}s^{-1}$, and since little evidence for the intermediate triene 32 is observed (UV, NMR assay of crude product), for the unimolecular rearrangement of triene 32 k_1 is assumed to be at least an order of magnitude larger, i.e. $4 \times 10^{-2}s^{-1}$. Using extrapolated values of k_1 for the rearrangement 6 → 11 at 36° (∿ $2 \times 10^{-7}s^{-1}$) gives the ratio k_1 (32)/k_1(6) ∿ 2×10^5 at 36°. This apparently dramatic increase in kinetic reactivity of triene 32 compared to 2H acceptor-substituted triene 6 combines both differential electronic effects and a steric component associated with the dichloro (or dimethoxy) methylene bridge and the developing s- dichloroethano bridge. Experiments with heterocyclic analogues of trienes 6 and 32 indicate that this steric component is not large however.

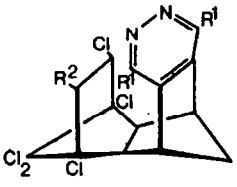
Part B Synthesis and Properties of Dihydropyridazines 36 - 38 and 2-Pyrazolines 42 - 45, and 53 - 55. Kinetic Comparison of 2H Group-Transfer in 2-Pyrazoline Derivatives

The synthesis of framework analogues of trienes 6 - 10 but with a heterocyclic system replacing the 1,3-cyclohexadiene element e.g. dihydropyridazines 36, 37 is readily realised utilising inverse electronic demand (4 + 2)Π cycloaddition with 1,2:4,5-tetrazine derivatives.[24] Thus isodrin 1 heated with 3,6-bisaryl-1,2:4,5-tetrazines at 110-136° gives products of dinitrogen extrusion from the initial adducts 34, 35, tetrazine addition being considerably faster than with tetra-arylated cyclopentadienones.[4,21] The products have ^{1}H NMR and UV spectra [24,25] characteristic of pyridazine derivatives 39 and 40, the rational products of comcomitant 2H group-transfer in the transiently formed dihydropyridazines 36 and 37. By contrast, dienophile 3, a more electron-rich dienophile than 1 (butadienoid Π - Π interaction), reacts considerably faster with 3,6-bis(2′-pyridyl) tetrazine (at 77°) giving only the expected intermediate 38 with little evidence of any 2H group-transfer, viz product 41, consonant with the relatively slower rearrangement of trienes 7, 8 and 27 with analogues vinyl-ether 2H acceptor sites, compared to triene 6. Dihydropyridazine 38 shows little propensity to rearrange at temperatures up to 180°.

These observations invited comparison of the dihydropyridazines 36 - 38 with similar structures but having a smaller heterocyclic ring element as 2H donor. The synthesis of a range of relevant model compounds by appropriate 1,3-dipolar cycloadditions with 1 and its analogues as dipolarophiles can be envisaged, and in particular 2-pyrazoline derivatives by adduction with 1,3-diarylnitrilimines[26]. 2,5-Diaryl-1,2,3,4-tetrazoles[27] which readily extrude nitrogen on mild thermolysis or photolysis[26,28] are particularly convenient sources of diarylnitrilimine 1,3-dipoles and accordingly isodrin 1 (in excess) heated (PhBr, 157°, N_2) with a range of diaryltetrazoles (Scheme 3) and preparative TLC product separation gives the 2-pyrazoline derivatives 42 - 45 in upto 80% yield. In every case a small quantity (∿6%) of an isomeric higher m.p. compound is also



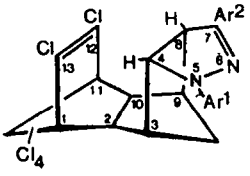


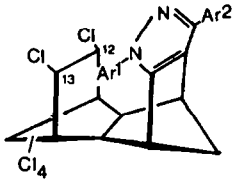


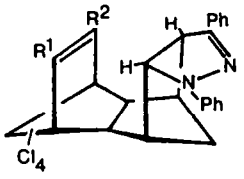
34 R^1 = Ph R^2 = Cl ⟶ [**36** R^1 = Ph R^2 = Cl] ⟶ **39** R^1 = Ph R^2 = Cl

35 R^1 = 2′-C_5H_4N R^2 = Cl ⟶ [**37** R^1 = 2′-C_5H_4N R^2 = Cl] ⟶ **40** R^1 = 2′-C_5H_4N R^2 = Cl

38 R^1 = 2′-C_5H_4N R^2 = OEt ⟶ **41** R^1 = 2′-C_5H_4N R^2 = OEt







42 $Ar^{1,2}$ = Ph ⟶ **46**

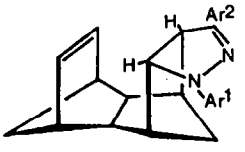
43 $Ar^{1,2}$ = p-MeC_6H_4 ⟶ **47**

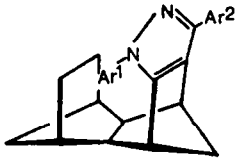
44 $Ar^{1,2}$ = p-ClC_6H_4 ⟶ **48**

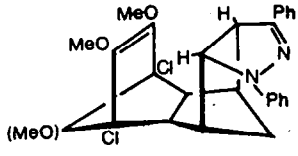
45 Ar^1 = p-MeC_6H_4 Ar^2 = p-ClC_6H_4 ⟶ **49**

50 R^1 = OEt R^2 = Cl

51 R^1 = Cl R^2 = OEt







53 $Ar^{1,2}$ = Ph ⟶ **56**

54 $Ar^{1,2}$ = p-MeC_6H_4 ⟶ **57**

55 $Ar^{1,2}$ = p-ClC_6H_4 ⟶ **58**

52

Scheme 3

isolated which lacks the intensity of striking visible blue fluorescence emission in daylight characteristic of the main 2-pyrazoline products; on prolonged heating (157°) each of the 2-pyrazolines **42** - **45** gives a quantitative yield of the respective isomer **46** - **49** identical to these minor products. The 2-pyrazoline - pyrazole rearrangements are most clearly seen to be quantitative from the m.p. behaviour; the pure 2-pyrazolines melt without decomposition in the range 220-250°, solidify and re-melt at the higher m.p. of the corresponding pure pyrazole isomers (*cf.* triene **8**[3]). The nature of the isomerisation as a 2H group-transfer is unambiguously apparent from the spectroscopic properties of the pyrazoline-pyrazole isomers; each of the isomer-pairs exhibit two ^{1}H NMR doublets (^3J = 9 - 10 Hz) in the range 3.4 - 4.4δ (H-4,8 and H-12,13), but for the pyrazolines further spin-coupling (principally to H-3,9) broadens the component signals; in the pyrazoles the pairs of doublets diverge (differential aromatic ring-current effects) and appear exceptionally sharp consistent with each of the relevant nuclei being in a non-protonated environment. Characteristic frequency differences are also seen in the electronic absorption and fluorescence emission spectra for the isomer pairs; besides short-wavelength aromatic bands, the 2-pyrazolines have a single medium wavelength absorption band near 340-360 nm ($\varepsilon\nu$ 1.5 - 2.2 x 10^4) contrasting with the pyrazoles which exhibit three hypsochromically shifted and generally more intense

absorption maxima in the range 280-300 nm ($\varepsilon\sim$ 2.0 - 2.6 x 10^4) and are transparent at 340-360 nm. Whilst striking visible blue fluorescence emission at 458.5 ± 6.5 nm characterises the 2-pyrazolines, shorter wavelength emission at 340.5 ± 5.5 nm characterises the pyrazoles. Systematic changes correspondingly appear in the IR (C=N stretching) region, 1400-1600 cm^{-1} the most noticeable being a shift of a strong band near 1400 cm^{-1} in the 2-pyrazolines to ca. 1460 cm^{-1} in the pyrazoles (increased ring-strain). During the TLC purification the rapid darkening of the yellow 2-pyrazoline in contact with silica and air in daylight (but not under N_2) indicates considerable sensitivity to oxygen, and attempted kinetic investigation in air showed non-first order behaviour; in addition what is apparently a peroxide can be isolated by heating pyrazoline 42 in air.

In the absence of air and despite fluorescence emission, Beers law holding at appropriate concentration ($\sim$3.6 x 10^{-5}M), UV absorption facilitates accurate kinetic comparison for the isomerisation of pyrazolines 42-44; heating their degased decalin solutions in vacuo in the range 185-205° and monitoring at λ_{max} gives first-order rate plots from which the rate constants (Table 1) and activation parameters (Table 2) can be obtained. These data may usefully be compared with those similarly obtained above for the air-stable triene 6. It is seen that all the 2-pyrazolines rearrange at comparable rates (e.g. k_1(23)/k_1(25) $\sim$ 1.5 at 196°) but much less readily than e.g. triene 6, and the aryl substituents have comparitively little effect. On the other hand, the 1,3-diphenylnitrilimine adducts 50 and 51 similarly made from dipolarophile 3, and the analogous adduct made from 23 do not isomerise detectably under similar conditions, superficially resembling the dihydropyridazine 38 in their stability.

Extrapolation of the data in Table 2 for pyrazoline derivative 42 gives $k_1 \sim 8.85 \times 10^{-12} s^{-1}$ at 36°; if in the absence of the chlorine substituents the rate of isomerisation is accelerated to a similar degree to that of triene 32 in comparison to its chlorinated analogue 6, k_1 for the rearrangement of pyrazoline derivative 53 at 36° is expected to be $\sim 1.8 \times 10^{-6} s^{-1}$, and the rates for rearrangements of dehalogenated 2-pyrazolines 53-55 are expected to be accurately measurable within reasonable temperature ranges. The required 2-pyrazolines 53-55 are readily synthesised as for the hexachloro- analogues using hexadechloro-1 as dipolarophile; dipolar cycloaddition is noticeably faster here (transannular Π-Π orbital mixing) and the products typically consist of mixtures of 2-pyrazolines with up to 50% of their pyrazole isomers, an indication of their more rapid isomerisation near 160°. Separation by preparative TLC and recrystallisation (under N_2) gives the required 2-pyrazolines and kinetic runs with representatives 53 and 55 (as for the chlorinated analogues) gives good first-order rate-plots, but with some deviation from linearity over long runs at lower temperatures. The rate constants and kinetic parameters are included for comparison in Tables 1 and 2. It is seen that the dechlorinated pyrazoline derivatives 53 and 55 rearrange only by an order of magnitude faster than their analogues 42 and 44; assuming that the steric requirements for 2H-group transfer at the acceptor site are approximately similar for the alicyclic trienes and 2-pyrazoline derivatives steric effects associated with the chlorinated framework should be comparable in triene 6 and pyrazoline 42, and for triene 32 and 2-pyrazoline 53 the attenuation of this effect should also be comparable. The dramatic increase in kinetic reactivity of triene 32 compared to triene 6 therefore appears to have a largely electronic origin.

Probably insufficient data are yet available to meaningfully discuss acceptor Π-bond substituent effects in terms of theoretical models for the transition state related to that developed by Ruedenberg[6]. However both Cl and MeO groups at the 2H receptor Π-bond retard rearrangement, radical or dipolar intermediates can be discounted and the group-transfers discussed here are best viewed as truly pericyclic processes whose rates may also show some dependance on a fine balance of effects associated with the proximity of the π-bond to the bonded hydrogens transferred[7,29] and the spatial requirements for rehybridisation at the acceptor carbons. Experiments designed to clarify these effects are in hand.

Experimental

The following apply unless otherwise indicated. NMR data refer to solutions in $CDCl_3$ (TMS), obtained using Jeol FX90Q, GX270 or PMX60 instruments; all signals had the correct relative intensities. UV spectroscopic data were obtained for solutions in EtOH using a PE 555 spectrometer. Fluorescence emission wavelengths were determined with a PE 3000 spectrometer. IR data were obtained for CH_2Cl_2 solutions with a PE 197 instrument. Mass spectra refer to probe samples analysed with an AEI-GEC MS902 machine with VG Micromass facilities; all ion clusters had the correct halogen isotope abundance ratios. Preparative TLC refers to 0.8 mm Merck type 60 GF silicagel coated plates, flash chromatography to type 60, 230-400 mesh silica. Petrol refers to the 60-80°b.p. fraction. Kinetic data are for solutions in decalin; for air-sensitive 2-pyrazoline derivatives 42, 43, 44, 53 and 55 solutions were prepared in N_2-purged decalin and degassed in vacuo by freeze-thaw cycles before sealing ampoules. Ampoules were heated in a Grant thermostat fitted with a calibrated thermometer. (±0.1°); temperatures cited in Table 1 represent the estimated mean values over runs, and solutions were monitored at the principal UV λmax using a PE 551 digital-display spectrometer. Rate constants in Table 1 for pyrazoline derivatives represent the best five correlating data-pairs from seven determined. Eyring activation parameters (Table 2) were obtained by computation.[23]

Part A. Synthesis of 1,4-Dichloro-2,3,7,7-tetramethoxynorbornadiene, 22.

(a) 1,3,4-Trichloro-2,5,5-trimethoxycyclopentadiene, 17: To a stirred solution of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene (16) (31.5g., 120 mmol) in dimethylsulphoxide (DMSO) (72 ml) was added a cooled solution of KOH (10.2g., 180 mmol) in MeOH (54 ml); the mixture was cooled, stirred at ~20° (18h) quenched in water and the product several times extracted with petrol; the extracts were washed with brine, dried (Na_2SO_4) and evaporated to give trichlorotrimethoxycyclopentadiene 17 (29.6g., 97%), ir νmax: 1 612, 1 650 - 1 660 vs cm^{-1} (ClC=CCl, ClC=COMe); δH: 3.25 and 4.12 (each s ratio 2:1, 5,5-and 2-OMe).

(b) 1,4-Dichloro-2,3,5,5-tetramethoxycyclopentadiene 18: (i) Trichlorotrimethoxydiene 17 (10.3g., 40 mmol) in DMSO (24 ml) was treated as above with a solution of KOH (6.8g., 120 mmol) in MeOH (20 ml); after ~20h the product was isolated as above giving a ca. 1:1 mixture of dichlorotetramethoxydiene 18 and cyclo-pentendione bis-acetal 19 (9.78g.). The oily product (4.89g.) was separated on Al_2O_3(Brockmann II + 5-6% H_2O, 150g.) in petrol (2ℓ), then 5:1 petrol-Et_2O (1.25ℓ) into crystalline bis-acetal 19 (1.9g.), a liquid fraction (60% diene 18 + 19, 620 mg.) and crystalline bis-vinylether 18 (1.73g.) (86% recovery). (ii) Tetrachlorodimethoxycyclopentadiene 16 (10.5g., 40 mmol) in DMSO (24 ml) was mixed with a solution of KOH (3.4g., 61 mmol) in MeOH (18 ml), the solution stirred overnight at ~20° and then poured onto freshly prepared KOMe [from potassium (4.7g., 120 mg atom) in MeOH (150 ml) followed by removal of MeOH in vacuo]. KOMe dissolved as the mixture was stirred and after 24h additional KCl precipitated. The product was isolated as above giving again a 1:1 mixture of bis-vinylether 18 and bis-acetal 19 (9.05g.) separated as before. Pure samples of 19 and 18 were obtained by recrystallisation from petrol; bis-acetal 19 m.p. ~57° (lit.[14] 60-61°), ir νmax:1 632, 2 850 vs cm^{-1} (ClC=CCl, OMe); δH: 3.41 and 3.45(each s ratio 1:1, MeOCOMe) 4.05(s HCCl); m/z:290($M^{+\cdot}$ scarce) 255($M-Cl^{+}$)100%. Bis-vinylether 18 had m.p. 53-54° (lit.[14] 54-55°), ir νmax:1 640, 1 675 vs and 2 850 vs cm^{-1} (MeOC=COMe, OMe): δH:3.23 and 4.08(each s ratio 1:1, 5,5- and 2,3-OMe); m/z: 254($M^{+\cdot}$), 239($M-CH_3^{+}$)100%, 219($M-Cl^{+\cdot}$),208 ($M-CH_3-CH_3O^{+\cdot}$)100%. [(iii) Bis-acetal 19(5.5g., 20 mmol) when treated with ^tBuOK (3.36g., 30 mmol) in DMSO 20 ml) with cooling, then at ~20°/24 h gave a product, isolated and separated as before giving 18(~60%) and unchanged 19].

(c) Adduction of Diene 18 with cis/trans-Dibromoethylene: Tetramethoxydiene 18(3.73g.,14.6 mmol) was heated with dibromoethylene (1.28:1 trans: cis mixture, 7.3g., 40 mmol) in sealed ampoules at 175-180°/24 h. Excess dibromoethylene was distilled off giving a brown viscous oil (4.74g., 74% conversion) containing a 2.6:1 mixture of stereoisomeric adducts 20 and 21, portions of which (900 mg.) subjected to flash chromatography (silicagel, 2:1 petrol-Et_2O) gave two fractions (i): 5,6-cis-endo-dibromo-1,4-dichloro-2,3,7,7-tetramethoxynorborn-2-ene 20 (650 mg.), m.p. 104-105°(petrol), δH: 3.51, 3.85(each s ratio 1:1, 7,7- and 2,3- OMe); 4.69(s - H - 5,6); m/z: 440($M+2^{+\cdot}$) scarce, 403($M-Cl^{+\cdot}$) 245($M-Br_2-Cl^{+\cdot}$),100%. (Found: C, 29.98; H,3.20. $C_{11}H_{14}Br_2Cl_2O_4$ requires C, 29.96; H, 3.20%). Fraction (ii) comprised a viscous non-crystallising oil (248 mg.), the trans-dibromo isomer 21 of adduct 20; δH: 4.25, 4.35 (each m H-5,6) and four bands resolved at 3.4-3.5(4 OMe). In several preparations crude product subjected to charcoal in petrol and the solution evaporated partially crystallised giving almost pure 20.

Diene 18 also gave a 1:1 adduct with vinylene carbonate when molar proportions were heated (110°) toluene, 24h, N_2); the oily product recrystallised from CCl_4 gave 1,4-dichloro-5,6,7,7-tetramethoxynorborn-5-ene-endo 2,3-diol cyclocarbonate (50%), m.p. 120 - 121.5°, δH: 3.57, 3.60, 3.87(each s ratio 1:1:2, 7,7- and 2,3- OMe); 5.07(s H-5,6); m/z: 340 ($M^{+\cdot}$)scarce, 305($M-Cl^{+\cdot}$) 100%. (Found: C, 42.15; H, 4.17. $C_{12}H_{14}Cl_2O_7$ requires C, 42.25; H, 4.14%).

(d) Debromination of Adduct 20 giving Dichlorodimethoxynorbornadienone Dimethyl Acetal 22: A solution of cis-endo-dibromo compound 20 (758 mg., 1.72 mmol) in 1:1 HOAc-Et_2O (7.5 ml) was vigorously stirred with fresh zinc dust (450 mg., 6.8 mg. atom) for 1.75h at ~0°; the reaction mixture was quenched in ice-water, the product extracted with several portions of pre-cooled Et_2O, the extracts bulked (ca. 50 ml) washed with satd. aqus. $NaHCO_3$, brine and dried (Na_2SO_4); the solution was rapidly evaporated in vacuo (water-bath, 30°) and the residual colourless oil briefly warmed to 35° in vacuo giving >95% pure norbornadienone acetal 22 (~100%) which crystallised on chilling, m.p. 68-70°; purified by prep. TLC followed by cautious recrystallisation (petrol) gave 1,4-dichloro-2,3,7,7-tetramethyoxynorborna-2,5-diene 22 (88%), m.p. 72-73°, δH: 3.38, 3.44(each s 7,7-OMe), 3.69(s 2,3-OMe), 6.43(s H 5,6);

at 7.5% conc. 22 and 2.5% conc. Yb(fod)$_3$ in $CDCl_3$ all signals shift to higher δ by 0.15–0.2 ppm but as expected OMe signals at 3.69 δ remain co-incident; m/z: 245(M-Cl$^{+\cdot}$)100%, 199 (M-Cl-$CH_3OCH_3^{+\cdot}$). (Found: C, 47.33; H, 5.11 $C_{11}H_{14}Cl_2O_4$ requires C, 46.99; H.5.02%). Several experiments indicated that longer exposure of bridge-acetal 22 to zinc/zinc salts resulted in decomposition; $CDCl_3$ solutions of the product were stable several days at 20–25°, but heated at 40° the bridge acetal had $\tau_{\frac{1}{2}}$ ~ 3h.

Bromination of Norbornadienone Dimethyl Acetal 22 with Pyridinium Hydrobromide Perbromide, and Solvolysis of the Product: Norbornadienone acetal 22 (112 mg., 0.4 mmol) was stirred with $C_5H_5NHBr_3$ (140 mg., 0.44 mmol) in CH_2Cl_2 (10 ml) for 0.5h, the solution washed with water and $Na_2S_2O_3$ soln., dried and evaporated to give 3-bromo-1,4-dichloro 3,7,7-trimethoxynorborn-5-en-2-one 25 138 mg., 93%), m.p. 115–116°(petrol), δH: 3.52(s 7,7-OMe), 3.60(s 3-OMe), 5.98, 6.24 (each d J~6.5 Hz, H-5,6); m/z: 309(M-Cl$^{+\cdot}$) scarce, 265(M-Br$^{+\cdot}$)100%, 230(M-Cl-Br$^{+\cdot}$)83%; ir νmax: 1 780 vs cm^{-1}(α,α-dihalogeno CO); the lachrymatory product slowly deteriorated in air, but was stable in a closed ampoule. This product was dissolved in MeOH (10ml) a little powdered chalk added, the solution stood at 20°/ 18h and then heated under reflux (2h) finally diluted with CH_2Cl_2 and the mixture washed with water dried and evaporated gave 1,4-dichloro-3,3,7,7-tetramethoxynorborn-5-en-2-one 26 (110 mg., 93%), m.p. 100–101.5° (petrol), δH: 3.43, 3.57, 3.59, 3.62 (all s 3,3,7,7 - OMe), 5.95, 6.34 (each d J~6.5 Hz, H-5,6); m/z: 281(M-$CH_3^{+\cdot}$), 261(M-Cl$^{+\cdot}$), 253 (M-CO-$CH_3^{+\cdot}$)86%, 105 [(MeO)$_3$C$^+$] 100%. (Found: C, 44.22, H, 4.77, $C_{11}H_{14}Cl_2O_5$ requires C, 44.46; H, 4.74%).

Cycloaddition of Norbornadienone Acetal 22 with Cyclopentadiene. Synthesis of endo-endo-exo-Pentacyclohexadecatriene 27: Norbornadienone acetal 22 (363 mg.) was dissolved in freshly cracked cyclopentadiene (6 ml) and the solution heated in a sealed-tube at 120–135° for 19h (the furnace pre-heated to 120°). Dicyclopentadiene was rapidly distilled from the crude product, and five fractions were isolated from the residual oil by prep. TLC (petrol-Et_2O mixtures); (i): dicyclopentadiene (144 mg.), (ii): 3,6-dichlorocatechol dimethyl ether 24 (87 mg., 32%), m.p. 30–31° δH, (CCl_4): 3.83 and 6.88(each s ratio 3:1, 2 OMe and H-4,5): m/z: 206(M$^{+\cdot}$) 100%, 191(M-$CH_3^{+\cdot}$) 44%; (iii): crude endo-endo adduct 23 (27 mg., 6%), identified by δH: 1.36, 1.60(each dm J~9.0Hz, CH_2 bridge), 2.87(m H-1,8), 2.93(s H-2,7) 3.51, 3.54(each s 11,11-OMe) 3.75(s 4,5 - OMe), 5.85("t" H - 9,10). Fractions (iv) and (v) contained carbonyl compounds - anticipated decomposition products of bridge-acetal 22.[11] Attempted further purification of fraction (iii) resulted in decomposition (hydrolytic decomposition on silicic acid?). The combined adduct 23-containing fractions (138 mg.) from a similar experiment (2 x scale) was saponified with KOH/MeOH to remove ester by-products and the CH_2Cl_2 extracts of the hydrolysis mixture dried and evaporated; the residual oil (118 mg., 13%) contained ca.50% adduct 23. This product (113 mg.) was heated with freshly prepared 2,3,4,5-tetrachlorothiophene dioxide[20] (TCTD)(45mg., 1.1 mol) in heptane (2 ml) at 98° for 3.5 h, the solvent evaporated in vacuo and the residue subjected to prep. TLC (3:1 petrol - Et_2O) giving unreacted TCTD (20 mg.) and a single major component; this, following successive prep. TLC (3:1 petrol - Et_2O then toluene) and recrystallisation of the relevant fraction (petrol) gave endo-endo-exo adduct 27 (18 mg.), m.p. 167–168° mix m.p. with the products of alternative synthesis (below) not depressed. [A solution of norbornadienone acetal 22 (30 mg.) in $CDCl_3$(0.4 ml) was treated with cyclopentadiene (6 fold excess) in the presence of Yb(fod)$_3$ (10 mg.); ^{1}HNMR monitoring of the solution indicated dimerisation of cyclopentadiene during 16 days but acetal 22 remained].

Adduction of Dichlorotetramethoxycyclopentadiene 18 with norbornadiene: Diene 18 (1.427g., 5.6 mmol, freshly purified) was heated with norbornadiene (10 ml, stabilised with quinol) in a sealed tube at 160–170°/50h. Excess C_7H_8 was distilled off in vacuo and the residual oil boiled in MeOH; insoluble polymer was removed and the filtrate evaporated in vacuo to give crude adduct (1.85g., 85%). ^{1}HNMR indicated a mixture of endo-exo- and endo-endo adducts 28 and 23 (ca. 6.7:1). Convenient separatory techniques failed to completely resolve the components, but recrystallised several times from MeOH the mixture gave endo-exo-3,6-dichloro-4,5,11,11-tetramethoxy-[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-diene 28, m.p. 63–64°, δH: 1.16, 1.85(each dm J = 9.9 Hz) CH_2; 2.35(s H-2,7), 2.76 (m H-1,8), 3.49, 3.51(each s 11,11-OMe), 3.85(s 4,5-OMe), 6.16(m H-9,10); δC: 140.7(C-9,10), 131.8 (C-4,5), 113.0(C-11), 74.0(C-3,6), 60.4(4,5-OMe), 54.6(C-12), 51.9(OCH_3), 51.2(OCH_3), 40.9(C-2,7), 40.4(C-1,8); ir νmax: 1 668 vs, 2 850 ms cm^{-1}(MeOC=COMe and OMe); m/z: 311(M-Cl$^{+\cdot}$)scarce, 245 (RDA, ^{30}M-Cl-$C_5H_6^{+\cdot}$) 100%. (Found: C, 55.33; H, 5.87. $C_{16}H_{20}Cl_2O_4$ requires C, 55.34; H, 5.81%). The adduct 28 was also characterised as the trans-dibromide m.p. 149–150°, δH: 1.73(nm CH_2), 2.30, 3.02(each d J = 8Hz, H-2,7), 2.50 (m H-1,8), 3.48, 3.51(each s 11,11 - OMe), 3.83(s 4,5-OMe), 3.65 (m H-10), 4.25(dd J~3 and 5Hz, H-9); m/z: 469(M-Cl$^{+\cdot}$) 100 m 245[RDA, $C_5Cl_2(OMe)_4^{+\cdot}$] 23%, (Found: C, 37.54; H, 3.99. $C_{16}H_{20}Br_2Cl_2O_4$ requires C, 37.89; H, 3.98%).

Synthesis of endo-exo-exo- and endo-endo-exo-Pentacyclohexadecatrienes 29 and 27: A mixture of adducts 23 and 28 obtained as above (346 mg.,1 mmol) was heated in heptane (5 ml) with TCTD(277 mg., 1.1 mmol) at the b.p (N_2) for 6h. The product which crystallised on cooling was separated off (412 mg.) and recrystallised[2] (CH_2Cl_2 - petrol) giving endo-exo-exo- 1,5,6,7,8,12 - hexachloro - 13, 14, 15,15 - tetramethoxypentacyclo -[10.2.1.1^{3,10}.0^{2,11}.0^{4,9}] hexadeca - 5,7,13-triene 29 (331 mg., 62%), m.p. 212–213° (after further recrystallisation, δH: 1.47, 1.79(each dm J = 12.2Hz, CH_2), 2.49(s H-2,11), 2.83(s overlapping m, H-4,9 and H-3,10). 3.56(s 15,15-OMe), 3.90(s 13,14-OMe): ir νmax: 1 619s and 1 670s cm^{-1}(conj. ClC=CCl and MeOC-COMe); m/z: 499(M-Cl$^{+\cdot}$) 100% (105, which is very abundant in the stereoisomer 27, absent). (Found: C, 44.57; H, 3.77. $C_{20}H_{20}Cl_6O_4$ requires C,44.72; H, 3.75%). The reaction and recrystallisation residues were combined; these cleanly resolved by prep. TLC (toluene eluent) into unreacted TCTD (36 mg.), further adduct 29 (40 mg., fraction 3) and a middle fraction, the stereoisomer of 29, endo-endo-exo- 1,5,6,7,8,12- hexachloro - 13,14,15,15 - tetramethoxypentacyclo [10.2.1.1^{3,10}. 0^{2,11}0^{4,9}] hexadeca-5,7,13-triene 27, (37 mg., 6.9%), identical to that prepared above, m.p. 169–171° (after further purification with the similar fraction from a duplicate experiment), δH: 1.49, 1.90(each dm J =10.7 Hz, CH_2), 2.89(bs H-2,3,10,

11), 3.33(d J = 1.3 Hz H-4,9), 3.56, 3.57(each s 15,15-OMe), 3.96(s 13,14-OMe); ir νmax : 1 620s, 1 675s (conj. ClC=CCl and MeOC=COMe), 1 308s(C=C-O), 1 200 vs, 1 150 vs cm^{-1}(C-O-C); m/z: 499 ($M-Cl^{+\cdot}$), 105$[(MeO)_3C^+]$ 100% (very intense relative to scale); λmax nm, (εmax)(decalin): 265 (4 666), 275(4 522), 287(6 109), 299(6 728), 313(3 988), (Found: C,44.70; H,3.79. $C_{20}H_{20}Cl_6O_4$ requires C,44.72; H, 3.75%).

Thermal Rearrangement of endo-endo-exo-Pentacyclohexadecatriene 27: The purified triene 27 (~25 mg.) in a little toluene was introduced into an ampoule, the solvent evaporated in vacuo, and the sealed ampoule heated at 130.2 ± 0.1°; the composition was determined (^{1}HNMR) after 8.5, 11.5 and 16.00h giving $\tau_{\frac{1}{2}}$ ca. 11.5h at this temperature. The product from this experiment was recrystallised (with difficulty) from aqus. MeOH giving the aromatic compound endo-endo-1,5,6,7,8,12-hexachloro-13,14,15,15-tetramethoxypentacyclo[10.2.1.1^{3,10}.0^{2,11}.0^{4,9}]hexadeca-4(9),5,7-triene 30 (15 mg.), m.p. 197-199°, δH: 1.83, 2.07(each dm J = 9.0 Hz, CH_2) 2.51(s H-13,14), 3.20(s 13,14-OMe) overlapping with 3.23(m H-2,11), 3.48,3.53(each s 15,15-OMe), 3.73(bm H-3,10); ir νmax:1 600 ms (aryl C=C), 1 190, 1 140 vs(C-O-C) cm^{-1}, bands at 1620 and 1675 characteristic of triene 27 absent; m/z: 499($M-Cl^{+\cdot}$), 251(RDA-H, $C_9H_3Cl_4^{+\cdot}$), 105$[(MeO)_3C^+]$, 100%; λmax nm(εmax): 275(382), 284(394), 294(280), cf. ref.3. (Found: C, 44.30; H, 3.79. $C_{20}H_{20}Cl_6O_4$ requires C,44.72; H, 3.75%).

Reaction of Trichlorotrimethoxycyclopentadiene 17 with norbornadiene: Diene 17 (5.15g., 20 mmol) was heated under reflux (N_2) with norbornadiene (25 ml) for 72h; excess dienophile was stripped off giving a viscous oil which slowly crystallised, (6.76g., 96%). A portion of the adduct (100 mg.) subjected to prep. TLC gave endo-exo-1,8,10-trichloro-9,11,11-trimethoxytetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-diene 28 (98 mg.), m.p.101-102°(MeOH), - δH: 1.2,1.75(each dm ^{2}J=10Hz, CH_2), 2.40(s H-2,7), 2.75 (bs H-1,8), 3.48(s 11,11-OMe), 4.0(s 5-OMe), 6.15(bs H-9,10); ir νmax: 1 643 vs, 2 850 ms cm^{-} (ClC=COMe); m/z: 315($M-Cl^{+\cdot}$)scarce, 249(RDA,^{30}M-Cl-$C_5H_5^{+\cdot}$) 100%. (Found: C,50.94; H,4.90. $C_{15}H_{17}Cl_3O_3$ requires C,51.23; H, 4.87%). In several similar experiments, little evidence was found for any stereoisomeric adduct.

Reaction of endo-endo-Tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-diene with Tetrachlorothiophenedioxide: Commercial samples of isodrin 1 were recrystallised from MeOH and dechlorinated with Li-^{t}BuOH-THF using the literature procedure.[31] Distilled samples of the product solidified as previously reported[3] to an air and moisture sensitive semi-crystalline wax; prep. TLC (petrol) indicated some contamination with polymer but diene 31 had the expected ^{1}HNMR spectrum [δH:1.45(bs CH_2), 2.55 (m H-1,3,6,8), 2.65(m H-2,7), 5.20("t" H-4,5,9,10), all signals in the correct ratio].

Tetracyclodiene 31 (freshly purified, 85.5 mg., 0.54 mmol) was dissolved in $CDCl_3$ (0.9 ml); this solution(0.3ml, 0.18 mmol) was mixed with a solution of TCTD (45.7 mg., 0.18 mmol) in $CDCl_3$ (0.2 ml); ^{1}HNMR monitoring of the mixture at 120s intervals (36°) showed vinylic proton signals characteristic of 31 rapidly diminishing in intensity as reaction occurred; the data showed acceptable second-order rate behaviour with half-completion time 720s and 75% signal attenuation after ca. 0.5h. The products from three similar experiments were combined (193 mg.) and purified by prep. TLC (5:1 petrol-Et_2O) giving aromatic compound 33 (106 mg., 56%). The product from a similar experiment, recrystallised from MeOH gave 5,6,7,8-tetrachloropentacyclo [10.2.1.1^{3,10}.0^{2,11}.0^{4,9}]hexadeca-4(9),5,7-triene 33, m.p. 138.5-139.5° not depressed on admixture with an authentic sample[3]; δH: 0.44, 0.98 (each symm. AA'XX'm, H-13,13,'14,14'), 1.36 and 1.66 (dq J=9.2, 2.9, 1.45 and dm J=9.2 Hz, H-15,15')1.93 and 2.05 (dt J = 8.8, 1.47 and dq J=8.8, 3.2 and 1.83 Hz, H-16,16'),2.26(m H-1,12) 2.73(m H-2,11), 3.48(two overlapping triplets J = 3.6, 1.8 and 1.8 Hz, H-3,10); δC: 23.2, 39.7, 46.3 (each CH_2), 47.3, 59.3 (each CH), 127.2, 128.7, 146.3 (each quat. C=, 1 signal obscure); m/z: 346($M^{+\cdot}$), 252(RDA, $C_9H_4Cl_4^{+\cdot}$), 95(RDA+1,$C_7H_7^+$)100%. Found: C, 55.14; H, 3.99 calc. for $C_{16}H_{14}Cl_4$ C, 55.21; H, 4.05%); λmax 213 nm (ε~20,000); absorbtion characteristic of the 1,2,3,4-tetrachlorocyclohexadiene chromophore[21] absent in the crude products of these experiments.

Pentacyclohexadecatrienes 6-8: Compounds 7 and 8 and their respective aromatic isomers 12 and 13[3] remained unchanged over 20 years! 7, δH: 1.54, 1.65 and 1.96, 2.09 (each m J = 11Hz, CH_2), 3.04 and 3.14(each m H-2,3,10,11 overlapping H-4), ~3.45 (dd J = 11.8 and 1.75 Hz, H-9), 4.14(s OMe); 12, δH: 1.89, 2.00(each m) and 2.20, 2.31(each t J = 9.65 and 1.75 Hz, CH_2), 2.99(d J = 7.9 Hz, H-13), 3.23(s OMe), 3.49-3.76(cm H-3,10), 3.68(d J = 7.9 Hz, H-14), 3.86-3.90(cm H-2,11); 8, δH: 1.42 and 4.47(t and q OCH_2CH_3), 1.54, 1.64 and 1.96, 2.08(each m J = 10.9Hz, CH_2), 3.03(m H-3,10), 3.14(m H-2,11), ~3.15 and 3.47(each dd J = 11.8 and 1.3Hz, H-4 and H-9); 13, δH: 1.03 and 3.38(t and q OEt), 1.89, 1.99 and 2.19, 2.30(all t J = 9.7,1.31 and 1.75 Hz, CH_2), 2.90 and 3.65(each d J=7.9 Hz, H-14,H-13), 3.5-3.65(cm H-3,10), 3.86(cm H-2,11). (UV, IR[3], m/z[30]).

Original[3] samples of triene 6 had completely rearranged; fresh samples were made as before by addition of diene 16 to dienophile 1, hydrolysis of the adduct (H_2SO_4) giving bridge-carbonyl compound which was heated (after vacuum drying at 45°) in CCl_4 until IR monitoring indicated almost complete disappearance of ir νmax 1830-1847 cm^{-} (75% decomp. in 2.5h); the product, purified by prep. TLC gave unchanged bridge-acetal adduct and decachloropentacyclohexadecatriene 6, δH: 1.54, 1.68 and 1.98, 2.11(each t or m J = 11 and 1.75 Hz, CH_2), 3.02 - 3.09(cm H-3,10), 3.13(d J=1.75 Hz, H-4,9), 3.25-3.30(m H-2,11); ir νmax: 1 600s, 1 620 ms cm^{-1} (non-conj., conj. ClC=CCl); λmax nm, (ε): 265(1 829), 276(2 744), 287(2 989), 299 (4 493), 313(2 732); the rearrangement product of 6, compound 11 had δH: 1.90, 2.01 and 2.20, 2.32 (each t or m J = 9.63 and 1.75 Hz, CH_2), 3.62-3.67 (m H-2,11), 3.75(s H-13,14), 3.87-3.93(m H-3,10). Other data see refs 3, 30).

Part B. The Reaction of Isodrin 1 with 3,6-Diphenyl-1,2:4,5-tetrazine: Pyridazine 39: Isodrin 1 (320 mg., 0.88 mmol) was boiled in xylene (25 ml) with 3,6-diphenyltetrazine[24] (200 mg., 0.85 mmol) for 16h, the colour fading; some solid crystallised on cooling, and removal of solvent, dissolution of the residue in $CHCl_2$(10 ml) followed by dilution with petrol gave colourless crystals of pyridazine derivative 39 (200 mg., 44% from CH_2Cl_2 - petrol), m.p. indefinite >300°(decomp.), δH: 1.97, 2.17(each dt J=9.9, 1.5 and 1Hz, CH_2), 3.91(m H-2,11), 3.95(m H-3,10), 4.14(s H-13,14), 7.56-7.68 and 8.02-8.07(ArH); m/z: 568($M^{+\cdot}$) 533($M-Cl^{+\cdot}$), 498($M-Cl_2^{+\cdot}$); λmax nm(ε): 220(111 000), 274(40 362),

299sh(38 715) [cf. 3,6-diphenylpyridazine (Carboni and Lindsay[24]) λmax 280(ε-29 000)]; ir νmax (nujol): 1 578w 1 543w, 1 493w 1 448vs; 773vs, 703vs cm^{-1} (aryl C=C, C=N; C_6H_5). (Found: C, 54.82; H, 2.93; N, 5.06, $C_{26}H_{18}Cl_6N_2$ requires C, 54.67; H, 3.17; N, 4.91%). Similarly prepared from 1 (1 mmol) and 3,6-di(2'-pyridyl)- 1,2:4,5 - tetrazine (0.9 mmol) (110°, 18h), pyridazine derivative 40 (438 mg., 82%) m.p. >285°(decomp.), δH: 1.88, 1.99 (each dt J=9.9,1.5 and 1Hz, CH_2), 3.87(t J= 2Hz, H-2,11), 4.36(m H-3,10), 4.28 (s H-13,14), 7.45, 7.95, 8.59 and 8.81(each dq or dt, 2 x C_5H_4N); m/z: 570($M^{+\cdot}$)scarce; 535($M-Cl^{+\cdot}$)100%, 501($M-Cl_2+H^{+\cdot}$); λmax nm(ε): 224(76 579), 282(30 361), 294sh (25 320); ir νmax(nujol): 1 588m, 1 575m, 1.555w; 790vs 740vs cm^{-1}(C=C, C=N; C_5H_4N). (Found: C, 50.59; H, 2.66; N, 9.95. $C_{24}H_{16}Cl_6N_4$ requires C, 50.29; H, 2.81; N, 9.78%).

The Reaction of Dechloroethoxyisodrin 3 with 3,6-Di(2'-pyridyl)-1,2:4,5-tetrazine: Dihydropyridazine 38: Dechloroethoxyisodrin 3[10] (420mg., 1.12 mmol) was boiled in CCl_4(25ml) with 3,6-di-(2'-pyridyl) tetrazine (240 mg., 1 mmol) for 8h, the solvent taken off and the residue recrystallised from CH_2Cl_2 - petrol giving bright yellow crystals of dihydropyridazine derivative 38 (330 mg., 68%), m.p. 170-175°(decomp.) after further recrystallisation; δH: 1.35 (t J = 6.9 Hz, CH_3), 1.39 and 1.58(dm and dt J = 10.8, 1.7 and 1.5Hz, H-16,16' bridge-CH_2), 3.93, 4.20(each dd J = 11.9 and 0.9 Hz, allylic H-4,9), 2.84, 2.92(each d J=3.2 Hz, H-3,10), 3.06, 3.16 and 3.07, 3.15(each d J= 11.4 Hz, H-2,11), 4.41-4.64 (cm OCH_2), 7.34, 7.76, 8.36 and 8.7 (qd, td, qt and tm, 2xC_5H_4N); m/z: 545($M-Cl^{+\cdot}$); λmax nm(ε): 222(52 356), 267sh(11 832) 275sh(13 459), 282(14 435), 305(14 305), 234sh (10 797), 336sh(7 099), 356sh(2 070) [cf.ref.25]; ir νmax: 1 640vs; 1 600vs, 1 565m, 1 545m (ClC=COEt; C=C, C=N). (Found: C, 53.85; H, 3.61; N, 9.83. $C_{26}H_{21}Cl_5N_4O$ requires C 53.58; H, 3.63; N, 9.61%).

The Reaction of Isodrin 1 with 2,5-Bisaryl-1,2,3,4-tetrazoles giving the Bisarylpyrazoline Derivatives 42-45: In a typical experiment, isodrin 1 (365 mg., 1 mmol, 100% excess) was heated in PhBr (1 ml) at the b.p. with 2,5-diphenyltetrazole[27] (111 mg., 0.5 mmol) under N_2 for 3h, the solvent blown-off (N_2) and the residue diluted with petrol; crystalline product separated (173 mg.) and the liquid residue was subjected to prep. TLC (5:1 petrol-Et_2O) giving besides recovered 1 (~200 mg.) further adduct 42 (76 mg., total yield 89%) and its colourless pyrazole isomer 46 (19 mg., 6.8%). Recrystallised from petrol, the pyrazoline derivative, endo-endo-exo-5,6-diaza- 1,11, 12,13,14,14-hexachloro-5,6-diphenylpentacyclo[9.2.1.$1^{3,9}0^{2,10}0^{4,8}$]pentadeca-6,12-diene 42 had m.p. 218-219°, solidifying at 255° and remelting at 277-278°(decomp.-see below); δH: 1.38, 1.50; 1.72 and 1.85(each cm, ^{2}J-12 Hz, H-15,15'), 2.90 and 3.02(each m H-3,9), 3.26-3.31(m H-10,H-2), 3.91 and 4.37(each dm, J-10Hz H-8,H-4), 6.75-7.70(cm 2xC_6H_5); m/z: 556($M^{+\cdot}$) and 521($M-Cl^{+\cdot}$) each 100% 486($M-Cl_2^{+\cdot}$)scarce; λmax nm(ε): 237(15 934), 301sh(6 150), 358(18 370); fluorescence emission 452 nm; ir νmax:1 602vs; 1 505vs, 1 498 vs,(1 3955) cm^{-1}(C=C,C=N). (Found: C,53.72; H, 3.28; N, 4.77. $C_{25}H_{18}C_6N_2$ requires C,53.70; H,3.24; N,5.01%). Similarly prepared, isolated and purified, adduct 43(94%), m.p. 229-231°, δH: 1.38, 1.41; 1.75 and 1.87(each cm J-12.3 Hz, H-15,15'), 2.28 and 2.37 (each s Me), 2.90 and 3.03(each m H-3,H-9), 3.24-3.3(m H-10,H-2), 3.88 and 4.35(each dm J-10 Hz, H-8, H-4), 7.05 and 7.37(each qm overlapping AA'XX' signals 2 x p-MeC_6H_4); m/z: 584($M^{+\cdot}$)100%, 549($M-Cl^{+\cdot}$), 514($M-Cl_2^{+\cdot}$)scarce; λmax nm (ε): 244(15 754), 305(7 803), 360(17 668); fluorescence emission 462 nm; ir νmax: 1 618s, 1 602s; 1 515, 1 392vs (1 380) cm^{-1} (C=C, C=N). (Found: C, 55.04; H, 3.67; N, 4.53. $C_{27}H_{22}Cl_6N_2$ requires C, 55.22; H, 3.77; N, 4.77%). [Isomer 47(5%) was also isolated]. Adduct 44 (71%), m.p. 251-252°, δH:1.44, 1.56; 1.72 and 1.84(each bm J-12Hz, H-15,15'), 2.89 and 3.02(each bm H-3,H-9), 3.30(bm H-2,10), 3.89, 4.86(each dm J-10 Hz, H-8, H-4), 7.12 and 7.48 (overlapping AA'XX'm's, 2 x p-ClC_6H_4): m/z: 624($M^{+\cdot}$) 100%, 589($M-Cl^{+\cdot}$), 555($M-Cl+H^{+\cdot}$)scarce; λmax nm(ε): 236sh(14 160). 247(16 870), 254sh(15 546), 312sh(7 326). 320sh(8 312), 366(22 411); fluorescence emission 465 nm - very intense. (Found: C, 47.63; H, 2.47; N, 4.44. $C_{25}H_{16}Cl_8N_2$ requires C, 47.80; H, 2.57; N, 4.46%). [Isomer 48 (5%) was also isolated]. Adduct 45 (71%), m.p. 228-229.5°, δH: 1.40, 1.52; 1.72 and 1.85(each bm J-10 Hz, H-15,15'), 2.27(s Me), 2.87 and 3.04(each bm H-3, H-9), 3.26(m H-2,10), 3.87 and 4.39(each dm J = 10Hz, H-8,H-4), 7.04 and 7.46(each qm overlapping AA'XX' signals, p-MeC_6H_4- and p-ClC_6H_4; m/z: 604($M^{+\cdot}$)100%, 569($M-Cl^{+\cdot}$), 534, 499 very scarce; λmax nm(ε): 235sh(15 877), 245(18 930), 255sh(15 266), 308(5 954). 371(21 068)- fluorescence emission 454 nm; ir νmax: 1 618, 1 602 ms; 1 518, 1 498 vs; 1 410 ms, 1 380-1 390s cm^{-1}(C=C,C=N). (Found: C, 51.65; H, 2.98; N, 4.35. $C_{26}H_{19}Cl_7N_2$ requires C, 51.39; H, 3.15; N, 4.61%). [Also isomer 49 (4.5%)].

Thermolysis of Pyrazoline Derivatives 42-45 giving Pyrazole Derivatives 46-49: In a typical experiment di-(p-tolyl)pyrazoline derivative 43 (50mg.) was heated in PhBr (3 ml, N_2) at 157° for ~100h, the pale yellow colour fading; the solvent was evaporated in vacuo and the residue subjected to prep. TLC (4:1 petrol - Et_2O) gave as major fraction colourless pyrazole derivative, endo-endo- 5,6-diaza-1,11,12,13,14,14-hexachloro-5,7-di(p-tolyl) pentacyclo[9.2.1.$1^{3,9}0^{2,10}0^{4,8}$]pentadeca-4(8),6-diene 47 (40 mg., 80%), m.p. 257-258° (CH_2Cl_2 -petrol), δH: 2.08, 2.19; 2.58 and 2.68(each m J = 10 Hz, H-15,15'), 2.40(s 2 x Me), 3.74-3.90 (cm H-2,3,9,10 signals overlapping), 3.61 and 4.49(each d J = 10 Hz, H-12, H-13), 7.2 - 7.8 (cm overlapping AA'XX' signals, 2 x p - $Me-C_6H_4$); m/z: 584($M^{+\cdot}$) 100%, 549($M-Cl^{+\cdot}$), 514($M-Cl_2^{+\cdot}$); λmax nm(ε): 222(20 148), 235sh(14 391), 283(22 882), 288(23 170), 295(22 163) transparent at 360 nm; fluorescence emission 343 nm; ir νmax: 1 612w; 1 522,1 510vs; 1 465, 1 452 ms cm^{-} (C=C, C=N). (Found: C,54.89; H,3.51; N, 4.77. $C_{27}H_{22}Cl_6N_2$ requires C,55.22; H,3.77; N, 4.77%). Similarly prepared and purified pyrazole derivative 46, mp. 277-279°, δH: 2.04, 2.18; 2.57 and 2.68(each m J = 10 Hz, H-15,15') 3.7-3.9(cm H-2,3,9,10 overlapping signals), 3.62 and4.47(each d-J 9Hz, H-12,H-13), 7.3-7.9(cm 2xC_6H_5); m/z: 556($M^{+\cdot}$)100%, 521($M-Cl^{+\cdot}$) 486($M-Cl_2^{+\cdot}$); λmax nm(ε):220(20 128), 280(19 848), 285(20 547), 291(20 128), transparent at 358 nm; fluorescence emission 335 nm; ir νmax: 1 601 vs; 1 523, 1 515 vs; 1 465, 1 452 ms cm^{-} (C=C, C=N). (Found: C, 53.87; H, 2.99; N, 4.72. $C_{25}H_{18}Cl_6N_2$ requires C, 53.70; H, 3.24; N, 5.01%). Heating adduct 42 in air gave a product m.p 217-219° (decrepitation ~150°), δH: 1.54, 1.66; 1.77 and 1.90(each m J~12.8 Hz, H-15,15'), 3.08, 3.14(each m H-3,9), 3.25(s H-2,10), 3.31 and 3.92(each dm J=8.5 Hz, H-8,H-4), 6.88 - 7.22(cm 2 x C_6H_5); m/z: 572($C_{25}H_{18}Cl_6N_2O$). Possibly the product of autosensitized peroxidation of 42. (Found: C, 51.13; H, 3.05; N, 4.56. $C_{25}H_{18}Cl_6N_2O_2$ requires C, 50.79; H, 3.06; N, 4.74%). Pyrazole derivative 48, m.p. 266-268°, δ_H: 2.08, 2.23; 2.60 and 2.74(each m J~9.6 Hz, H-15,15'), 3.3(cm H-3,9), 3.74(m H-2,10), 3.46 and 4.32(each d J~11Hz, H-12,H-13), 7.14 - 7.80(overlapping m's, 2xp-ClC_6H_4); m/z: 624($M^{+\cdot}$), 589($M-Cl^{+\cdot}$) both scarce, 554($M-Cl_2^{+\cdot}$), 520($M-H_2Cl_3^{+\cdot}$);

λmax nm (ε): 222(18 470), 238(16 008), 286sh(24 319), 291(25 612), 299(25 612); fluorescence emission 342 nm. (Found: C, 47.29; H, 2.43; N, 4.21. $C_{25}H_{16}Cl_8N_2$ requires C, 47.80; H, 2.57; N, 4.46%). Pyrazole derivative 49, m.p. 258-259°, δH: 2.12,2.21; 2.60 and 2.71(each bm J~10 Hz, H-15,15'), 2.41 (s Me), 3.61 and 4.42(each d J=10 Hz, H-12,H-13), 3.72-3.90(bm H-2,3,9,10), 7.40 and 7.70(each q of m's - overlapping AA'XX' signals, p - MeC_6H_4 and p-ClC_6H_4); m/z: 604($M^{+\cdot}$) 100%, 549(M-$Cl^{+\cdot}$), 534(M-$Cl_2^{+\cdot}$) 499(M-$Cl_3^{+\cdot}$); λmax nm(ε): 222(18 930), 234(14 961), 288(24 426) 297sh(22 136; fluorescence emission 346 nm; ir νmax: 1 605w; 1 522, 1 510 vs; 1 462, 1 448s cm^{-1}(C=C and C=N). (Found: C,51.58; H, 3.04; N, 4.44. $C_{26}H_{19}Cl_7N_2$ requires C, 51.39; H, 3.15; N, 4.61%).

The Reaction of Dipolarophile 3 with 1,3-Diphenyl-nitrilimine: Dechloroethoxyisodrin 3 treated in boiling PhBr (N_2) with 2,5-diphenyltetrazole as for isodrin (above) and product-isolation by crystallisation and prep TLC of the residues gave a single pale yellow fluorescent product (m.p. 220-221°) (50%) with only unreacted 3 and diphenyltetrazole; ^{1}HNMR indicated a 1:1 mixture of regioisomeric pyrazoline derivatives 50 and 51 e.g. δH: 3.95 and 4.54(each dmm H-8,H-4) for isomer A; and 4.26 and 4.70(each dmm H-8, H-4) for isomer B, these and other data being consistent with pyrazoline structures [e.g. Δδ(H-8,H-4) ~0.48 ppm in pyrazolines 42-45, but for pyrazoles 46-49 Δδ(H-12,H-13) ~0.85 ppm]; λmax nm(ε): 358(20,000). (Found: C,56.74; H, 4.19; N,4.67. Calc. for $C_{24}H_{23}Cl_5N_2O$: C, 57.01; H, 4.07; N, 4.92%). The mixture of pyrazoline derivatives 50,51 was recovered unchanged (TLC, NMR) after thermolysis (PhBr, 157° N) for ~100h.

The Reaction of Hexadechloroisodrin (31) with 2,5-Bis-aryltetrazoles; Pyrazoline Derivatives 53-55 and their Thermal Isomerisation to Pyrazoles 56 - 58: In a typical experiment dipolarophile 31 (purified as above, 316 mg., 2 mmol) was heated with 2,5-diphenyltetrazole (222 mg., 1 mmol) in PhBr (2-3 ml, 157°,N_2) for 3.5h and the products isolated by prep. TLC (3:1 petrol-Et_2O) giving two fractions, (i)endo-endo-exo-5,6-diaza-5,7-diphenylpentacyclo[9.2.1.1^{3,9}.0^{2,10}.0^{4,8}]pentadeca-6,12-diene (53) (168 mg., 48%), m.p. 176-177° (from petrol, N_2), δH: 1.62 and 1.86(each dm J = 7.7 and 1.5 Hz H-14,14'), 1.44 and 1.60(each dm J = 10.3 and 1.7 Hz, H-15,15'), 2.86(bm H-1,11), 2.53, 2.62 and 2.64(each m H-3,9 H-2,10), 3.52 and 3.98(each dd J = 9.4 and 0.9Hz, H-8, H-4), 6.14(pent. H-12,13), 6.78-7.80 (cm 2xC_6H_5); m/z: 352($M^{+\cdot}$) 100%, 258(RDA,M-$C_7H_{10}^{+\cdot}$) 86%; λmax nm(ε): 250sh (15 611), 316sh(7 493), 361(22 417). (Found: C,84.94; H, 6.93. $C_{25}H_{24}N_2$ requires C,85.18; H,6.86%); fraction (ii) was endo-endo-5,6-diaza-5,7-diphenylpentacyclo[9.2.1.1^{3,9}.0^{2,10}.0^{4,8}]pentadeca-4(8),6-diene 56 (135 mg., 38%), m.p. 146-147° (petrol), δH: 0.34[cm endo-H-12(or 13)], 0.82-1.05[cm exo-(H-12,13) and endo-H-13(or 12)], 1.38, 1.72(each dm, J = 9, 1.2 and 1 Hz, H-14,14'), 2.17, 2.47 (dt and dq, J = 8.15, 1.8 and 1.2 Hz, H-15,15') 2.27(bs H-1,11), 2.81, 2.91(each dt J=11.6 and 3.6 Hz H-2,10); 3.42,3.50(each dt J = 3.6 and 1.8 Hz, H-3,9), 7.22 - 7.93(cm 2 x C_6H_5); m/z: 352($M^{+\cdot}$) 91%, 258(RDA,M - $C_7H_{10}^{+\cdot}$) 100%; λmax nm(ε): 232(12 144), 280sh(21 795), 287(22 574) transparent at 361 nm. (Found: C, 85.37; H, 6.99%). Over longer reaction times fraction (ii) - (56) - increased at the expense of fraction (i) - (53), and a sample of the pure crystalline pyrazoline derivative 53 (~25 mg.) sealed in vacuo and heated at 185.7±0.1° for 2.0h followed by TLC purification gave pyrazole derivative 56 (22 mg.) and unchanged 53 (2 mg.)- 88% conversion i.e. 2h≈3 x $\tau_{\frac{1}{2}}$ at this temperature.

Similarly made and characterised, adduct 54, m.p. 186-187°, m/z: 380($M^{+\cdot}$), 286(RDA, M-C_7H_{10}). (Found: C,84.96; H,7.63; N,7.26. $C_{27}H_{28}N_2$ requires C,85.22; H,7.41; N,7.36%); and its pyrazole isomer 57, m.p. 129-130°, m/z: 380($M^{+\cdot}$), 286(RDA as for 56). (Found: C,85.19, H,7.57; N,7.53). Adduct 54 and its thermal isomer 57 had spectroscopic properties closely similar to 53, 56 above further exemplified in adduct 55, m.p. 206-207° from petrol, N_2), δH: 1.59 and 1.86(each dm J = 8.0 Hz, H-14,14'), 1.45 and 1.56(each dm J~11Hz, H-15,15'), 2.86(bm H-1,11), 2.47, 2.60, 2.62(each m H-3,9 and H-2,10), 7.47 and 3.93(each dm, J = 9.2 Hz, H-8, H-4), 6.13(m H-12,13), 6.97-7.64(cm overlapping AA'XX' signals for 2 x p-ClC_6H_4); m/z: 420($M^{+\cdot}$) 100%, 326(RDA, M-$C_7H_4^{+\cdot}$), 95%; λmax nm(ε): 236sh(13 322), 248(16 407), 256sh(14 724), 326sh (10 166), 370(26 048), (Found: C,71.45; H,5.57; N,6.56. $C_{25}H_{22}N_2Cl_2$ requires C,71.25; H,5.26; N,6.65%), and its thermal isomer 58, m.p. 180.5-181.5°, δH: 0.2 - 0.25[m endo-H-12(or H-13)], 0.90[m exo-(H-12,13) and endo-H-13(or H-12)], 1.38 and 1.72(each dm J = 9.3 and 1.0, and 9.3 Hz, H-15,15'), 2.18 and 2.46(dt and dq J = 8.1 and 1.3 Hz, H-14,14'), 2.25(bs) H-1,11; 2.81 and 2.91(each dt J = 11.5 and 3.7 Hz H-2,10); 3.38 and 3.47 (each dt J = 3.7 and 1.7 Hz, H-3,9), 7.37-7.46 and 7.63 - 7.87(each dt's, AA'XX' signals for 2 x p-ClC_6H_4); m/z: 420($M^{+\cdot}$) 81%, 326(RDA, M - $C_7H_{10}^{+\cdot}$) 100%; λmax nm(ε): 222sh(16 666), 238sh(15 087), 246sh(14 737), 292sh(26 666), 301(28 596), transparent at 370 nm. (Found: C, 71.49; H, 5.43; N, 6.60%). δC: 22.3, 23.1, 39.3, 39.8, 40.9, 42.6, 46.75, 48.18, 49.1, 63.9 (CH and CH_2), 120.3, 127.4, 128.9, 129.5 (aromatic CH), 128.1, 131.2, 131.9, 133.4, 138.6, 145.3, 152.2 (quat. aryl and heteroaryl).

Pyrazoline Derivative 52: A mixture of adducts 28 and 23 (23 = 20%) (180 mg., 0.52 mmol) was heated with 2,5-diphenyltetrazole (126 mg., 0.57 mmol) in PhBr(0.5ml, 157°, N_2) for 5h, the solvent blown-off (N_2) and the residue subjected to prep. TLC (5:1 petrol-Et_2O) giving one major fraction containing the exo diphenylnitrilimine adduct of compound 28 (268 mg., 95%) which twice recrystallised (CH_2Cl_2- petrol (107 mg.) had m.p. 229-231°, δH: 1.25, 1.66(each dm J = 12.2Hz, CH_2), 2.58(q J~8Hz, H-2,10), 2.76 and 2.93(each bs H-9,3), 3.59, 3.63(each s MeOCOMe), 3.84, 3.85(each s 12,13-OMe), 4.08(dm J = 11.8Hz H-4) 3.6(obscured dm H-8), 6.7-7.82(bcm 2 x C_6H_5); m/z: 540($M^{+\cdot}$), 505 (M-$Cl^{+\cdot}$), 258 (RDA-N_2, $C_7H_8CPh_2^{+\cdot}$), 243 and 245, 100%. (Found: C, 64.69; H, 5.74. $C_{29}H_{30}Cl_2N_2O_4$ requires C, 64.35; H, 5.74%). Rechromatography of the crystallisation residues gave the stereoisomeric thermally stable, diphenylnitrilimine adduct, 52, (45 mg., 16%) which recrystallised (CH_2Cl_2-petrol) had m.p. 211-212° unchanged after cooling; δH: 1.34, 1.66(each dm J = 10.5 Hz CH_2), 2.79(bs H-3,9), 2.90(bs H-2,10), 3.59,3.62(each s MeOCOMe), 3.94,3.96(each s 12,13 OMe), 4.10 and 4.58(each dm J = 9.2 Hz H-8, H-4), 6.7-7.8 (bcm 2 x C_6H_5); m/z: 540($M^{+\cdot}$), 211 100%. (Found: C,64.39; H,5.58%).

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Since completion of this paper, W.-D. Fessner, G. Sedelmeier, P.R. Spurr, G. Rihs and H.Prinzbach (J. Amer. Chem. Soc., 1987, 109, 4626) have also reported the qualitatively rapid conversion of chlorocarbon 32 into the aromatic isomer 33 and illustrated the utility of dechlorinated derivatives of compound 11 in the synthesis of [1.1.1.1]pagodane (a precursor of dodecahedrane, see e.g. W.-D. Fessner, B.A.R.C. Murty, J. Worth, D. Hunkler, H. Fritz, H. Prinzbach, W.D. Roth, P. von R. Schleyer. A.B. McEwen and W.F. Maier, Angew. Chemie Internat. Ed., 1987, 26 452 and references cited).