On intramolecular dyotropy: structural effects on reaction rates and crystal structure-molecular mechanics correlations for some new examples

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In an earlier paper we discussed the effect on reaction rate for thermal intramolecular dyotropy exhibited for a series of trienes, 1–4 and pyrazolines 6–9 having identical structural elements proximate to the 2 H receptor π-bond. Both sets of compounds displayed closely similar rate-ratios across the series correlating with structural modification. The set of homopyrazolines 14–17 analogous to 6–9, now reported, correlate similarly and all three sets of compounds obey a linear free energy relationship log $k_1^A = m \log k_1^B + C$, suggestive of a common reaction mechanism for H dyotropy for these compounds. We also report on the kinetic behaviour of new, oxygen-bridged trienes 22 and 23, analogues of triene 1; over quite large temperature ranges, translating into a rate-spread of ~ 10^5, Arrhenius plots for rearrangement of 1 and 23 are essentially linear, indicating that these compounds behave classically with scant evidence for quantum tunnelling from this result and the previously reported indecisive PDKIE data. We also describe solvent effects on the rearrangement rates for representative analogues of triene 1, and for trienes 22 and 23, and briefly report on the solid-state thermochemical behaviour of the triene 3, analogous to 1. A new molecular framework exhibiting relatively slow thermal H dyotropy is also reported. The information we have obtained rather strongly suggests a concerted, but non-synchronous transfer of 2 H in the dyotropic process.

Introduction

Compounds which readily form crystals suitable for X-ray or neutron diffraction structural analysis and are amenable to kinetic analysis of their rearrangement reactions without undue difficulty, invite attempts to correlate experimentally determined structural features with observed reactivity, and also to compare the experimental data with calculated structural and thermochemical data when this is possible. Such an approach has been demonstrated recently for a series of compounds, *e.g.* trienes **1–4** which undergo *irreversible* exothermic ($4\sigma + 2\pi$) intramolecular dyotropy, yielding quantitatively their respective dyotropomers, **1D–4D**,[1a] (Scheme 1). In an alternative approach elsewhere, a series of compounds containing similar donor/acceptor elements to those present in the reaction cavity of trienes **1–4** and which display *reversible* dyotropic equilibria, have been investigated; here correlations are found between reactivity and crystallographically determined steric proximity (d_{CH}) of transferred Hs to sp^2 receptor Cs,[1b] and with ground state strain systematically introduced (*e.g.* in analogues of compound **21**, Scheme 3, below), in the absence of significant changes in d_{CH} or of perceivable electronic effects.[1c] The impetus for these investigations is the observation that intramolecular reactions are often extremely fast processes compared to intermolecular analogues, but very few detailed studies of the effects on reaction rates concomitant with experimentally determined structural changes for sets of compounds undergoing an identical intramolecular transformation have been reported.‡,[2,3] The early observation[1a,b] that a modulation in d_{CH} of only 0.1–0.17 Å translates into a rate spread of 10^4 s^{-1} has added further impetus to the search for other rate-controlling factors in intramolecular dyotropy.[1a,c]

In our recent work we have disclosed[1a] precise kinetic behaviour for the dyotropically active series of trienes **1**, **2**, **3** and **4**, and compared their reactivity in terms of unimolecular rearrangement rate constants, k_1; activation parameters, E_a, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and log A; reactant ground-state strain energies E_s and changes in overall π-energies for the rearrangement, ΔE_π, as well as with changes in theoretically and experimentally determined internuclear proximity d_{CH}. As expected for a series of structurally similar compounds undergoing an identical transformation, k_1 values were found to correlate with reactant strain energy E_s, but not with reactant–product ΔE_s, a consequence of the reactant-like transition states for strongly exothermic processes (ΔH *ca.* −23 kcal mol^{-1}).§ Variation in the exothermicity of the process with structural changes across a series of analogous trienes, *e.g.* **1–4**, would be expected to be reflected in relative reaction rates. Since rearrangement exothermicity is certain to be influenced by overall π-energy change, ΔE_π, during aromatisation of the 2 H donor ring and saturation of the acceptor π-bond, a correlation of reaction rate with this parameter is expected. In fact an approximate correlation of ln k_1 with ΔE_π can be discerned for the triene group **1–4**. The range of ΔE_π values is, however, narrow compared to a similar correlation of ln k_1 with E_s over a range of > 20 kcal mol^{-1} for this group of trienes.[1a] Such correlations

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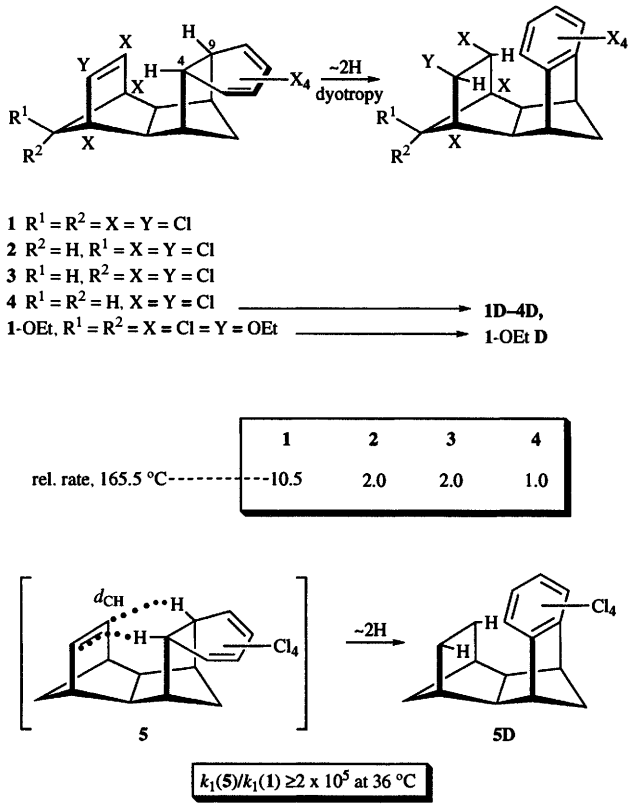
‡ A referee has expressed total disbelief in the relevance of intramolecular H dyotropy to enzyme mechanisms. Such a point of view *might* be appropriate in the specific sense. We[1a] and others[1b,3] believe that, in the general sense, proximity of the substrate and the enzyme active centre must be important in determining the specificity and accelerated rates associated with enzymic catalysis, however proximity is affected.

§ 1 cal = 4.184 J.



Scheme 1

would only be expected provided d_{CH} for this group of compounds is essentially constant (an isoapostatic series [1a]), as is observed. The influence of d_{CH} and ΔE_π is more dramatically seen for the norbornene-unsubstituted compound **5** which cannot be isolated at 25 °C; k_1 for this triene at 36 °C is estimated to be $\geqslant 4 \times 10^{-2}$ s^{-1} yielding a rate differential k_1 (**5**)/k_1(**1**) $\geqslant 2 \times 10^5$ at 36 °C, where the rate of rearrangement of **1** is slow, but measurable (see below, with $k_1 \sim 1.5 \times 10^{-7}$ s^{-1} at this temperature). The calculated mean d_{CH} for the elusive triene **5** is 2.38 Å—smaller by *ca.* 3% than the average experimental value of d_{CH} for the triene set **1**, **2**, **3** and **4**[1a] and this, together with a relatively large change in ΔE_π (10%) compared to much smaller changes in the series **1**–**4** (~1%), conspire to deliver exceptional reactivity for **5**. From these facts it can reasonably be concluded that (i) dyotropy for the series of trienes **1**–**4** (and most probably also **5**) occurs by the same mechanism; (ii) internuclear proximity d_{CH} and reactant strain-energy E_s influence reaction rate; and (iii) the transition state (TS) is particularly sensitive to incipient changes in E_π, as reflected in ΔE_π. As we have previously observed, small changes in π-energy at the receptor π-bond occasioned by the proximity of polarising substituents on the adjacent methylene bridge contribute to the modest rate-spread observed for the essentially isoapostatic series of trienes **1**–**4** of about an order of magnitude at 100 °C, and there is evidence for this effect in other examples.[1a] Here, the assumption is made that release of resonance energy, consequent on aromatisation of an identical donor diene ring, will make the same contribution to ΔE_π for each of the trienes **1**–**4**, and also their analogues.

Comparison of systems containing pyrazoline donor elements, which display intramolecular H dyotropy, with trienes 1–4. Some new examples and inter-series free energy relationships

In our earlier report we also compared the kinetic behaviour of a series of pyrazolines exhibiting intramolecular dyotropy, **6**, **7**, **8** and **9** (Scheme 2), having identical structural features in the norbornene receptor element, proximate to the receptor π-bond, as for the triene group **1**–**4**. The group of pyrazolines are much less reactive generally than the trienes, but at 214.9 °C the measured values of k_1 for the series **6**–**9** are in the ratio 7.3:2.4:1.4:1.0. The relative rates seen here strongly resemble those for the group of trienes extrapolated to this temperature from respective E_a and log A factors, being 7.2:1.8:1.7:1.0 for **1**–**4**, strongly suggesting a linear free energy relationship between the two sets of compounds and hinting at a common mechanism. In the present work we have therefore made the corresponding set of bridge-expanded (homo) pyrazolines **15**, **16** and **17** for comparison with the known analogue **14**,[1a] and with the pyrazolines **6**–**9** and trienes **1**–**4**. This series of compounds is noticeably more reactive than the set of pyrazolines **6**–**9**. Consequently, a lower temperature (165.5 °C) proved most convenient for kinetic comparisons, and experimental rate data for the homopyrazolines **14**–**17** at this temperature are compared to data extrapolated to this temperature for the pyrazolines **6**–**9** and trienes **1**–**4**, as shown in Table 1.

Table 1 Unimolecular rate-constants, k_1, and rate ratios for dyotropy of trienes, pyrazolines and homopyrazolines at 165.5 °C. Inter-series correlations: log k_1 (P) = 0.8726 log k_1 (HP) − 2.8420 (R^2 = 0.998); log k_1 (T) = 0.8544 log k_1 (P) + 2.9968 (R^2 = 0.950); log k_1 (T) = 0.7656 log k_1 (HP) + 0.9475 (R^2 = 0.955)

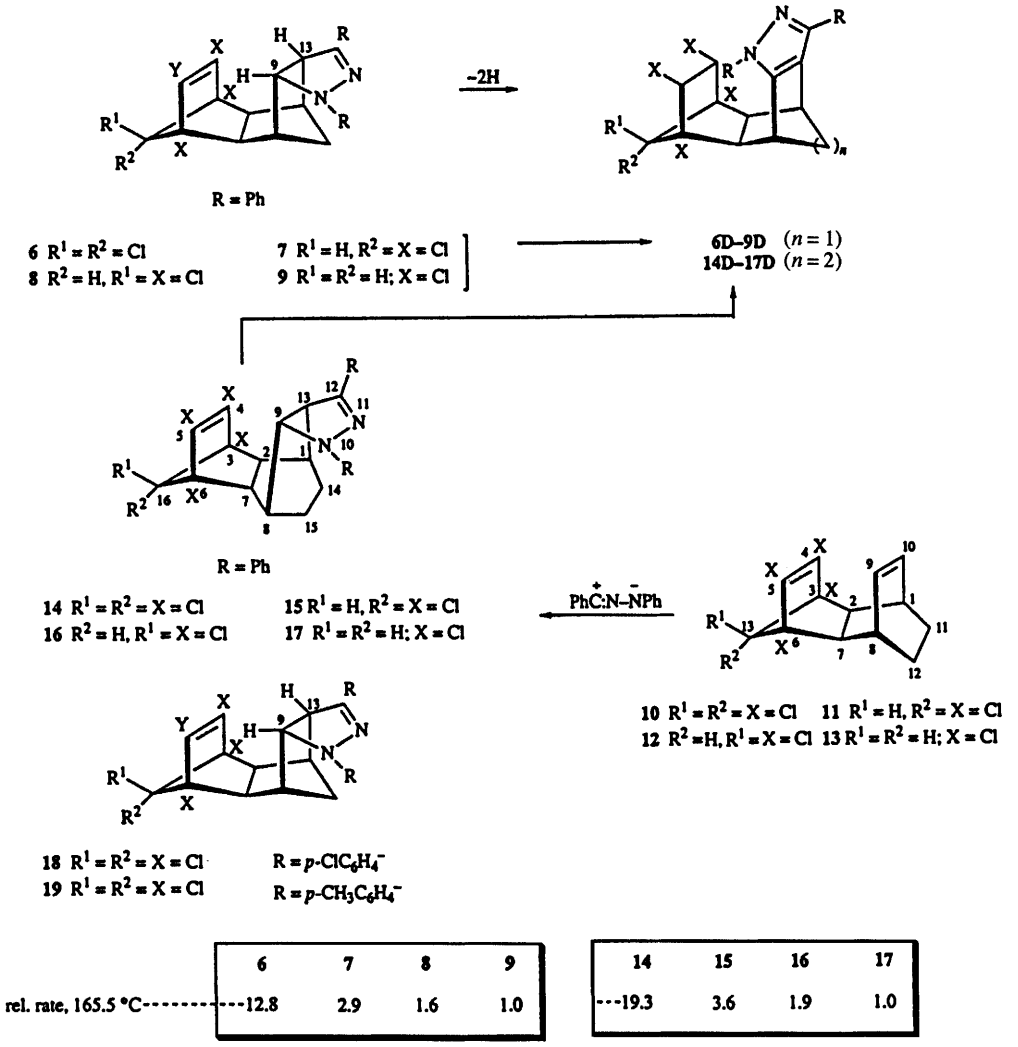
Compound	k_1/s^{-1} [a]	Relative rate
Trienes (T)		
1	35.8	10.5
2	6.99	2.0
3	6.91	2.0
4	3.42	1.0
Pyrazolines (P)		
6	57.4	12.8
7	12.98	2.9
8	7.10	1.6
9	4.48	1.0
Homopyrazolines (HP)		
14	67.4	19.3
15	12.7	3.6
16	6.74	1.9
17	3.48	1.0

[a] T: $10^3 \times k_1$ (calc.); P: $10^7 \times k_1$ (calc.); HP: $10^5 \times k_1$ (expt.).

The relative rates are clearly rather similar across each of the sets of compounds, and for different sets of compounds, analogous within each set, undergoing an identical transformation, the free energy relationship log $k_1^A = m$ log $k_1^B + C$ should hold.[4] Here we find a virtually linear relationship for the pyrazolines (P) and homopyrazolines (HP), but the correlation between trienes (T) and pyrazolines, and between trienes and homopyrazolines is slightly less perfect. The overall correlation between the three sets of compounds is nevertheless suggestive of a common mechanism for dyotropy for all these particular compounds.[1a,5]

Do non-classical effects contribute to dyotropic rearrangement kinetics?

In our earlier work we alluded to the possibility of a quantum tunnelling contribution to the kinetics for dyotropy of triene **1** and of pyrazoline **18** and reported on the primary deuterium kinetic isotope effect (PDKIE) observed for the $^2H_2$ isotopologues of these compounds. It is believed that in ~90% of reactions which involve transfer of H$^\bullet$, H$^+$ or H$^-$, a non-classical (quantum tunnelling) component contributes to the overall kinetics,[6] and when there are particularly favourable circumstances H$^\bullet$ tunnelling provides the sole mechanism for H-transfer.[7] When tunnelling occurs, Arrhenius plots of ln k_1 *vs.* K^{-1} may exhibit significant curvature in the temperature range employed to measure k_1 experimentally, and, at low enough temperatures, the reaction may become temperature indepen-



Scheme 2

dent.[8a,b,c] For a heavy atom isotopologue displaying a primary kinetic isotope effect, curvature is less pronounced when tunnelling occurs, and depending on the experimental temperature range used for kinetic studies, the experimentally derived pre-exponential factor, log A, derived from the Arrhenius intercept (ln A) may actually be larger for the heavy atom species, due to the experimental tangent of the real ln k_1/K^{-1} curve being steeper. Consequently an indication of tunnelling is a fractional value of the ratio A^{2H}/A^{2D} in PDKIE studies with the dyotropically active trienes and pyrazolines.[9a] Two other criteria need to be met if tunnelling is to be established with reasonable certainty:[9b] (i) a large $k_1{}^{2H}/k_1{}^{2D}$ ratio at 25 °C and (ii) a steep temperature dependence in $\ln(k_1{}^{2H}/k_1{}^{2D})$ *vs.* K^{-1}. In our earlier work,[1a,d] we found all three criteria were met in the kinetic behaviour of the isotopologues [9, 13-$^1H_2$] and [9,13-$^2H_2$]pyrazoline **18** with $k_1{}^{2H}/k_1{}^{2D}$ 4.60 ± 0.29 at 207.6 °C and 28.2 at 25 °C; $\ln(k_1{}^{2H}/k_1{}^{2D})/10^3$ K^{-1} 1.420; and A^{2H}/A^{2D} 0.284 ± 0.143. In addition, for **18** $\Delta(E_a{}^{2D} - E_a{}^{2H})$ = 2.80 ± 0.5 kcal mol^{-1}, the mean value being in excess of the ground-state C–2H/C–2D vibrational energy difference (2 × 1.22 kcal mol^{-1}). This result is consistent with an exothermic process having a thermochemically unsymmetrical transition state, where relevant C–H(D) vibrations do not entirely vanish.[4] For the isotopologues of triene **1** the situation is less clear-cut,[1d] and we have therefore studied triene **1** rather carefully over an extended temperature range (26.6–99.9 °C, Table 2) in the expectation that tunnelling, if present, will be revealed by curvature in the Arrhenius plot.[8b] In fact, a perfectly linear relationship ln k_1/K^{-1} (R^2 = 1.000) is found for the unimolecular decay of triene **1**. In order to check this result over a wider temperature range, additional values of k_1 were determined, slightly less precisely, at 110.3 °C where reaction is quite fast, and at ~0 °C for the very slow conversion of **1** into **1D**. The values of k_1 obtained, 6.0 × 10^{-4} and ~1 × 10^{-9} s^{-1}, respectively, lie very close to the values of k_1 calculated at these temperatures from the data in Table 3 derived from the rate-data given in Table 2. Thus the Arrhenius relationship for triene **1** is essentially linear over a rate spread of 10^5 s^{-1}, generally regarded as a reliable indicator for the absence of tunnelling.[8b] Significantly, a solution of triene **1** stored at an average temperature of −10 °C showed no change (within experimental error) after a period of nine months, indicating the absence of any significant temperature-independent processes. Thus the experimental evidence points to an absence of significant non-classical behaviour in H dyotropy of triene **1**.

Quantum tunnelling is most likely to occur when there is a high activation barrier, and the H traverse is of the same order as the de Broglie wavelength, λ_{dB}. For the pyrazoline **18**, E_a = 31.4 (3) ± 0.2 kcal mol^{-1} compared to E_a = 25.0(9) ± 0.10 kcal mol^{-1} for triene **1**, a very significant difference. In the triene series the H traverse from *neutron* diffraction crystallographic data appears to be ~1.3 Å and approximately the same for the pyrazoline **18**, in the ground state.[1a] In the vibrationally excited state the actual traverse, due to vibrational compression of the donor H atoms into the reaction cavity, will actually be considerably smaller than 1.3 Å. For a particle of mass 1.0 with 20 kcal energy, λ_{dB} is 0.31 Å, and 0.22 Å for an isoenergetic particle of mass 2.0.[10] This suggests that for **18** tunnelling is occurring near to the narrow top of the barrier, but for triene **1** E_a is low enough for 'normal' kinetic behaviour, and *a priori*, tunnelling

Table 2 Unimolecular rate constants k_1, and standard deviations (%) for dyotropy of trienes

Compound	T/ °C	$k_1/10^{-6}$ s^{-1}	$\sigma_{(n-1)}/k_1 \times 100$
1	99.9	262.0	1.7
	96.0	184.0	1.8
	95.0	166.0	0.5
	90.0	106.0	1.2
	87.7	84.6	1.2
	84.8	62.6	0.6
	82.2	48.5	2.5
	79.8	38.5	1.5
	75.0	23.4	1.5
	49.8	1.34	0.3
	40.0	0.401	0.8
	30.0	0.104	2.0
	26.6	0.071	1.4
23	110.0	561.0	1.1
	105.0	365.0	0.9
	100.0	242.0	0.7
	95.0	154.0	0.8
	94.9	151.0	0.6
	90.2	98.0	0.8
	87.0	72.8	0.6
	84.5	57.3	0.2
	75.1	23.4	1.1
	49.8	12.5	3.0
	40.1	0.40	1.3
	30.0	0.115	2.0
	26.3(5)	0.067	1.3
22	115.0	185.0	0.5
	109.8	118.0	0.4
	105.1	78.4	1.6
	99.9	47.4	0.7
	94.0	26.7	0.3
	89.7	17.6	0.7

Table 3 Activation parameters for dyotropy of trienes

Compound	E_a[a]	Log A
1	25.0(9) ± 0.1	11.1(1) ± 0.0
22	26.1(5) ± 0.1	10.9(8) ± 0.1
23	24.7(1) ± 0.1	10.8(4) ± 0.0

[a] kcal mol^{-1}, converted from computed data in kJ mol^{-1}. Deviations are standard deviations.

is less likely if the reaction involves the transfer of 2 H in the rate-limiting step. Another consequence of curvature in the ln k_1/K^{-1} plots is that the experimental tangent to the real curve, when tunnelling occurs, leads not only to a smaller intercept ln A, but clearly also a reduced slope, E_a/R. In this connection, the (slightly revised[5]) value of E_a for the bis-tolyl analogue **19** of **18** is 33.2(0) ± 0.3 kcal mol^{-1} compared to that for **18** which has apparent E_a = 31.1(1) kcal mol^{-1}, and yet **19** appears to rearrange faster than **18**. Preliminary results from PDKIE experiments with the isotopologues of pyrazoline **19** provide little evidence for a tunnelling contribution here however, indicating that **18** may be exceptional in its kinetic behaviour. There is then the possibility that E_a for **19** is the intrinsic barrier, close to the critical value for the onset of tunnelling, the intrinsic barrier for **18** being actually a little larger than 33 kcal mol^{-1} (see below).

Mechanism for H-dyotropy

For the dyotropic processes we describe, a concerted synchronous transfer, or a concerted but rather asynchronous transfer with or without tunnelling in each case can be envisaged. For a two-step process involving a single H$^{\bullet}$ transfer as the rate limiting step, reasoned from our data for triene **1** and pyrazoline **18** by Smedarchina and Siebrand[11a] and for reversible dyotropic equilibria as recognised by Paquette *et al.*[1b,c] and discussed by Houk *et al.*,[11b] reaction would almost certainly be accompanied by a significant tunnelling contribution. The Siebrand model ingeniously envisages an oscillating barrier-width associated with 'in–out' vibrational modes of the donor-ring, bringing one transferring H into closer proximity to the receptor site, resulting in single H$^{\bullet}$ barrier-avoiding tunnelling. Our results, and some new examples discussed below, certainly reveal scant experimental evidence for tunnelling in the triene systems typified by **1**. With regard to the two-step mechanism, one might also expect that the ethoxy triene **1**-OEt would rearrange much faster than is observed when the significant asymmetry in the relevant d_{CH} values (2.548 and 2.373 Å, Δd_{CH} = 0.175 Å) (Table 4) places one of the transferable H atoms closer to a receptor sp^2 carbon, which also has an amplified π-orbital component due to polarisation caused by the donor group OEt; and yet **1**-OEt rearranges more than an order of magnitude *slower* than the slightly more symmetrical compound **1** (Δd_{CH} = 0.150 Å), both compounds having an identical mean value of d_{CH} (2.46 Å). The rate ratio k_1 (**1**):k_1 (**1**-OEt) is actually ~13 at 100 °C. For the sets of compounds, trienes **1–4**, and homologous pyrazolines **6–9** and **14–17** discussed above, the essentially linear free energy relationships suggest a common mechanism, and that a diradical intermediate is therefore unlikely.¶ The pyrazolines would be expected, with their donor ring N frameworks and aryl substituents, to deliver much more stable free-radical elements when one H$^{\bullet}$ is transferred in a rate limiting step, than expected for the trienes, and to rearrange more rapidly—the opposite of what is actually found.

All of the examples of dyotropy which we have discussed[1a,d] are also exothermic and irreversible processes.‖ Quantitatively, differential scanning calorimetry (DSC) yields, *e.g.* triene **4**, a value of ΔH = −22.63 ± 0.41 kcal mol^{-1} for the exothermicity of the rearrangement. From this value of the exothermicity (usually defined as ΔE), the expected activation energy, $E_{a,o}$, for an identical thermoneutral process can be calculated from ΔE and the measured value of E_a for triene **4**, 28.3 (3) ± 0.3 kcal mol^{-1}, using the Koeppl–Kresge correlation[15,16] $E_a = E_{a,o}(1 + \Delta E/4E_{a,o})$,[2] which reduces to $E_a = E_{a,o} + \Delta E/2$ when higher, relatively insignificant, terms (< 1 kcal mol^{-1}) in the expansion are neglected. Thus from the data for triene **4**, $E_a = E_{a,o} - 11.3$, and $E_{a,o}$ = 39.6 kcal mol^{-1}. This figure is rather close to E_a experimentally estimated for dyotropy of the furano compound **20** described by Vogel *et al.*,[17] E_a ~35–39 kcal mol^{-1}. For the disulfone **21** described by Paquette *et al.*,[1b] a mean k_1 of 4.25 × 10^{-4} s^{-1} at 160 °C is reported and from Table IV in their paper, k_1 is 23.6 times slower at 130 °C, with a mean k_1 = 1.80 × 10^{-5} s^{-1}. These data yield E_a = 36.4 kcal mol^{-1} for the nearly thermoneutral rearrangement of disulfone **21**.** By comparison, for the hydrocarbon analogue of the disulfone (**21**, R = H), *ab initio* calculations[11b] for the concerted thermoneutral pathway yield E_a = 39.9 kcal mol^{-1}. This value is

¶ The fast dyotropy observed in certain porphyrin-type compounds has, however, been accommodated in a two-step asynchronous model.[12]

‖ This is indicated by the mp behaviour of micro and macro samples. In several instances samples melt, usually at 180–250 °C, then resolidify, and finally melt again at the mp of the pure dyotropomer. On a macro scale (~500 mg) crystals of **1**-OEt slowly raised in temperature in a small tube inserted into an oil bath, melt suddenly near 180 °C; the temperature of the melt rises 25 °C above the oil-bath temperature before the sample finally crystallises.[13] Resonance energy released is *ca.* 35 kcal mol^{-1} for the homocyclic compounds, and 27–40 kcal mol^{-1} for the pyrazoline–pyrazole conversion[14] and will contribute to the exothermic drive for these reactions.

** The kinetic data for this compound more recently reported by Paquette *et al.*,[18] k_1 = 4.43 × 10^{-6} s^{-1} (130 °C) and 4.25 × 10^{-4} s^{-1} (160 °C), translates into a value for E_a of *ca.* 50 kcal mol^{-1} and appear to be incorrectly recorded.

Table 4 Heats of formation ΔH_f, strain E_s and π-energies E_π (kcal mol^{-1}), and experimental and calculated d_{CC} and d_{CH} internuclear distances (Å)

Compound	ΔH_f[a]	E_s	E_π	δ_{CC}	δ_{CH}	Dyo	ΔH_f	E_s	E_π	δ_{CC}	δ_{CH}	$\Delta\Delta H_f$	ΔE_π	k[b]/10^{-5} s^{-1}	Relative rate
1	49.965	109.74	−272.94	3.14[c]	2.46[c]	**1D**	14.407	117.68	−315.28	—	—	−35.558	−42.34	23.01	1
				3.072(7)[d]	2.50(5)[d]										
				3.041(7)[d]	2.35(5)[d]										
				Avg. 3.057	Avg. 2.43										
23[e]	6.003	113.02	−272.80	3.136[c]	2.413[c]	**23D**	−26.989	123.633	−314.140	3.080[c]	—	−32.992	−41.341	20.7	0.9
				3.050	2.39(6)					3.093	2.364				
				3.067	2.44(9)					3.090	2.354				
				Avg. 3.054	Avg. 2.42					Avg. 3.091	Avg. 2.359				
22[e]	13.324	110.987	−272.95	3.124[c]	2.354[c]	**22D**	−18.171	122.95	−314.925	3.081[c]	—	−31.495	−41.976	4.75	0.21
				3.157[c]	2.538[c]					3.080[c]	—				
				Avg. 3.141	Avg. 2.446					Avg. 3.080	—				
1-OEt	13.300	105.42	−272.73	3.079	2.373	**1-OEtD**	−20.443	109.30	−315.26	3.051	2.260[f]	−33.733	−42.530	1.70	0.07
				2.998	2.548					2.955	2.111				
				Avg. 3.038	Avg. 2.46					3.017	2.187				
										3.04	2.188				
26	78.997	69.728	−586.297	2.850[c]	2.454[c]	**26D**	39.662	61.302	−630.349	2.80[c]	2.575[c]	−39.335	−44.052	3.84 × 10^{-3}	1.67 × 10^{-4}
				2.823[c]	2.549[c]										
				Avg. 2.836	Avg. 2.501										
				2.802	2.42										
				2.819	2.47										
				Avg. 2.811	Avg. 2.44										
24	65.000	45.431	−483.210	2.707											
				(π/π)											

[a] E_π (ene) included in ΔH_f calc., HC=CH, −11.94; ClC=CCl, −13.40 eV. [b] At 100 °C. [c] Calc. value. [d] 4,9-Dideuterio-compound. [e] For **22** Cl-14 tilts 3° *exo*, Cl-13, 1° *exo*; for **23** Cl-13, 14 tilt equally 2° *exo* (*endo*-pyramidalisation). [f] Two independent molecules.

remarkably close to $E_{a,o}$ calculated as above from experimental data.

It would be very remarkable for such a favourable correlation to exist between the activation energies $E_{a,o}$ for the essentially thermoneutral processes exhibited by **20** and **21**, and the highly exothermic transformation of triene **4**, if the observed dyotropy involved biradical intermediates, given the very different molecular frameworks in **4**, **20** and **21**. In fact, for the biradical pathway for thermoneutral dyotropy of analogues of compound **21**, calculation[11b] delivers an unreasonably high value of E_a, 63–65 kcal mol^{-1}, indicating the process to be unlikely. It should also be pointed out that the Koeppl–Kresge correlation holds, strictly speaking, only for identical processes involving a single step in the rate-limiting event. For the dyotropic processes we have described, a picture may be conjectured in which during 'in–out' vibration of the donor element, one of transferring Hs incipiently passes over the barrier, or through it near to its apex, when at minimum width during oscillation, followed by the second H in a concerted but non-synchronous process taking advantage of the lower energetic cost of pericyclicity in an orbital symmetry-allowed process.[19a,b] The former process occurs when the barrier is below a critical height, as for the triene series of compounds typified by **1**; but above a critical height, barrier-avoidance becomes significant, as for pyrazoline **18**.††

Solvent effects

The possibility that dyotropy with these trienes and pyrazolines involves concerted but significantly non-synchronous processes‡‡ prompted a brief study of solvent effects on the kinetics of rearrangement of triene **1** and its *syn*-dechloro-analogue **3**. For an asynchronous transfer of 2 H, the transition state (TS) will develop greater charge separation than for a synchronous transfer, where charge separation will approximate that of the ground state reactant (particularly for a reactant-like TS).[22] The rate constant, k_1, for dyotropy of triene **1** at 90 °C ranges from 1.06×10^{-4} s^{-1} in decalin (decahydronaphthalene) to 2.70×10^{-4} s^{-1} in nitromethane—a modest rate-spread; other data are included in Table 5, together with similar data for triene **3**, which is seen to be a little less kinetically solvent-sensitive than the more highly chlorinated analogue, **1**. A correlation is found for log k_1 with the Reichardt solvent parameter E_T, which is reasonably linear in trend for trienes **1** and **3**. For these compounds the slopes (log k_1/E_T) are positive, +0.020 for triene **1** and +0.010 for analogue **3**, and typically are the results to be expected in homopolar (concerted) pericyclic reactions. For reactions involving radical or biradical intermediates Reichardt plots usually have zero or negative slopes.[23]

Dyotropy of triene 1 in the solid state

Whilst triene **1**-OEt stored at room temperature for 25 years was found to be quite stable, even older samples of triene **1**, originally large transparent crystals (2 × 3 mm) had become opaque; NMR analysis showed the sample to be 100% pure dyotropomer, **1D**! From the solution data E_a, log A values, the half-life of triene **1**, $\tau_{\frac{1}{2}}$ at 20 °C, is 369.7 days; however, there are indications that crystalline samples survive for much more than a year, at ~20 °C, suggesting, as might be expected, that reaction is significantly slower in the solid state. A large rectangular crystal of triene **1** when viewed through a hot-stage microscope at T ~ 100 °C was seen to develop an opaque zone at one edge, which travelled uniformly through the crystal during the course of *ca.* 1 min. Because triene **3** is somewhat less reactive than analogue **1**, promising better control of solid-state kinetic measurements, well formed single crystals of triene **3** (of X-ray diffractable quality, largely free of defects) were accurately weighed and heated at 124.9 °C in sealed capillary tubes inserted into thermostat ampoules containing decalin as the heat transfer medium. The extent of conversion to dyotropomer **3D** was measured by dissolution of each of the crystals in ethanol and UV absorption. The results are depicted in Fig. 1. The extraordinarily large induction period before the onset of significant reaction implies that either crystal packing forces prevent vibrational activation of the C–H bonds involved in dyotropy, and/or that the large deformation required of the donor ring in achieving the TS is strongly inhibited; *if* sufficient thermal energy can be acquired by one of the C–H bonds involved for transfer of H$^{\bullet}$ in a two-step process, the donor-element ring deformation required to achieve radical stabilisation would be similarly inhibited. The overall result might then be that the second H$^{\bullet}$ transfer could become rate-limiting, with the first step becoming an equilibrium process. This would imply that the initially formed biradical has a significant life-time, and that other fragmentation processes might supervene, but from the behaviour of triene **1** in the solid state, there is no evidence for any other products than the dyotropomer **1D**. The solid-state behaviour is rather typical in general terms;[24] reaction only becomes rapid after defect centres in the solid, usually at the crystal edges, allow relaxation of crystal forces in their locality, promoting molecular rearrangement and the increasingly rapid consequent spread of crystal defects, until *e.g.* after 90% conversion, triene **3** exists as a solid solution in its dyotropomer. This of course rationalises the mp behaviour observed for many of these types of compound.‖

Table 5 Influence of solvent polarity on dyotropic rates for trienes. Slope of Reichardt correlation, log k_1 *vs.* E_T ($\Delta \ln k_1/2.303\Delta E_T$): **1**, + 0.020; **3**, +0.010; **22**, +0.004; **23**, +0.009 ($R^2 > 0.840$ in each case)

	$K_1/10^{-4}$s^{-1}				
Solvent	**1**[a]	**3**[b]	**22**[c]	**23**[d]	E_T/kcal mol^{-1}
Decalin	1.06	1.15	0.91	0.92	33.6
C_6H_5Me	1.35	—	—	—	33.9
C_6H_5Cl	1.51	1.40	0.93	1.08	37.5
C_6H_5CN	2.05	1.77	1.13	1.21	42.0
$MeNO_2$	2.70	1.75	—	—	46.3
AcOH	2.46	1.89	1.07	1.37	51.7

[a] 90° C. [b] 115° C. [c] 107° C. [d] 89.5° C.

Some new examples of structures displaying intramolecular (4σ + 2π) thermal dyotropy

Other than the many and variously structured compounds which we have investigated (including dihydropyridazines analogous with *e.g.* triene **1**[5]) which exhibit irreversible H dyotropy in the temperature range 20–230 °C, with an extrapolated rate-spread of ~10^{12} normalised to the rate for the most reactive compound studied, triene **5** at 36 °C, a very significant number of *syn*-sesquinorbornene derivatives have been investigated by Paquette *et al.*,[1b,c,18] which, however, show a much narrower rate spread. Isolated examples of (4σ + 2π) dyotropy have also been recognised[17,25] or inferred,[26b,c,d,e] together with an example of (4σ + 2π) dyotropy.[26f] In the latter example, the measured E_a correlates well with E_a for

†† Some indications that this picture may be correct are provided by the following. From a diagrammatic reaction coordinate, the isotopic increment to E_a, $\delta E_a(v_o)$ arising from lowest-level vibrational C–H/C–D energy differences between ground state and transition state can be seen to be $\delta E_a(v_o) = \delta E_a(v_o)_{gs} - \delta E_a(v_o)_{ts}$. The PDKIE data for triene **1** and pyrazoline **18** and the known value for $\delta E_a(v_o)_{gs}$, 1.22 kcal mol^{-1} per D atom,[20] gives values of $\delta E_a(v_o)_{ts}$ of +0.35 kcal and −0.20 kcal mol^{-1}, respectively, implying that $(v_o)_{ts}$ is above the barrier apex for triene **1**, but below it for pyrazoline **18**. For the di-*p*-tolylpyrazoline **19**, none of the criteria for a tunnelling contribution discussed appear to be met. The E_a value for **19** does therefore suggest a measure of the barrier height above which tunnelling may become apparent.

‡‡ There is other evidence for asynchronicity in pericyclic reactions from work on isotope effects for the Claisen rearrangement.[21]

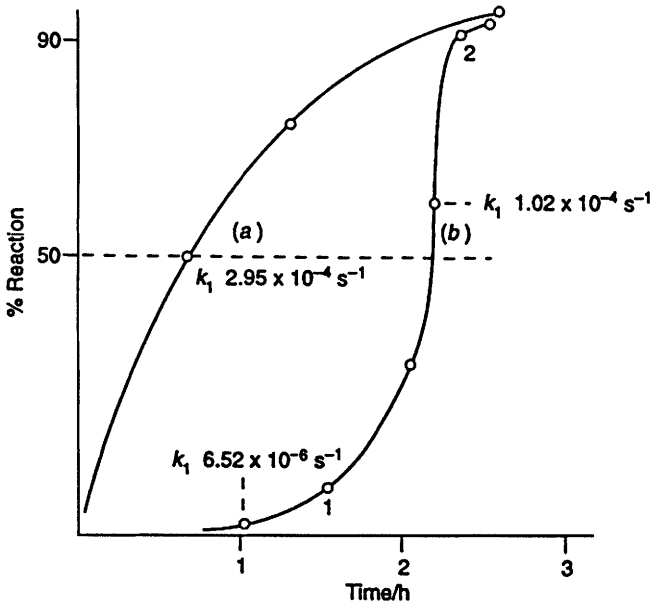
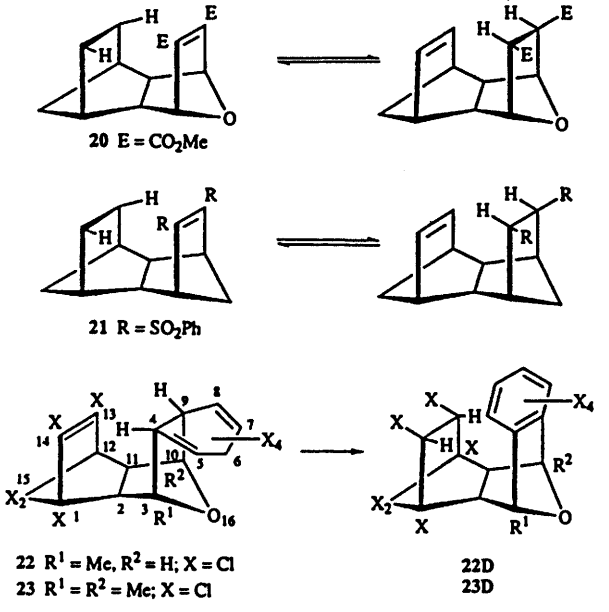


Fig. 1 Single-crystal kinetic behaviour of triene **3** (*b*) compared to unimolecular decay in solution (*a*). At point 1, crystals are transparent, becoming opaque at point 2.

trienes **1–4**, when allowance is made for conformational effects, and the kinetic isotope effect at 160.7 °C, k^{2H}/k^{2D} = 3.16, is comparable with that for triene **1** extrapolated to this temperature to give a value of 5.6. Our main objective has been to uncover a range of compounds with different structural features and to analyse within selected groups how structural changes affect kinetic reactivity, and to find correlations for kinetic and thermochemical effects with structural changes common to individual classes of compounds as illustrated for trienes **1–4**, pyrazolines **6–9** and homopyrazolines **14–17**. The general idea that molecular features remote from the actual reaction cavity might influence reactivity by either steric or electronic effects (or both), led us to make the oxygen-bridged compounds analogous to triene **1**, **22** and **23**, (Scheme 3 and



Scheme 3

also **22**, R^1 = Et, R^2 = H)[27] for structural and kinetic comparisons. The oxygen-bridged compounds show clean kinetic behaviour in air, as for triene **1**. We find that the kinetic and thermochemical data for triene **23** is almost identical to that for triene **1**, (Tables 2 and 3), and this prompted us to study the

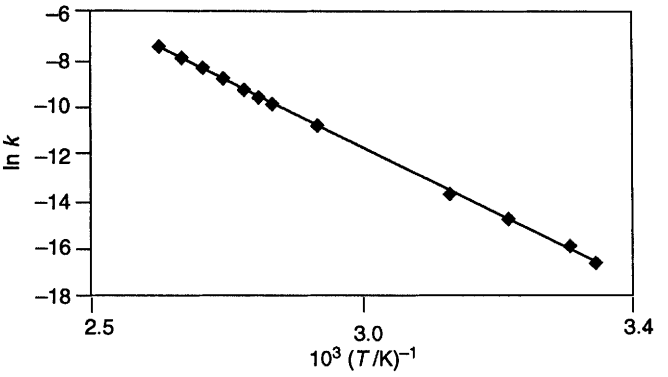


Fig. 2 Arrhenius plot for triene **23** in the temperature range 26.3–110 °C

kinetic behaviour of **23** over a wide temperature range yielding, as for triene **1**, a perfectly linear Arrhenius plot (Fig. 2). For trienes **23** and **1**, the mean d_{CH} values (Table 4) are identical if allowance is made for the difference (0.01 Å) in C–H and C–D bond lengths, the more kinetically stable [4,9-$^2H_2$] isotopologue of triene **1** having been used in X-ray/neutron diffraction experiments. The values for ΔE_π for these two compounds and their dyotropomers, **1D**, **23D**, are significantly different (−42.34 and −41.34 kcal mol^{-1}) and there is no correlation with the ln $k_1/\Delta E_\pi$ data for trienes **1–4**.[1a] The reactant strain-energies E_s are rather similar, however (109.74 and 113.02 kcal mol^{-1}) and here there is a good correlation with ln k_1/E_s data for trienes **1–4** [for which ln k_1 = −(21.96–0.122 E_s) ± 0.24]. These data predict k_1 for **23** to be in the range 2.23–3.59 × 10^{-4} s^{-1} at 100 °C, whilst the experimental value is 2.07 × 10^{-4} s^{-1} at this temperature.

The monomethyl-compound **22** is almost isoapostatic in *mean* d_{CH} with trienes **1** and **23**, and k_1 at 100 °C (Table 2) is noticeably smaller by a factor of ~5. For **22** neither E_s nor ΔE_π correlate with the triene group **1–4** data, despite the close similarity in E_s values, although the ΔE_π factors are significantly different, (Table 4). However, the calculated values of d_{CH} for **22** are noticeably disparate, 2.354 and 2.538 Å (Δd_{CH} = 0.184° Å), compared to triene **23** where these values are 2.396 and 2.449 Å (Δd_{CH} = 0.05 Å) from the crystallographic data. The difference in the d_{CH} values for triene **22** is the largest seen in all the trienes so far investigated, but resembles the experimental values for the similarly distorted triene, **1**-OEt, discussed above (2.548 and 2.373 Å, Δd_{CH} = 0.175 Å). Significantly, the rate-ratio k_1(**1**): k_1(**1**-OEt) is ~13 at 100 °C compared to k_1(**23**):k_1 (**22**) 5 at this temperature. In our earlier paper[1a] we identified **1**-OEt as anomalously unreactive compared to triene **1**, especially since ΔE_π for **1**-OEt ⟶ **1**-OEt **D** is slightly more favourable than for **1** ⟶ **1D** (Table 4), and showed that the ln k_1/E_s and ln $k_1/\Delta E_\pi$ correlations with the triene **1–4** data failed completely. We proposed a possible cause of this effect in the perturbation of the π-system by the π donor oxygen in EtOC=CCl, leading to transition-state distortion occasioned by the inequality of the π-orbital coefficients at the receptor carbons, likely to be an important effect in a concerted 2 H transfer. The comparison of trienes **1**, **22** and **23** now reveals that molecular distortion of this order of magnitude (Δd_{CH} ~0.175–0.184 Å) is also an important rate-retarding effect, trebled in rate terms by the additional π-orbital distortion in **1**-OEt, where the mean d_{CH} is nearly isoapostic with **1** and **22**, (2.46 Å). In considering the mechanism of reaction, another important point emerges. Since in **22** one of the H atoms in the donor ring is closer to a receptor carbon by 0.04 Å compared to the nearest donor ring H in **23**, it would be expected that **22** would be more reactive in a single H$^\bullet$ transfer process than **23** (or at least more closely similar in rate), particularly when it is recalled that in all the compounds investigated, receptor C atoms and donor H atoms are well within the sum of the van der Waals radii for sp^2 C and sp^3 H,

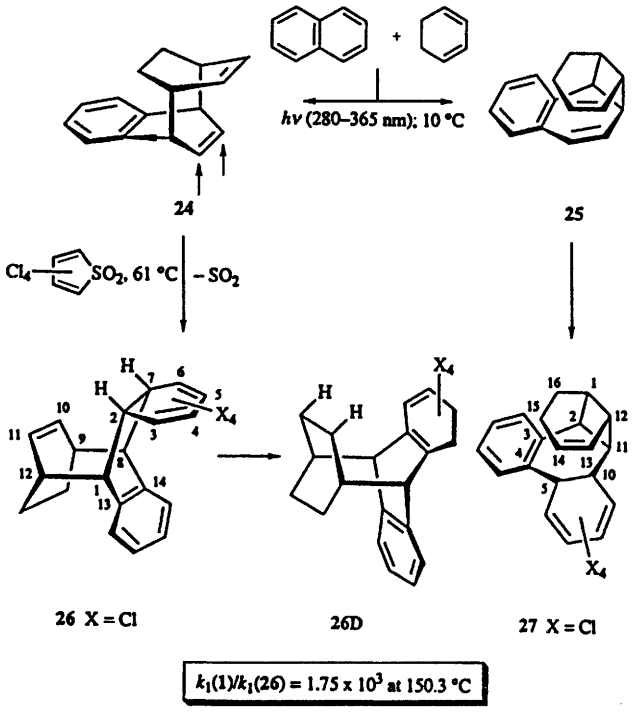
appropriate to the onset of chemical reaction,§§[28] and given the sensitivity of dyotropic rate to modulation in d_{CH}.[1a,b]

In pursuing the idea that molecular distortion plays a significant role in modulating kinetic behaviour, we attempted to make the 3-Bu^t-analogue of the bridgehead methylated triene **22** (**22**, R^1 = Bu^t, R^2 = H), since molecular modelling (MM) calculations suggest even more disparate values for the proximity factors d_{CH}, here 2.226 and 2.651 Å. Whilst the required precursor 2-*tert*-butylfuran–hexachloronorbornadiene *endo–endo* adduct proves accessible, this compound is thermally unstable, and unreactive towards tetrachlorothiophene dioxide, foiling isolation of **22** (R^1 = Bu^t).

A limited study of the solvent effect on reaction rate and Reichardt correlations shows, as expected, a smaller change in polarisation for trienes **22** and **23** in accessing the transition state from already more polarised reactants, than is found for trienes **1** and **3** (Table 5). Triene **22** has a log k_1/E_T slope of +0.004, whereas the triene **23** is slightly more sensitive to increasing solvent polarity, with a slope of +0.009 for the similar Reichardt plot.

Dyotropy of a triene with a more flexible framework

All of the compounds which display dyotropy discussed here are characterised by considerable framework rigidity. Another potentially adjustable parameter which might be varied is the framework flexibility of structures which potentially exhibit dyotropy, as indicated from the kinetic investigation of (4σ + 6π) dyotropy by Grimme *et al.*[26f] To this end we have made the (4π + 4π) photo-adduct of naphthalene and cyclohexa-1,3-diene, **24**,[29] which is formed together with *ca.* 10% of its Cope rearrangement product **25** in the photo-addition at ~10 °C (Scheme 4). Attempted separation of **24** and **25** by preparative



Scheme 4

TLC, surprisingly catalysed conversion of **24** into **25**, and therefore the mixed photo-adduct was exposed directly to tetrachlorothiophene dioxide (TCTD) in $CDCl_3$ and the cycloaddition reaction monitored by NMR spectroscopy. Reaction was complete after 24 h at 61 °C, and repeated crystallisation of the solid tarry products obtained by evaporation gave the desired triene **26** (30% purified yield), mp 232–235 °C. On cooling, the mp sample solidified, and re-melted at 198–220 °C, suggesting slow dyotropic reaction. The adduct was stable in solution at 125 °C (3 h) with no detectable change in the NMR spectrum, but at 150 °C in decalin, UV monitoring of the characteristic 1,2,3,4-tetrachlorocyclohexa-1,3-diene chromophore showed unambiguous evidence of rearrangement. A sample of **26** dissolved in hexachlorobutadiene (0.105 M) with a trace of $(CD_3)_2CO$ was heated at 160.1 °C for 3 h, after which time ^{1}H NMR signals characteristic of dyotropomer **26D** appeared; after a total of 10.5 h at 160.1 °C the ratio of **26**:**26D** was 1:1, giving the half-life at this temperature and $k_1 = 1.83 \times 10^{-5}$ s^{-1}, (*cf.* Table 6). No other reaction products were detected. In pilot studies to establish conditions for obtaining kinetic data using dilute solutions of **26** in decalin (typically ~0.002 M), anomalous behaviour was observed, traced to dissolved air in the sample. In none of the trienes previously investigated here, or in the original work[1a,5,13] had air interfered with kinetic measurements, although this problem had been encountered earlier with the pyrazolines,[5] whose kinetic behaviour was accordingly examined using degassed solutions *in vacuo*. A similar strategy with air sensitive triene **26** delivered the rate data in Table 6 and thermochemical data E_a 31.7(7) ± 0.3 kcal mol^{-1} (converted from computed data expressed in kJ and J) and log A 11.2(6) ± 0.2.

From the data in Table 4, the mean crystallographic d_{CH} for **26** (2.44 Å) is closely similar to that for triene **1**, but the rate ratio at 150.3 °C, k_1 (**1**):k_1 (**26**), obtained by extrapolation for **1** (Table 3 data) is 1.75×10^3. The data in Table 4 show the reactant strain-energy E_s less favourable for **26** compared to **1** (69.728 and 109.74 kcal, respectively), but ΔE_π is much more favourable by 1.7 kcal mol^{-1}, given the high sensitivity of reaction rate towards this factor displayed in the group of trienes **1**–**4**. The difference in activation energy for trienes **1** and **26** (6.7 kcal mol^{-1}) is of the correct order of magnitude to be associated with a rocking motion of the appended cyclohexene receptor element perhaps required to promote reaction. For the present, this must remain a rather speculative explanation, for additionally the receptor π-bond is at lower energy (less strained) than for a norbornene 2 H receptor and the consequent reduction in exothermicity will also translate into reduced dyotropic rate.

In the cycloadition product **27** of the Cope rearranged photo-adduct **25** with TCTD, the X-ray crystal structure (Fig 4, Experimental section) shows quite severe distortion with respect to the potentially dyotropic H atoms, H-5 and H-10, and receptor π-element C-13, C-14, and no evidence has been found for dyotropy with this compound.

One point of further interest concerns the regiospecific addition of TCTD with photo-adduct **24**. Calculations indicate that a homoallylic interaction (of bond order 0.025) occurs between the aromatic ring and the adjacent double bond. This has two effects; a raised HOMO energy, and increased orbital coefficients (0.4833 and 0.4826) compared to those on the remote double bond (0.4312 and 0.4320).¶¶ Both factors will favour rapid reaction in an inverse electronic demand (4π + 2π) cycloaddition.[19a,30] Preliminary experiments indicate that when this dienophilic site is made unreactive by substitution of H by electronegative groups, cycloaddition occurs at the alternative alkene site.[31] The regiospecific reaction of **24** with TCTD is thus seen to be a kinetic effect, as expected from the calculations.

§§ Arguments based on crystal-structure proximity effects assume that inequality in d_{CH} values persist in solution. There is evidence for this in the NMR spin-coupled systems H-2,7 and H-1,8 in the dyotropomers **19** and **19D**, analysed for solution data.[1a]

¶¶ In the original report describing the photo-adduct **24**, spectroscopic properties were interpreted in terms of transannular π–π interaction.[29]

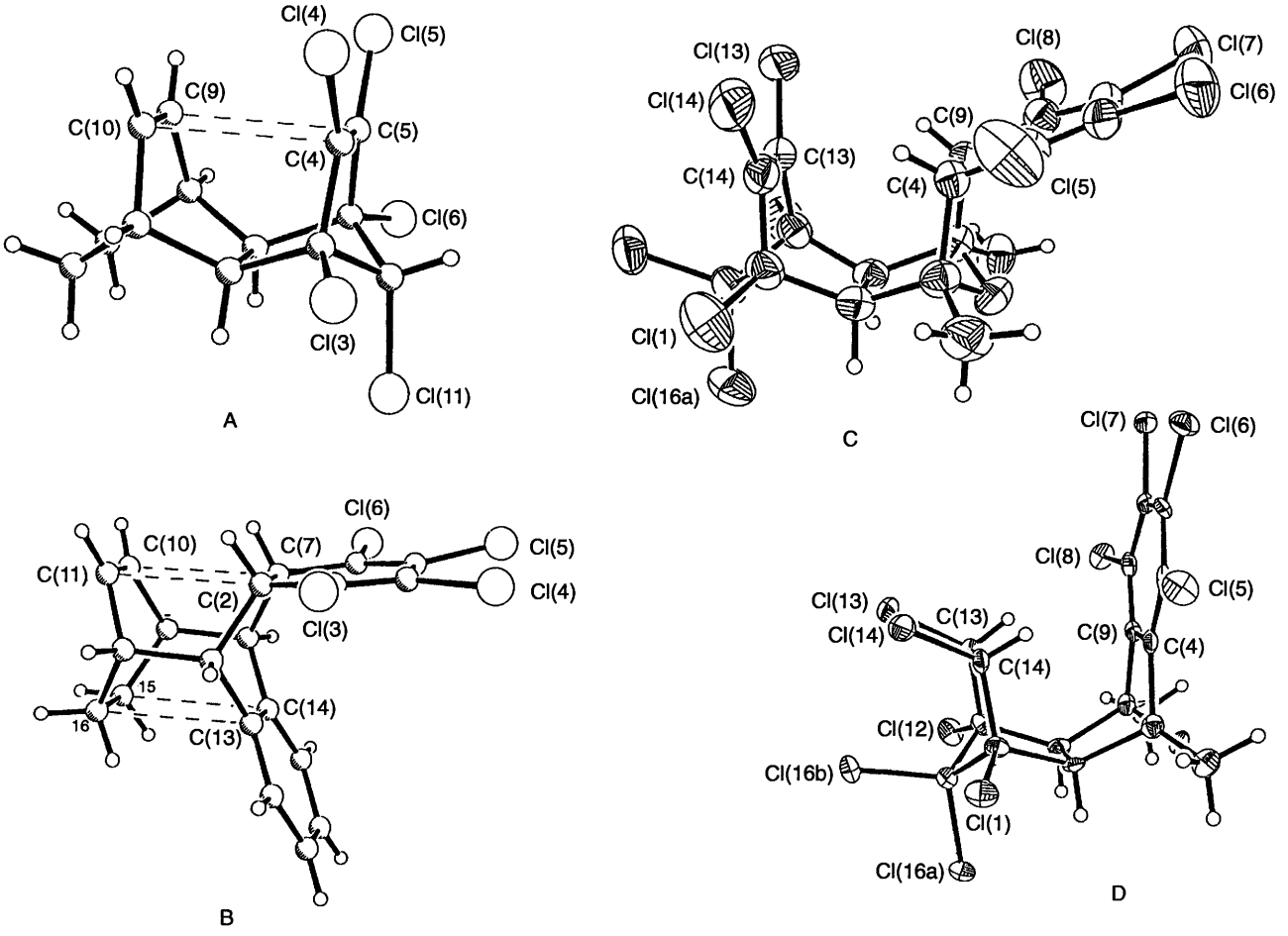


Fig. 3 Representative single-crystal X-ray structures: **A**, 11-*syn*-dechlorohomoisodrin **11**; **B**, dyotropomerically active triene **26**; **c**, triene dyotropomer **23**; **D**, aromatic dyotropomer of triene **23**, **23D**. d_{cc} (Å): **A**, C(5)–C(9) 2.957, 2.958; C(4)–C(10) 2.956, 2.976. **B**, C(13)–C(16) 2.834; C(14)–C(15) 2.849. Other data, Table 4.

Table 6 Unimolecular rate constants k_1, and standard deviations (%) for dyotropy of triene **26**

Compound	T/°C	$k_1/10^{-5}$ s^{-1}	$\sigma_{(n-1)}/k_1 \times 10^2$
26	175.4	6.30	2.9
	170.3	4.03	3.8
	165.6	2.82	3.0
	160.3	1.79	4.2
	155.0	1.16	4.5
	150.3	0.744	1.6

Conclusions

In this paper and our earlier report,[1a] insight into factors governing relative kinetic behaviour of dyotropomers which involve interlocking stereoelectronic effects can clearly be facilitated by consideration of quite small modulation in ground state strain energy, E_s, exothermicity, ΔE_π, and internuclear sp^2 C–sp^3 H proximity effects, d_{CH}. This may be particularly the case for the compounds we describe, where the relevant reactive centres are constrained at less than the van der Waals distance, appropriate to the onset of chemical reaction.[28] However, in several instances both calculated and X-ray/neutron diffraction structural information for the sets of analogous compounds studied indicates different degrees of pyramidalisation of receptor sp^2 C atoms. The ground state molecules thus display geometrical features foreshadowing transition state access to a greater or lesser extent. The differing extent to which ground state molecules in an analogous set resemble the transition state geometry will translate into kinetic effects superimposed on to those due to other factors (E_s, ΔE_π and d_{CH}). This may be one reason why the correlation of internuclear separation, d_{CH}, with relative reactivity is far from perfect.[1a,b] This effect might also contribute to the weakening of the correlation of ln k_1 with E_s and particularly ΔE_π, for some of the trienes analogous with the triene group **1**–**4** which we have discussed here.

Experimental

The following apply unless otherwise indicated. NMR data refer to solutions in $CDCl_3$ (Me_4Si) using JEOL GX270, GX400 or GSX500 instruments. All signals have the correct relative intensities. J values are given in Hz. In the NMR data, n represents narrow. UV spectroscopic data required for kinetic monitoring were acquired for solutions in decalin with PE 555 and PE 552 instruments. EI mass spectra were obtained with probe samples using an AEI MS902 machine with VG Micromass facilities or with a Fisons Autospec machine; all ion-clusters have the correct characteristic halogen isotope abundance ratios in appropriate cases. Preparative TLC refers to 0.8 mm Merck Type 60 GF_{254} silica gel coated plates visualised under UV light. Light petroleum refers to the 60–80 °C bp fraction redistilled. Kinetic data are for solutions in decalin. For air-sensitive compounds (pyrazolines **14**, **15**, **16**, **17** and triene **26**) decalin solutions were air-purged by freeze–thaw cycles (−196 °C) under N_2 and then under vacuum, before ampoules were sealed *in vacuo*. For solvent effect studies, commercially available solvents were redistilled before use. Ampoules were heated in a Grant thermostat fitted with a calibrated thermometer (±0.1 °C); temperatures cited represent the estimated mean value over runs, solutions being monitored by digital display PE 555, PE 552 spectrometers at a principal UV λ_{max} and corrected for solvent background absorption.

Kinetic runs were conducted over time intervals of 1–3 half-lives, it having been established that unimolecular rearrangements proceeded to completion on prolonged heating (——→*D*, solvent background absorption, 0.1 cm cell). Replicate runs consistently indicated reproducibility of k_1 values to within 2%. Arrhenius plots had residual factors > 0.998. Further kinetic data, spectra, Arrhenius plots and tables for compounds **1**, **14**, **22**, **23** and **26** have been deposited as supplementary material at the British Library.‖‖ X-Ray crystal structure data, tables of fractional coordinates, bond lengths, bond angles and other data have been deposited with the CCDC.‖‖

Synthesis of pyrazolines 14, 15 16 and 17***

Homoisodrin **10** (*endo-endo*-3,4,5,6,13,13-hexachlorotetracyclo[6.2.2.$1^{3,6}0^{2,7}$]trideca-4,9-diene), was prepared by the method of Edward *et al.*[32] and converted to pyrazoline **14** accompanied by dyotropomer **14D** by heating with 2,5-diphenyltetrazole as previously described.[1a] The *syn*-**14** and *anti*-**14** bridge-methylene dechloro-compounds **15** and **16** were similarly made from *syn*- and *anti*-13-dechlorohomoisodrin (**11**, **12**) prepared as follows. In a typical run a zinc–copper couple was prepared by heating zinc powder (720 mg, 0.011 g atom washed with dil. aq. HCl, then 3 × MeOH and finally diethyl ether) with CuBr (1.58 g, 0.01 mol) in diethyl ether (10 ml) with vigorous stirring.[33] To the finely divided chocolate-brown suspension of Cu–Zn, homoisodrin (7.664 mg, 2.0 mmol in Et_2O, 5 ml) was added and the mixture heated and stirred for 3 h, and then gently boiled for 46 h; the cooled reaction mixture was diluted with diethyl ether, the ethereal solution carefully decanted and combined with several diethyl ether washings of the residual solid, then washed and dried (Na_2SO_4). The solid product obtained by evaporation contained two components (TLC); these were separated by prep. TLC (10% EtOAc–light petroleum) into *syn*- and *anti*-13-dechlorohomoisodrin **11** and **12**, respectively. *endo,endo*-3,4,5,6-*anti*-13-Pentachlorotetracyclo[6.2.2.$1^{3,6}0^{2,7}$]trideca-4,9-diene **11** (267 mg, 40%); mp 152.5–153.5 °C (MeOH); δ_H 1.28 and 1.47 (each m, A_2B_2, H-11,11′,12,12′), 2.71 (m, H-2,7), 3.83 (s, H-13), 5.97 (t, H-9, 10); *m*/*z* 342 (M^+, 5%); 307 (M–Cl^+, 36%), 236 ($C_5HCl_5^+$, RDA,††† 10%), 78, 79 and 80 ($C_6H_n^+$, RDA, 28, 31 and 18%) (Found: C, 45.10; H, 3.23. $C_{13}H_{11}Cl_5$ requires C, 45.32; H, 3.22%). X-Ray single crystal structure data, *syn*-13-dechlorohomoisodrin **11**: $C_{13}H_{11}Cl_5$ M = 344.5; *a* = 12.147(2), *b* = 13.934(2), *c* = 8.830(2) Å; α = 91.16(2)°, β = 92.78°, γ = 110.41 (2)°; space group $P\bar{1}$ *V* = 1397.9(4) Å^3; *Z* = 4, D_c = 1.637 g cm^{-3}; *F*(000) 696; *R*, (*R*′) 0.0874, (0.1037), 6528 data. Also isolated, *syn*-13-chloro *isomer* **12** (97 mg, 14%); mp 125.5–126.5 °C (MeOH); δ_H 1.28 and 1.46 (each m, A_2B_2, H-11,11′,12,12′), 2.57 (m, H-2, 7 at higher field due to absence of proximate Cl-13), 2.77 (m, H-1, 8), 4.23 (s, H-11), 5.96 (t, H-9, 10); *m*/*z* 342 (M^+, 7%), 307 (M – Cl^+, 66%), 236 ($C_5HCl_5^+$, RDA, 14%), 78, 79, 80 ($C_6H_n^+$, RDA, 45, 53 and 37%) (Found: C, 45.28; H, 3.24%).

Preparation of 13,13-didechlorohomoisodrin, 13. Homoisodrin (2.40 g, 6.3 mmol) was heated with excess zinc powder (2.4 g, 0.04 g atom) in redistilled acetic acid (10 ml) with stirring for 4.25 h. The acetic acid was removed *in vacuo*, and the cooled product was stirred with water to remove $Zn(OAc)_2$, and the solution extracted with several portions of diethyl ether; the combined extracts were washed, dried (Na_2SO_4) and evaporated to give a waxy solid product (2.02 g); 100 mg

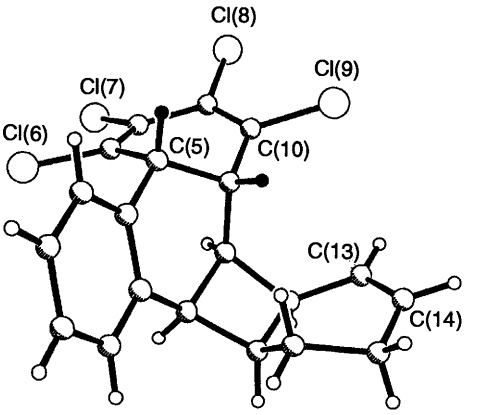


Fig. 4 X-Ray crystal structure of thermally stable triene **27**

portions of this product were resolved into a mixture of mono-dechlorohomoisodrin (**12**) and di-dechloro compound (**13**) (ratio 2:3) and unreacted homoisodrin (10–15%). The mixed mono- and di-dechlorohomoisodrin fraction from a number of experiments (60 mg in 0.5 ml CH_2Cl_2) was finally resolved, using 20 × 20 cm Al-backed silica plates (0.2 mm) with 10% EtOAc–light petroleum into di-dechlorohomoisodrin **13** (33 mg, 49% extrapolated yield) mp 125.5–127° (from MeOH). *endo–endo*-3,4,5,6-tetrachlorotetracyclo[6.2.2.$1^{3,6}.0^{2,7}$]trideca-4,9-diene **13**; δ_H 1.15–1.46 (overlap m, H-11, 11′, 12, 12′), 2.30 (ABq, H-13, 13′), 2.60 (n m, H-2, 7), 2.75 (br m, H-1, 8), 5.95 (t, H-9, 10); *m*/*z* 308 (M^+, 10%), 273 (M – Cl^+, 100%), 202 ($C_5H_2Cl_4^+$, 44%), 78, 79, 80 ($C_6H_n^+$, RDA, 87, 50, 14%) (Found: C, 50.26; H, 4.05. $C_{13}H_{12}Cl_4$ requires C, 50.36; H, 3.89%). Mono-dechloro compound **12** (20 mg, 27% extrapolated yield); mp and ^{1}H NMR identical to the sample derived (Zn–Cu) above was also isolated.

Pyrazolines 15, 16 and 17. In order to avoid excessive conversion of the dyotropically active pyrazolines into their corresponding pyrazole isomers, advantage was taken of the expected slower rearrangements of these compounds in decalin compared to their preparation in PhBr as previously described,[1a,5] reaction times also being limited to low conversion. In a typical experiment *syn*-dechloro-dipolarophile **11** (67 mg, 0.2 mmol) was heated with 2,5-diphenyltetrazole (22 mg, 0.1 mmol) in decalin (5 ml) at 154–156 °C for 4 h, under N_2. The cooled reaction mixture was evaporated and the crude product subjected to preparative TLC (50% CH_2Cl_2–light petroleum) giving *endo,endo,exo*-3,4,5,6-*anti*-16-pentachloro-10,12-diphenyl-10,11-diazapentacyclo [6.5.2.$1^{3,6}.0^{2,7}.0^{9,13}$]-hexadeca-4,11-diene, **15**, (9 mg, 17% from CH_2Cl_2–light petroleum) mp: yellow crystals turn opaque and colourless ~225 °C (concomitant dyotropy), melting 301–302 °C; δ_H 1.57 (obscured) and 1.85 (m, H-14, 14′, 15, 15′), 2.48 and 2.64 (each m, H-8, H-1), 3.01 (m, H-2, 7), 3.85 and 4.42 (each d m, H-9, H-13), 4.19 (s, H-16), 6.8–7.8 (5 m, ArH); *m*/*z* 536 (M^+, 22% +538, 36%), 501 (M–Cl^+, 25%) 271 ($C_{19}H_{14}N_2^+$ + H, RDA, 100%); λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 360 (20 129) (Found: C, 57.59; H, 3.96; N, 5.04. $C_{26}H_{21}Cl_5N_2$ requires C, 57.96; H, 3.96; N, 5.20%). Similarly made and purified, isomer **16** (15%), mp: yellow crystals turn opaque and colourless 230–240 °C, melting 328–330 °C; δ_H 1.52 and 1.82 (overlap. m, H-14, 14′, 15, 15′), 2.47 and 2.63 (each m, H-8, H-1), 2.86 (m, H-2, 7 shielded compared to isomer **15** by absence of proximate Cl-16), 3.85 and 4.38 (each dm, H-9, H-13), 4.35(s, H-16), 6.8–7.7(5 m, ArH) (NMR spin-couplings for **15** and **16** are closely similar to those found for pyrazoline **14**[1]); *m*/*z* 536 (M^+, 40%, 538, 65%), 501 (M – Cl^+, 29%), 271(RDA as for **15**, 100%); λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 359 (18 868) (Found: C, 57.53; H, 3.94 N, 4.96%). For the didechloro pyrazoline analogue **17** (18%) mp: yellow crystals turn opaque and colourless 180–200 °C, melting 225–226 °C; δ_H(300 MHz)

‖‖ Supplementary material has been deposited at the British Library [Suppl. Pub. 57152 (17 pp.)], and crystallographic data has been deposited at the Cambridge Crystallographic Data Centre (CCDC) [Reference no. 188/105]. Any request to either the British Library or the CCDC should give full literature citation and reference number.

*** For the numbering system used for compounds **10–17**, **22**, **23**, **26** and **27** see the structures shown earlier.

††† RDA = Retro-Diels–Alder.

1.22, 1.55 and 1.83–1.87 (each m, H-14, 14′, 15, 15′, *cf.* **14**)[1a], 2.49 (m, H-8), 2.64, 2.66 and 2.69–2.71 (q, ^2J 7.32, H-16, 16′), 2.66 (m, H-1), 2.82–2.92 (octet, H-2, 7), 3.83, 3.87 and 4.39–4.44 (each m, H-9 and H-13), 6.82–7.63 (m, ArH); *m/z* 502 (M^+, 54%, 504, 72%), 467 ($M - Cl^+$, 29%), 271 (RDA as for **15**, **16**, 100%); λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 365 (14 744) (Found: C, 61.65; H, 4.54; N, 5.45. $C_{26}H_{22}Cl_4N_2$ requires C, 61.92; H, 4.40; N, 5.56%).

Oxygen-bridged trienes 22 and 23 and their dyotropomers 22D and 23D

These compounds were made as recently described.[27]

Spectroscopic properties. Dyotropomer **22D**, mp 233–235 °C; δ_H(300 MHz) 2.02(s, CH_3), 3.44(d, *J* 12.99, H-2), 3.59 and 3.72 (each d, *J* 8.79 H-14, H-13), 3.91 (dd, *J* 12.99 and 5.13, H-11), 5.45(d, *J* 5.13, H-10); *m/z* closely similar to **22**[27] (Found: 565.748 077. Calc. for $C_{16}H_8Cl_{10}O$, 565.746 042) X-Ray crystal structure data were obtained for the dyotropomer of **22**, **22D** and for the dyotropomeric pair, triene **23** and **23D**. Attempts to make diffractable crystals of triene **22** proved intractable.

Crystal structure data. Triene **23**; $C_{17}H_{10}Cl_{10}O$; *M* = 584.75; *a* = 15.300(3), *b* = 8.364(2), *c* = 17.015(3) Å; *β* = 93.34°; space group $P2_1/c$, *V* = 2173.7(8) Å^3; *Z* = 4; D_c = 1.787 g cm^{-3}; *F*(000) = 584.75; *R* (*R*′) = 0.0849 (0.1006), 4840 data.

Dyotropomer **23D**; $C_{17}H_{10}Cl_{10}O$, *M* = 584.75; *a* = 17.216(3), *b* = 13.462(3), *c* = 17.947(4) Å; space group *Pbca*; *V* = 4159(2) Å^3; *Z* = 8; D_c = 1.868 g cm^{-3}; *F*(000) = 2320; *R*(*R*′) = 0.0492 (0.0628), 2521 data.

Neutron diffraction crystal structure data for [4,9-$^2H_2$]triene 1 (Table 4)

We previously reported brief details of this experiment;[1a] more complete data are as follows for $C_{16}D_6H_2Cl_{10}$ at 15 K: *M* = 560.7; *a* = 8.664(1), *b* = 14.047(2), *c* = 16.184(2) Å; *Z* = 4; space group $P2_12_12_1$ (orthorhombic); *V* = 1969.6 Å^3; D_c = 1.871 g cm^{-3}; *R*(*F*^{2}) = 0.0516, *wR*(*F*^{2}) = 0.0616, 4689 data collected. ^{2}H distribution, % (NMR *data*): C-3, 94 (*97*); C-4, 98 (*98*); C-9, 97 (*98*); C-10, 92 (*97*); C-16a, 93(*96*); C-16b, 92 (*97*); C-2, 9 (*0*); C-11, 2 (*0*).

Photoaddition of cyclohexa-1,3-diene to naphthalene: synthesis of triene 26

A solution of naphthalene (0.31 g, 2.4 mmol, 0.01 M) and cyclohexa-1,3-diene (19.2 g, 22.83 ml, 240 mmol, 1.0 M) in benzene (240 ml) was irradiated with a water-cooled 125 W Hg arc-lamp through a Pyrex filter, 3.5 h, the temperature of the solution remaining at ~10 °C during this time. Benzene and excess cyclohexadiene were evaporated under partial vacuum. ^{1}H NMR indicated the product contained mainly the photoadduct **24**[29] and a little of the Cope rearrangement product **25**. An attempt to separate these products using TLC (silica gel) delivered instead a product which proved to be mainly **25**. For this reason a portion of the crude product was used in reaction with tetrachlorothiophene dioxide (TCTD). The crude photoproduct (1.74 g, 8.4 mmol) was heated with TCTD (0.6 g, 2.4 mmol) in $CDCl_3$ (2 ml) under gentle reflux reaction, progress being monitored by ^{1}H NMR, being complete after 24 h. Evaporation of the solvent and several recrystallisations of the dark-coloured product gave the required adduct **26**, 13,14-*benzo*-3,4,5,6-*tetrachlorotetracyclo*[6.4.2.2^{9,12}.0^{2,7}]*hexadeca*-3,5,10-*triene* (180 mg, 20% based on TCTD) mp: colourless transparent crystals turn opaque 225–230 °C, melting 230–231 °C (from CH_2Cl_2–hexane); δ_H 1.26 and 1.34 (each m; H-15, 15′, 16, 16′), 3.04 (m, H-9, 12), 3.79 (s, H-2, 7), 4.36 (d, H-1, 8), 6.50 (m, H-10, 11), 7.01 and 7.13 (each m, ArH); *m/z*, see dyotropomer **26D**; λ_{max}(Shimadzu 160 data)/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 260.6 (3461), 269.0 (3483), 279.8 (3320), 292.8 (4614), 304.1 (5158), 317.4 (3339) (Found: C, 60.05; H, 4.09. $C_{20}H_{16}Cl_4$ requires C, 60.33; H, 4.05%). Crystal structure data **26**: $C_{20}H_{14}Cl_4$ *M* = 396.11; *a* = 8.276(2), *b* = 9.127(2), *c* = 12.369(2) Å; *α* = 83.10°, *β* = 72.39°, *γ* = 73.70°; space group $P\bar{1}$; *V* = 854.1 Å^3; *Z* = 2; D_c = 1.540 g cm^{-3}; *F*(000) 404; *R* (*R*′) 0.0687 (0.0745), 2745 data.

Also isolated, the product of reaction of **25** with TCTD, *syn*-1,2-*syn*-11,12-3,4-benzo-6,7,8,9-tetrachlorotetracyclo[10.4.0.-0^{2,11}.0^{5,10}]hexadeca-6,8,13-triene **27** (*ca.* 10%) mp 176–177 °C (from CH_2Cl_2–light petroleum); δ_H 0.98, 1.48 and 1.76 (each cm, H-15, 15′, 16, 16′), 3.98 (t, H-10), 4.29 (d, H-5), 5.86 (dm, H-13, 14); *m/z* 396 (M^+, 9.6%), 361 ($M - Cl^+$, 0%, *cf.* **26D**[27]), 314 ($M - C_6H_{10}$, 3%), 281 ($M - Cl - C_6H_{10}^+$, 62%), 246 ($M - 2Cl - C_6H_{10}^+$, 84%), 80 ($C_6H_8^+$, 100%) (Found: C, 60.90; H, 4.14. $C_{20}H_{16}Cl_4$ requires C, 60.33; H, 4.05%).

Crystal structure data for compound 27

$C_{20}H_{14}Cl_4$, *M* = 396.11; *a* = 5.2160(5), *b* = 16.5800(10), *c* = 20.2510(10) Å; *β* = 91.42°; space group $P2_1/c$; *V* = 1750.79(14) Å^3; *Z* = 4; D_c = 1.510 g cm^{-3}; *F*(000) 816; *R*(*R*′) 0.0868 (0.0988), 3079 data. The dyotropomer of **26**, **26D**, had δ_H 1.11–1.43 (cm, 10, 11, 15, 16 CH_2s), 2.84 (dm, H-9,12), 4.86 (d, H-1,8), (*cf.* anthracene–maleic acid adduct, bis-benzyl H, 4.65), 7.18 (m, ArH); *m/z* 396 (M^+, 5.6%), 361 ($M - Cl^+$, 5.5%), 314 ($M - C_6H_{10}^+$, 75%, 316, 100%) (Found: C, 60.33; H, 3.65. $C_{20}H_{14}Cl_4$ requires C, 60.33; H, 4.05%).

endo,*endo*-1-*tert*-Butyl-3,4,5,6,12,12-hexachloro-11-oxatetracyclo[6,2,1,1^{3,6}.0^{2,7}]dodeca-4,9-diene (potential precursor of 22, R^1 = Bu^t, R^2 = H)

This compound was made by exposure of hexachloronorbornadiene (0.4 g, 1.34 mmol) to 2-*tert*-butylfuran (0.5 g, 4.0 mmol) in a sealed Young's tube at 110 °C for 20 h. The cooled contents of the sealed tube were subjected to flash chromatography on silica gel using 7% ETOAc in pentane as eluent. The desired adduct eluted with some unreacted hexachloronorbornadiene, and was then resolved from recovered reactant using preparative TLC using CCl_4 as eluent, giving the *adduct* (51 mg, 10%) mp 111.5–112.5 °C (decomp.); δ_H 1.08 (s, $C_4H_9^t$), 3.48 (d, *J* 8.79, H-2), 3.70 (dd, *J* 4.89 and 8.79, H-7), 4.86 (dd, *J* 5.13 and 1.79, H-8), 6.31 (dd, *J* 5.86 and 1.71, H-9), 6.33 (*d*, *J* 5.86, H-10); *m/z* 385 ($M - Cl^+$, 10%, 387, 16%), 124 ($C_8H_{12}O^+$, RDA. 28%), 109 ($C_8H_{12}O - CH_3^+$, 90%), 57 (C_4H_9, 100%) [Found: 419.917 297 ($M^{\cdot+}$). Calc. for $C_{15}H_{14}Cl_6O$ 419.917 582] (Found: C, 43.26; H, 3.31. $C_{15}H_{14}Cl_6O$ requires C, 42.60; H, 3.34%). Crystal structure data: $C_{15}H_{14}Cl_6O$, *M* = 422.96; *a* = 10.621 (2), *b* = 13.730 (3), *c* = 13.885 (3) Å; *α* = 111.57 (3)°, *β* = 110.07 (3)°, *γ* = 90.53 (3)°; space group $P\bar{1}$, *V* = 1747.3 (6) Å^3; *Z* = 4; D_c = 1.608 g cm^{-3}; *F*(000) = 856; *R*(*R*′) = 0.0814 (0.0958), 7592 data. This compound proved to be thermally unstable and could not be brought into reaction with TCTD.

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