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COPE REARRANGEMENTS OF DIELS–ALDER ADDUCTS CONTAINING NORBORNENE AND NORBORNENONE SYSTEMS

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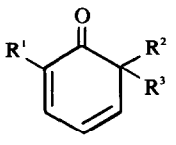
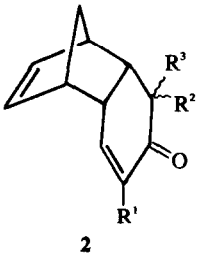
Abstract—The product formed from cyclopentadiene and the cyclo-octatetraene dimer **5a** has been shown to possess structure **6a**, probably resulting from Cope rearrangement of an initial adduct **4a**. The reaction of tetraphenylcyclopentadienone with 1 - methoxybuta - 1,3 - diene yields a mixture of the *exo*-adduct **14** and the rearranged *endo*-adduct **13**. Rearrangement of the norbornenone derivative **27** gives the Cope product **29**. Treatment of the 4,5-fused 2,3,4,5-tetrachlorocyclopent-2-enones **29**, **40** and **41** with powdered sodium hydroxide in tetrahydrofuran results in ring-cleaveage with the formation of 2,3,5-trichlorobuta-2,4-dienoic acid derivatives, **36**, **43** and **44** respectively.

In certain Diels–Alder systems in which each component is in principle capable of acting either as diene or dienophile, cycloaddition may be followed by Cope rearrangement of the initial *endo*-adduct, so that the isolated product may appear (deceptively) to have been formed from a reaction in which the true diene component acted as a dienophile (and *vice versa*). For example, the cyclohexa-2,4-dienones **1** react with cyclopentadiene to form, initially, the *endo*-adducts **2**; these norborene derivatives may be trapped by phenyl azide, but in its absence they rearrange (even at room temp.) to give products of structure **3**.[1] The driving force for this facile rearrangement presumably derives from the relief of strain in the norbornene system.

The possibility of such a rearrangement operating in the reaction of cyclopentadiene with cyclo-octatetraene at 190° led us to scrutinize the structure **4** assigned[2] to



1



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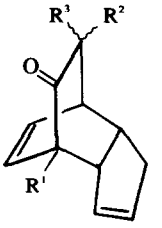
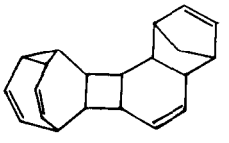


3

R^1	R^2	R^3
H	Me	Me
H	Me	Ph
H	Me	OAc
Me	Me	OAc

the product, which was shown to be an adduct of cyclopentadiene and the cyclo-octatetraene dimer **5**. The NMR spectrum† did not distinguish between structure **4** and its possibile rearrangement product **6**, but the observed lack of reactivity towards phenyl azide cast doubt on the formulation involving a norbornene system.



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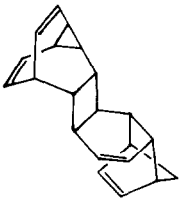
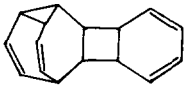


4a



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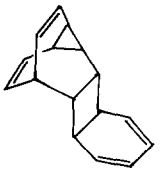
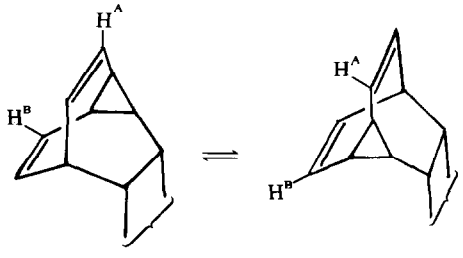


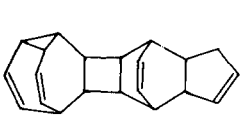
5a

†The original authors[2] assigned resonances centred at τ 4.06 (1H) and 4.30 (1H) (100 MHz spectrum; soln in $CDCl_3$) to the vinylic protons of the cyclohexene ring of structure **4**. In our experience[3,4] these double doublets (J = 9 and 9 Hz) are highly characteristic of the two homotropilidene protons H^A and H^B which retain their vinylic character throughout the fluxional process (see also Ref. 5).

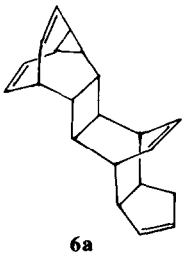


[The 3,4-homotropilidene systems of structures **4–9** are fluxional, but in each case only one of the two interconverting forms is illustrated].

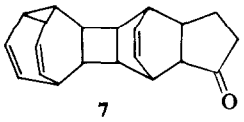
In order to confirm structure **6** an authentic sample was synthesized, as follows. Reaction of cyclopent-2-en-1-one with an excess of cyclo-octatetraene under reflux gave the adduct **7** of the cyclo-octatetraene dimer **5** (see Refs. 3 and 6). Reduction of the ketone **7** with sodium borohydride yielded the alcohol **8**; this was converted into the toluene - *p* - sulphonate **9**, which in refluxing



6



6a



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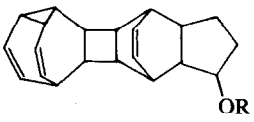
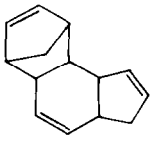


8: R = H
9: R = p-MeC$_6$H$_4$SO$_2$

collidine then gave the desired hydrocarbon **6**, identical with the product derived from cyclopentadiene and cyclo-octatetraene.

In the reaction of cyclopentadiene with the cyclo-octatetraene dimer **5**, the cyclopentadiene would not be expected to adopt an exclusive dienophilic role, and it is likely that at least some of the observed product **6** is formed by Cope rearrangement of an initial adduct **4**. Since the stereochemistry of the dimer is known to be represented by **5a**,[7] it follows that addition of cyclopentadiene must give the *endo*-adduct **4a** (only the *endo*-structure is capable of rearrangement); the final product may therefore be formulated as **6a**.

Similar considerations apply to the product obtained from cyclopentadiene and 8,9-dihydroindene at 200°, originally assigned structure **10**.[2] This is not consistent with its lack of reactivity towards phenyl azide, and we therefore suggest that this product is likely to possess the rearranged structure **11** or **12** (possibly a mixture).



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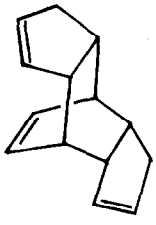
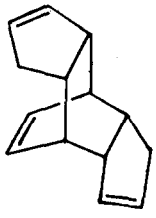


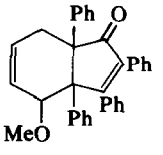
11



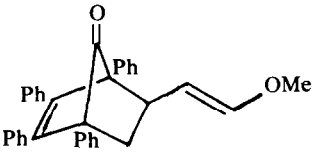
12

In its Diels–Alder reactions tetraphenylcyclopentadienone (tetracyclone) normally operates as the diene component. However, reaction with 1 - methoxybuta - 1,3 - diene at *ca.* 100° was found[8] to give an adduct formulated as **13** (together with a minor amount of a second product which was not characterised), and it has been concluded[9] that in this case tetracyclone must have behaved as a dienophile. Reexamination of this reaction has now shown that structure **13** is indeed correct for the major product, and that the minor product is the *exo*-adduct **14**. Proof of this structure was obtained as follows.

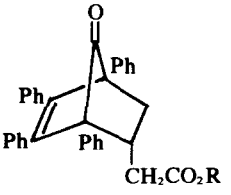
Reaction of tetracyclone with vinylacetic acid yielded a mixture of *endo*- and *exo*-adducts, **15** and **16** respectively, which were separated via their methyl esters, **17** and **18**. The stereochemistry of the *endo*-carboxylic acid **15** was proved by its conversion into a bromo-lactone, formulated as **19**, by the action of aqueous sodium hydrogen carbonate and bromine (see Ref. 10). That of the *exo*-isomer **16** was shown by reduction of the carbonyl bridge with sodium borohydride, followed by acidification, which resulted in the lactone **20**. Treatment of the minor product from tetracyclone and 1-methoxybutadiene with aqueous chromic acid-sulphuric acid, and subsequent esterification with methanolic sulphuric acid, was then found to give a methyl ester identical with the *exo*-compound **18**.



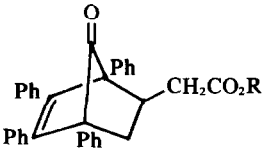
13



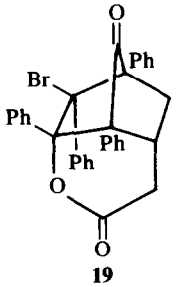
14



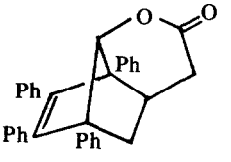
15: R = H
17: R = Me



16: R = H
18: R = Me



19



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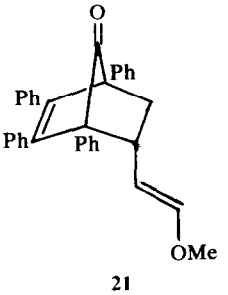
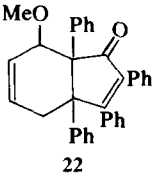


21

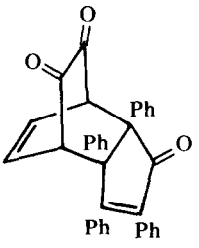


22

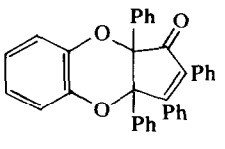
The absence of an *endo*-adduct **21** in the products obtained by reaction of tetracyclone with 1-methoxybutadiene strongly suggests that it rearranges to the observed product **13**; it should be noted that Cope rear-

rangement of **21** would result in the exclusive formation of **13** and that none of the isomer **22** would be produced.

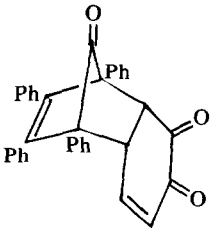
In a second alleged example of the adoption of a dienophilic role by tetracyclone, reaction with *o*-benzoquinone was found to afford the two adducts **23** and **24**.[11] However, the former could have arisen by rearrangement of an *endo*-adduct **25**, and the latter from the *spiro*-adduct **26**, and it therefore appears that the ability of tetracyclone to act as a dienophile has not yet been established.



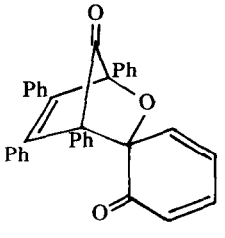
23



24



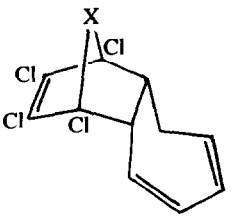
25



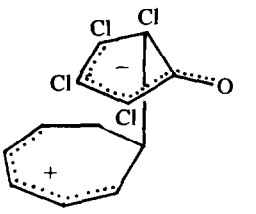
26

Although thermal rearrangements of the Cope type may proceed in a concerted fashion by a symmetry-allowed suprafacial-suprafacial [3, 3] sigmatropic shift,[12] in some cases dipolar or diradical intermediates may be involved (see, e.g. Refs. 13–16). If the rearrangement of the system **27** is contemplated, it is evident that the intervention of an intermediate such as **28** might lead to a structure other than the Cope product **29**, and it was therefore of interest to investigate this reaction. The carbonyl-bridged compound **27** was prepared by hydrolysis of the 1:1 5,5 - dibenzyloxy - 1,2,3,4 - tetrachlorocyclopentadiene - cycloheptatriene adduct **30**[17] with aqueous trifluoroacetic acid (98.5%). When **27** was heated in refluxing xylene, it rearranged smoothly to give a single product. The IR carbonyl absorption (ν_{max} 1745 cm^{-1}) was consistent with the presence of a 4,5-fused 2,3,4,5 - tetrachlorocyclopent - 2 - enone ring.[13,14] While the NMR spectrum provided support for structure **29**, the evidence was not entirely unambiguous; in particular, it did not distinguish conclusively between structures **29** and **31**. The rearranged product was therefore converted, by a procedure (see Ref. 13) involving treatment with sodium methoxide followed by acid hydrolysis of the resulting vinyl ether **32**, into the enolic 1,3-diketone **33** or **34**. In the NMR spectrum of this product, the magnetic non-equivalence of the methine (bridgehead) protons was maintained (a) in the presence of trifluoroacetic acid, when the interconversion **33** ⇌ **34** would be expected to be very fast, and (b) after treatment with NaOD in D_2O to generate the enolate anion **35**. These experiments eliminated the possibility that the original rearrangement product might have structure **31**.

In contrast with the action of sodium methoxide on compound **29**, powdered sodium hydroxide in tetrahydrofuran effected cleavage of the tetrachlorocyclopentenone ring to afford the trichlorocarboxylic acid **36** (see Ref. 18). The reaction is presumably initiated by attack of hydroxide ion on the carbonyl group of **29**, and subsequent ring-cleavage occurs with the ejection of chloride ion.



27: X = CO
30: X = $C(OCH_2Ph)_2$



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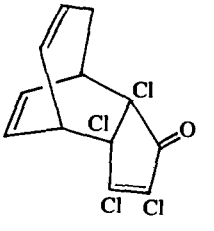
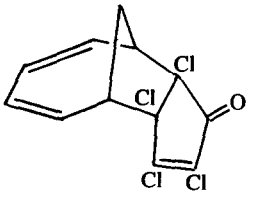
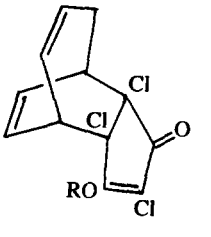


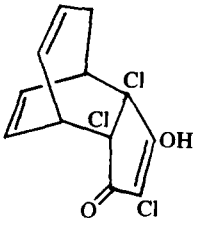
29



31



32: R = Me
33: R = H



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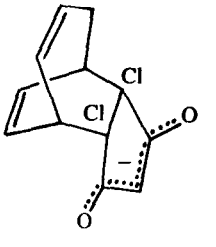

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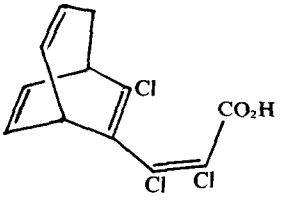

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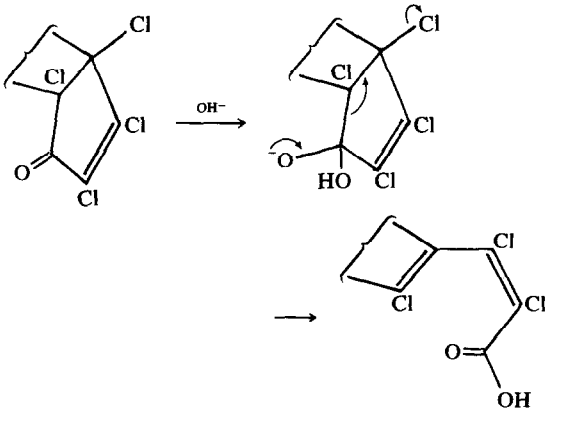
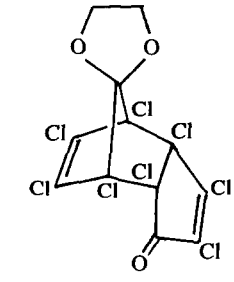
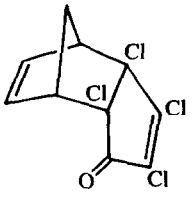


The generality of this reaction was tested in five other systems **37–41**, and it was found that while it failed for the norbornene and norbornane derivatives **37**,[19] **38**[13] and **39**,[13] the compounds **40**† and **41**,[20] containing the bicyclo[2.2.2]octene system, were cleaved in high yield to furnish the carboxylic acids **43** and **44** respectively. When each of these was subjected to thermolysis, 3,4-dichlorocoumarin **45** was produced, the expected retro-Diels–Alder reaction being accompanied by lactonization.



37



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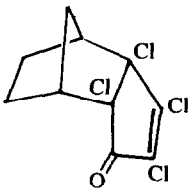
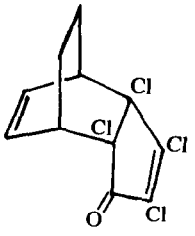


39



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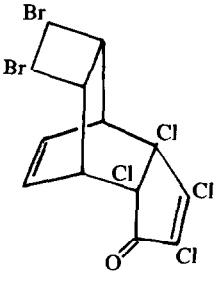

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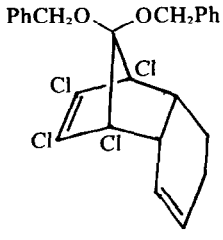
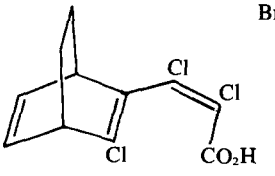
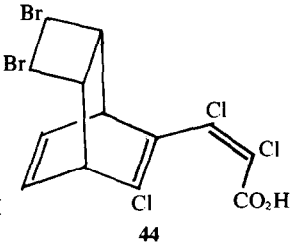


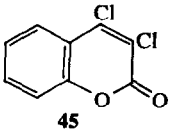
42



43



44



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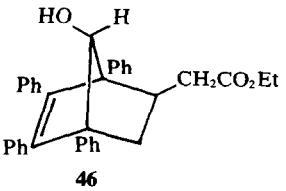

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EXPERIMENTAL

Unless stated otherwise, NMR spectra were measured at 100 MHz for solns in $CDCl_3$; light petroleum means the fraction of b.p. 40–60°. IR spectra were determined for Nujol mulls.

The adduct **7**. A mixture of cyclo-octatetraene (4.2 g) and cyclopent - 2 - en - 1 - one (0.9 g) was heated under reflux (N_2 atmosphere) for 4 h. The volatile material was then removed under reduced pressure, and the residue was treated with light petroleum at 0° to give the adduct **7** (0.16 g, 5%), m.p. 155–156° (from light petroleum) (Found: C, 87.0; H, 7.7. $C_{21}H_{22}O$ requires: C, 86.9; H, 7.6%); IR ν_{max} 1725, 1638 cm^{-1}; NMR τ 3.6–3.9 (2H), 4.10 (1H, dd, J 9 and 9 Hz), 4.34 (1H, dd, J 9 and 9 Hz), 6.0–6.5 (4H), 6.95–7.2 (1H), 7.2–8.9 (13H).

The alcohol **8**. A mixture of the ketone **7** (70 mg) and sodium borohydride (20 mg) in ethanol (10 ml) was stirred (N_2 atmos) at room temp. for 3 h. The reaction mixture was acidified with hydrochloric acid and the product was collected in light petroleum. Removal of the solvent afforded the alcohol **8** (56 mg, 80%), m.p. 135–136° (from light petroleum) (Found: C, 85.9; H, 8.2. $C_{21}H_{24}O$ requires: C, 86.3; H, 8.3%); IR ν_{max} 3320 br, 1640 cm^{-1}; NMR τ 3.4–3.8 (2H), 4.08 (1H, dd, J 9 and 9 Hz), 4.32 (1H, dd, J 9 and 9 Hz), 5.7–6.5 (5H), 7.2–7.5 (2H), 7.6–9.2 (13H).

The hydrocarbon **6a**. A mixture of the alcohol **8** (105 mg) and toluene - *p* - sulphonyl chloride (138 mg) in dry pyridine (1 ml) was kept at 0° for 72 h, and then poured onto crushed ice. The product was collected in ether, removal of which gave the crystalline toluene - *p* - sulphonate (145 mg). This was heated in refluxing collidine (4 ml) (under N_2) for 16 h. The resulting soln was poured into water, and the product was extracted with light petroleum. The petroleum extract was washed successively with dil. hydrochloric acid and water, dried ($MgSO_4$), and evaporated, and the residue was crystallized from light petroleum to yield the hydrocarbon **6a** (55 mg, 62%), identical with a sample of the adduct from cyclo-octatetraene and cyclopentadiene (prepared as described by Baxter and Garratt[2]).

The adducts **13** *and* **14**. The reaction of tetracyclone with 1 - methoxybuta - 1,3 - diene was carried out as described by von Euler *et al.*,[8] except that heating was stopped as soon as decolorization of the tetracyclone was essentially complete (*ca.* 25 min).

Adduct **13** (53%), m.p. 188° (decomp) (lit.[8] 188°); IR ν_{max} 1690 cm^{-1}; NMR τ 2.6–3.35 (20H), 3.7–3.8 (2H), 5.4–5.5 (1H), 6.99 (3H, S), 7.0–7.15 (2H).

Adduct **14** (34%), M.P. 157–158° (Found: C, 87.3; H, 6.1. $C_{34}H_{28}O_2$ requires: C, 87.1; H, 6.0%); IR ν_{max} 1770, 1649 cm^{-1}; NMR τ 2.6–3.55 (20H), 3.72 (1H, d, J 12.5 Hz), 5.67 (1H, dd, J 12.5 and 10 Hz), 6.81 (3H, s), 6.92 (1H, dd, J 10 and 4 Hz), 7.10 (1H, d, J 11.5 Hz), 7.49 (1H, dd, J 11.5 and 4 Hz).

Treatment of the adduct **14** *with chromic acid.* Chromium trioxide in dil. H_2SO_4 (Jones reagent[21]) was added dropwise to a stirred soln of the adduct **14** (220 mg) in acetone (10 ml) until a yellow-brown colour persisted. Stirring was continued for 45 min, and then the mixture was poured into water. The product was collected in CH_2Cl_2, and after removal of the solvent the residue was esterified with methanolic sulphuric acid in the usual way. Preparative TLC of the resulting oil (200 mg) on silica [1:9 ethyl acetate-light petroleum (b.p. 60–80°)] gave a fraction (22 mg) of m.p. 208–210° (decomp) (from ether-light petroleum), which was identical with the methyl ester **18** of the tetracyclone-vinylacetic acid *exo*-adduct **16** (see below).

The adducts **15** *and* **16**. A mixture of tetracyclone (0.59 g) and vinylacetic acid (1.75 ml) was heated under reflux for 40 min. The excess of vinylacetic acid was removed under reduced pressure, the residue was taken up in ether, and the soln was filtered to remove polymeric material. The filtrate was evaporated, and the residue esterified with methanolic sulphuric acid in the usual way. Some *exo*-ester **18** (180 mg) separated from the reaction mixture; m.p. 209–210° (decomp) (from CH_2Cl_2-light petroleum) [Found: C, 84.5; H, 5.9%; M (mass spectrum), 484.

†Prepared from the adduct **42** of 5,5 - dibenzyloxy - 1,2,3,4 - tetrachlorocyclopentadiene and cyclohexa - 1,3 - diene, by hydrolysis of the acetal grouping and subsequent Cope rearrangement.

$C_{34}H_{28}O_3$ requires: C, 84.3; H, 5.8%; M, 484]; IR ν_{max} 1776, 1730 cm^{-1}; NMR τ 2.45–3.5 (20H), 6.34 (3H, S), 6.75–7.25 (2H), 7.3–7.65 (2H), 7.75–8.1 (1H).

The methanol-soluble fraction was poured into water, and the product was collected in ether. Evaporation of the solvent gave a semi-solid which was subjected to preparative TLC on silica [1:19 ethyl acetate-light petroleum (b.p. 60–80°)]. Extraction of the faster-moving band with CH_2Cl_2 afforded a further quantity of the *exo*-ester **18** (total yield 343 mg, 46%), and similar extraction of the second band gave the *endo*-ester **17** (194 mg, 26%), m.p. 187–188° (decomp) (from CH_2Cl_2-light petroleum) (Found: C, 83.7; H, 5.9%; M (mass spectrum), 484); IR ν_{max} 1782, 1738 cm^{-1}; NMR τ 2.4–3.4 (20H), 6.21 (3H, S), 6.2–6.5 (1H), 6.71 (1H, dd, J 15 and 3 Hz), 7.07 (1H, dd, J 12 and 9 Hz), 7.48 (1 H, dd, J 15 and 12 Hz), 8.02 (1H, dd, J 12 and 5 Hz).

The two stereoisomeric methyl esters **17** and **18** were then hydrolysed with refluxing aqueous trifluoroacetic acid (60–65%) to regenerate, respectively, the *endo*- and *exo*-adducts **15** and **16**.

Adduct **15** (*endo*): m.p. 231–232° (decomp) (from CH_2Cl_2-light petroleum) (Found: C, 83.5; H, 5.7. $C_{33}H_{26}O_3$ requires: C, 84.2; H, 5.6%); IR ν_{max} 1785, 1716 cm^{-1}; NMR τ (CO_2H proton omitted) 2.4–3.5 (20H), 6.1–6.5 (1H), 6.64 (1H, dd, J 16 and 3 Hz), 7.02 (1H, dd, J 12 and 9 Hz), 7.42 (1H, dd, J 16 and 12 Hz), 7.95 (1H, J 12 and 5 Hz).

Adduct **16** (*exo*): m.p. 228–229° (decomp) (from CH_2Cl_2–light petroleum) (Found: C, 84.2; H, 5.6); IR ν_{max} 1774, 1695 cm^{-1}; NMR τ (CO_2H proton omitted) 2.4–3.5 (20H), 6.8–7.6 (4H), 7.85 (1H, dd, J 17 and 12 Hz).

The bromo-lactone **19**. The *endo*-adduct **15** (44 mg) was taken up in hot ethanol (10 ml), and hot saturated sodium hydrogen carbonate soln was added slowly until the total vol was *ca.* 200 ml. The soln was cooled, and an excess of bromine (*ca.* 1 g) in water was added. After 15 min the resulting precipitate was collected by filtration, washed with water, dried, and recrystallized from ether-light petroleum to give the bromo-lactone **19** (13 mg, 26%), m.p. 164–166° [Found: C, 72.3, H, 4.7; Br, 15.2%; M (mass spectrum), 548 (^{79}Br). $C_{33}H_{25}BrO_3$ requires: C, 72.1; H, 4.6; Br, 14.5%; M, 548 (^{79}Br)]; IR ν_{max} 1769 cm^{-1}.

The lactone **20**. A mixture of the *exo*-adduct **16** (100 mg), sodium borohydride (400 mg), sodium hydroxide (200 mg) and ethanol (35 ml) was stirred at room temp. for 3 h. Conc. HCl (10 ml) was then added, and stirring was continued overnight. The resulting soln was poured into water and the product was collected in ether. After removal of the solvent, preparative TLC on silica (1:1 CH_2Cl_2-light petroleum) afforded the lactone **20** (30 mg, 30%), m.p. 182–184° (from ether-light petroleum) [Found: C, 87.0; H, 5.85%; M (mass spectrum), 454. $C_{33}H_{26}O_2$ requires: C, 87.2; H, 5.8%; M, 454] IR ν_{max} 1749 cm^{-1}; MNR τ 2.5–3.55 (20H), 4.76 (1H, s), 7.0–7.7 (5H).

Extraction of a slower-moving band on the TLC plate yielded a product which was apparently a hydroxy–ethyl ester† (29 mg, 27%), m.p. 184–185° (from CH_2Cl_2-light petroleum) (Found: C, 83.85; H, 6.5. $C_{35}H_{32}O_3$ requires C, 84.0; H, 6.45%): IR ν_{max} 3400 br, 1712 cm^{-1}; NMR τ 2.6–3.6 (20H), 5.38 (1H, d, J 2 Hz), 5.87 (2H, q, J 7 Hz), 7.0–7.7 (5H), 8.20 (1H, d, J 2 Hz), 8.76 (3H, t, J 7 Hz).

Hyrolysisis of the adduct **30** *and rearrangement of the carbonyl-bridged product* **27**. A mixture of the adduct **30**[17] (15 g), trifluoracetic adid (35 ml), and water (0.5 ml) was heated on the steam-bath, with continuous shaking, for 12 min. The resulting dark red soln was poured into ice-water, and the products were collected in CH_2Cl_2. The solvent was removed under reduced pressure to give an oil, the IR spectrum of which indicated the presence of benzyl trifluoroacetate (ν_{max} 1785 cm^{-1}), the carbonyl-bridged compound **27** (ν_{max} 1825 cm^{-1}), and a little of the rearranged product **29** (ν_{max} 1745 cm^{-1}). Most of the benzyl trifluoroacetate was removed at *ca.* 40°/0.02 mm, and the residue (which still contained very little of the rearranged product **29**, as estimated from the IR spectrum) was heated in refluxing xylene for 45 min. After removal of the solvent, the product was chromatographed on silica. Elution with 1:4 benzene-light petroleum then gave the rearranged ketone **29** (7.4 g, 85%), m.p. 125–126° [from light petroleum (b.p. 60–80°)] (Found: C, 46.3; H, 2.6; Cl, 45.45. $C_{12}H_8Cl_4O$ requires: C, 46.5; H, 2.6; Cl, 45.75%); IR ν_{max} 1745, 1605 cm^{-1}; NMR τ 3.7–4.5 (4H), 6.58 (1H, ddd, J 7, 6 and 1 Hz), 6.8–7.15 (2H), 7.5–7.9 (1 H).

The vinyl ether **32**. Sodium methoxide (95 mg) in dry methanol (2.5 ml) was added to a soln of the ketone **29** (500 mg) in dry ether (15 ml), and the mixture was stirred at room temp. for 19 h. The product, isolated by the addition of water and separation of the ether-layer, was chromatographed on silica. Elution with benzene then gave the vinyl ether **32** (350 mg, 71%), m.p. 159–160° (from $CHCl_3$–MeOH) (Found: C, 50.9; H, 3.5: Cl, 35.0. $C_{13}H_{11}Cl_3O_2$ requires: C, 51.1; H, 3.6; Cl, 34.8%); IR ν_{max} 1722, 1614 cm^{-1}; NMR τ 3.7–4.55 (4H), 5.60 (3H, s), 6.5–6.75 (1H), 6.85–7.2 (2H), 7.6–7.95 (1H).

The enolic 1,3-*diketone* **33** *or* **34**. The vinyl ether **32** (800 mg) in glacial acetic acid (4.5 ml) was heated on the steam-bath with 40% hydrogen bromide in glacial acetic acid (0.7 ml) for 4 h. The soln was evaporated under reduced pressure, and the oily residue was treated with methanol to afford the enolic 1,3-diketone **33** or **34** (610 mg, 80%), m.p. *ca.* 216° (decomp) [from CCl_4-light petroleum (b.p. 60–80°)] (Found: C, 49.0; H, 3.1; Cl, 36.5. $C_{12}H_9Cl_3O_2$ requires: C, 49.4; H, 3.1; Cl, 36.5%); IR ν_{max} 2600, 2450, 1690, 1560 cm^{-1}; NMR τ 1.68 (1H, s; identified as O–H by D-exchange), 3.7–4.55 (4H), 6.62 (1H, dd, J 7.5 and 7.5 Hz), 6.8–7.25 (2H), 7.55–7.95 (1H).

Treatment of the ketone **29** *with sodium hydroxide in tetrahydrofuran.* Freshly powdered sodium hydroxide (2.5 g) was added, with cooling, to a soln of the ketone **29** (2.4 g) in tetrahydrofuran (15 ml), and the mixture was stirred overnight at room temp. The solvent was removed under reduced pressure, and the residue was treated successively with water and hydrochloric acid. Collection of the product in CH_2Cl_2 then gave the carboxylic acid **36** (1.4 g, 62%), m.p. 158.5–159° (decomp) (from benzene) (Found: C, 49.45; H, 3.2; Cl, 36.2. $C_{12}H_9Cl_3O_2$ requires: C, 49.4; H, 3.1; Cl, 36.5%); IR ν_{max} 1700, 1572 cm^{-1}; UV ($CHCl_3$) λ_{max} 251 nm (ϵ 6030); NMR τ (0.71) (1H, br s), 3.25–3.5 (1H), 3.7–4.05 (2H), 4.65–4.95 (1H), 6.6–7.0 (2H), 7.35–8.1 (2H).

The adduct **42**. A mixture of 5,5 - dibenzyloxy - 1,2,3,4 - tetrachlorocyclopentadiene[14] (4.6 g) and cyclohexa - 1,3 - diene (1.0 g) in xylene (10 ml) was heated under reflux for 24 h (N_2 atmos). After removal of the solvent, the residue was chromatographed on silica. Elution with ethyl acetate-light petroleum (1:19) gave the adduct **42** (5.0 g, 91%), m.p. 93–94° [from light petroleum (b.p. 60–80°)] (Found: C, 60.5; H, 4.5; Cl, 28.5. $C_{25}H_{22}Cl_4O_2$ requires: C, 60.5; H, 4.5; Cl, 28.6%); IR ν_{max} 1605, 1599 cm^{-1}; NMR τ 2.4–2.95 (10H), 3.8–4.35 (2H), 4.98 (2H, s), 5.02 (2H, s), 6.7–7.15 (2H), 7.8–8.9 (4H).

Hydrolysis of the adduct **42** *and rearrangement of the carbonyl-bridged product.* Treatment of the adduct **42** (4.0 g) as described above for the adduct **30** gave the rearranged ketone **40** (1.87 g, 81%), m.p. 122–123° [from light petroleum (b.p. 60–80°)] (Found: C, 43.9; H, 2.6; Cl, 47.9. $C_{11}H_8Cl_4O$ requires: C, 44.3; H, 2.7; Cl, 47.6%); IR ν_{max} 1738, 1598 cm^{-1}; NMR τ 3.55–4.15 (2H), 6.5–7.1 (2H), 7.4–8.0 (2H), 8.3–8.9(2H).

The carboxylic acid **43**. Treatment of the ketone **40** (1.1 g) as described above for the ketone **29** led to the carboxylic acid **43** (0.91 g, 88%), m.p. 146–147° (from CH_2Cl-light petroleum) (Found: C, 47.6; H, 3.3; Cl, 38.5. $C_{11}H_9Cl_3O_2$ requires: C, 47.3; H, 3.25; Cl, 38.05%); IR ν_{max} 1700, 1569 cm^{-1}; UV ($CHCl_3$) λ_{max} 253 nm (ϵ 4730); NMR τ 0.13 (1H, br s), 3.45–3.8 (2H), 6.15–6.45 (2H), 8.1–8.8 (4H).

The carboxylic acid **44**. Similar treatment of the ketone **41**[20] (2.0 g) gave the carboxylic acid **44** (1.2 g, 62%), m.p. 181–182° (decomp.) (from CH_2Cl_2-light petroleum) (Found: C, 33.9; H, 1.9; Br, 34.3; Cl, 22.7. $C_{13}H_8Br_2Cl_3O_2$ requires: C, 33.7; H, 2.0; Br, 34.5; Cl, 23.0%); ν_{max} UV (EtOH) λ_{max} 256 nm (ϵ 3740); NMR τ [$(CD_3)_2CO$] (CO_2H proton omitted) 3.05–3.25 (1H), 3.3–3.5 (1H), 5.1–5.3 (1H), 5.8–7.2 (3 H), 6.35–6.65 (1H), 6.7–7.0 (1H).

Thermolysis of the carboxylic acids **43** *and* **44**. (i) The carboxylic acid **43** (200 mg) was kept at 150–155° (oil-bath) under N_2 for 1 h, and the products were separated by preparative TLC on silica (3:2 CH_2Cl_2-light petroleum). Extraction of the faster-moving band with CH_2Cl_2 yielded 3,4-dichlorocoumarin (61 mg,

†Presumably possessing structure **46**.

39%), m.p. 107–108° (lit[22] 106.5–107.5°) (from light petroleum) [Found: M (mass spectrum), 214 (^{35}Cl). Calc. for $C_9H_4Cl_2O_2$: M, 214 (^{35}Cl)]; IR ν_{max} 1736, 1597 cm^{-1}; NMR τ 2.05–2.7 (4H).

(ii) Similar treatment of the carboxylic acid **44** (250 mg) at 180–190° also gave 3,4-dichlorocoumarin (79 mg, 68%).

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REFERENCES

[1]D. M. Bratby and G. I. Fray, *J. Chem. Soc.* (C), 970 (1971).
[2]C. S. Baxter and P. J. Garratt, *Tetrahedron* **27**, 3285 (1971).
[3]R. R. Deshpande, A. Gilbert, G. I. Fray and R. G. Saxton, *Tetrahedron Letters* 2163 (1971).
[4]R. G. Saxton, Ph.D. Thesis, Bristol (1973).
[5]R. Merényi, J. F. M. Oth and G. Schröder, *Chem. Ber.* **97**, 3150 (1964).
[6]J. Daub and V. Trautz, *Tetrahedron Letters* 3265 (1970).
[7]G. Schröder and J. F. M. Oth, *Angew. Chem. Internat. Edn.* **6**, 414 (1967).
[8]H. von Euler, H. Hasselquist, G. Haushoff and A. Glaser, *Chem. Ber.* **86**, 969 (1953).
[9]M. A. Ogliaruso, M. G. Romanelli and E. J. Becker, *Chem. Rev.* **65**, 261 (1965).
[10]K. N. Houk and L. J. Luskus, *J. Am. Chem. Soc.* **93**, 4606 (1971).
[11]W. M. Horspool, J. M. Tedder and Z. U. Din, *J. Chem. Soc.* (C), 1692 (1969).
[12]R. B. Woodward and R. Hoffmann, *Angew. Chem. Internat. Edn.* **8**, 781 (1969).
[13]P. Yates and P. Eaton, *Tetrahedron* **12**, 13 (1961).
[14]L. S. Besford, R. C. Cookson and J. Cooper, *J. Chem. Soc.* (C), 1385 (1967).
[15]M. J. S. Dewar and L. E. Wade, *J. Am. Chem. Soc.* **95**, 290 (1973).
[16]D. C. Wigfield, S. Feiner, G. Malbacho and K. Taymaz, *Tetrahedron* **30**, 2949 (1974).
[17]I. A. Akhtar, D. M. Bratby and G. I. Fray, *J. Chem. Soc.* (C), 2716 (1969).
[18]A. Eschenmoser and A. Frey, *Helv. Chim. Acta* **35**, 1660 (1952).
[19]K. V. Scherer, R. S. Lunt and G. A. Ungefug, *Tetrahedron Letters* 1199 (1965).
[20]G. I. Fray and D. P. S. Smith, *J. Chem. Soc.* (C), 2710 (1969).
[21]A. Bowers, T. G. Halsall, E. R. H. Jones and A. J. Lemin, *J. Chem. Soc.* 2548 (1953).
[22]M. S. Newman and S. Schiff, *J. Am. Chem. Soc.* **81**, 2266 (1959).