On the Preparation and Chemical Reactivity of 2-Benzopyrylium-4-olate

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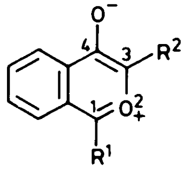
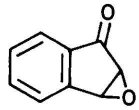
An efficient route to 1-acetoxy-1*H*-2-benzopyran-4(3*H*)-one is described. This acetate readily liberates the title compound 2-benzopyrylium-4-olate (**3**) under thermal or base-catalysed conditions. The 1,3-dipole (**3**) undergoes cycloadditions with a wide range of dipolarophiles and the regioselectivity of these processes follows frontier molecular orbital predictions.

Substituted derivatives of 2-benzopyrylium-4-olate such as the 1,3-diphenyl compound (**1**)[1] have been described previously and other substituted derivatives have been obtained as reactive intermediates, for example the methoxy compound (**2**).[2]

Nilsen and Undheim[5] claimed to have generated the parent system (**3**) by acid treatment of the reduced dichlorodicyano-1,4-benzoquinone adduct (DDQH) (**10**) or tetrachloro-1,2-benzoquinone adduct (TBQH) (**11**), the intermediates dimerising to the products (**12**). However, the fact that the precursors (**10**) and (**11**) gave different ratios of the dimers (**12**) under similar reaction conditions and the failure to trap the supposed zwitterion (**3**) with added dipolarophiles argue against it as an intermediate.



(**1**) $R^1 = R^2 = Ph$
(**2**) $R^1 = OMe, R^2 = H$
(**3**) $R^1 = R^2 = H$



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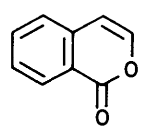
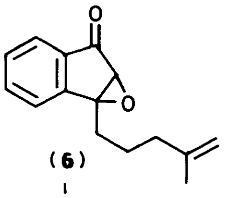
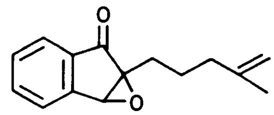


(**5**)



(**6**)



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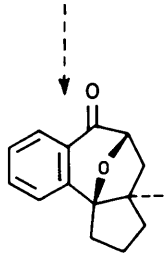

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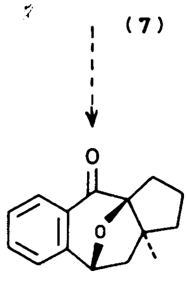
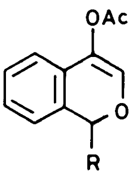
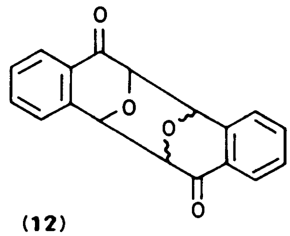


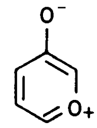
(**9**)



(**10**) R = DDQH
(**11**) R = TBQH



(**12**)



(**13**)

Attempts to generate system (**3**) by photolysis of 2,3-epoxyindanone (**4**), however, gave instead the isocoumarin (**5**) as the major product.[3] Feldman has recently reported[4] that irradiation of the mono-substituted epoxyindanones (**6**) and (**7**) gave the tricyclic compounds (**8**) and (**9**) respectively, presumably *via* an intramolecular cycloaddition to the transient 2-benzopyrylium 4-olate zwitterion.

Recently we have described a new route to the parent 2-benzopyrylium-4-olate from the precursor acetate (**18**).[6] Since it was expected that the ylide (**3**) would not be susceptible to the intermolecular dimerisation characteristic of the non-fused heterocycle, pyrylium-3-olate (**13**),[7] a more complete study of its

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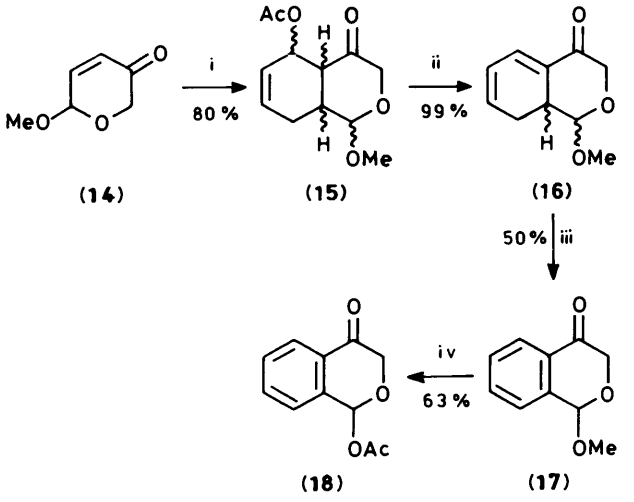
chemical behaviour towards a wider range of dipolarophile trapping agents is possible.

The synthesis of the precursor acetate (**18**), summarised in Scheme 1, commences with the known pyran-3(6*H*)-one (**14**).[8]

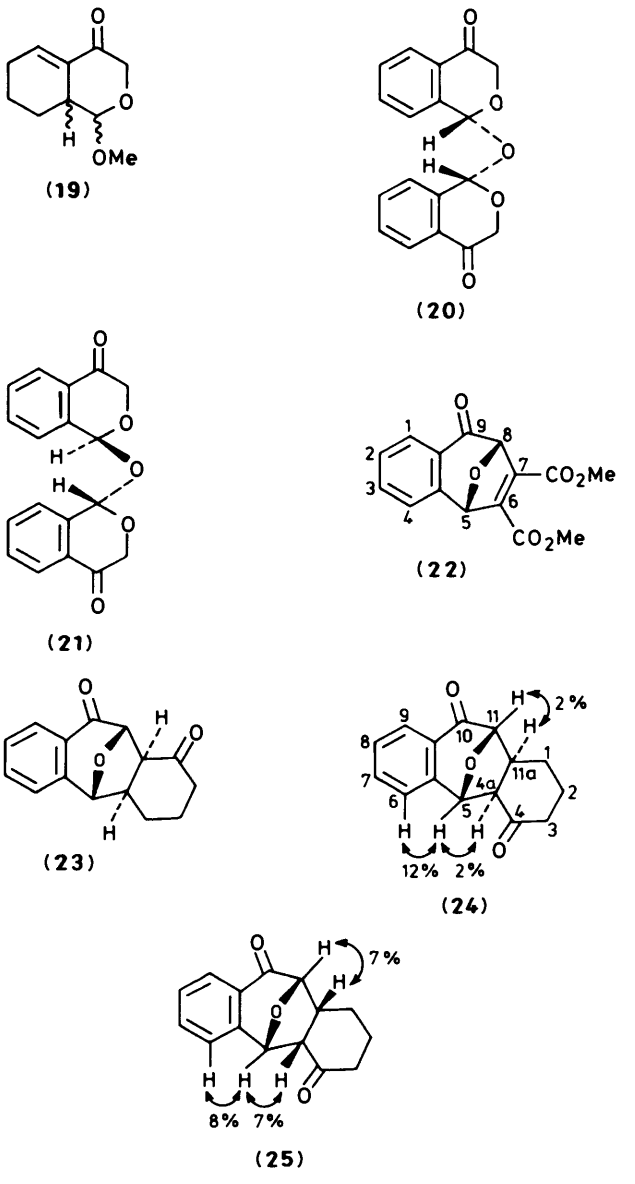


Scheme 1. *Reagents and conditions:* i, 1-acetoxybutadiene, 14 days, room temp.; ii, NEt_3; iii, Pd–C toluene, 110 °C, 2.5 h; iv, Ac_2O, AcOH, reflux, 1 h

Diels–Alder additions to such systems have been reported previously[9] and a similar approach to benzopyranosides described.[10] The 1-acetoxybutadiene adduct (**15**) was unstable and, with mild base, rapidly lost acetic acid to generate the diene (**16**), obtained as a mixture of anomers. Dehydrogenation of the diene was effected by 5% palladium-on-charcoal in toluene at reflux, to give the aromatic compound (**17**) (50%) together with smaller amounts of the tetrahydro compound (**19**) (34%). The relative amounts of oxidised and reduced products were not substantially altered by use of higher temperatures (180 °C in refluxing *o*-dichlorobenzene), a large excess of catalyst, or the use of cyclohexene, maleic acid, or air as hydrogen acceptors. The two derivatives could be easily separated by column chromatography. Attempted hydrolysis of the acetal (**17**), using dilute sulphuric acid, was complicated by co-formation of the dimeric acetals (**20**) and (**21**) and, therefore, a more direct method was employed for exchange of the methoxy group using refluxing acetic acid and acetic anhydride.

2-Benzopyrylium-4-olate (**3**) may be generated in solution from the acetate (**18**) by base-catalysed or thermal elimination of acetic acid.[6] Thus treatment of the acetate in dichloromethane with triethylamine as base and in the presence of dimethyl acetylenedicarboxylate as dipolarophile gave the adduct (**22**) in 88% yield, confirming the expectation that the zwitterion (**3**) can act as a carbonyl ylide across the 1,3-positions. Under thermal conditions, namely in acetonitrile in a sealed tube at 160 °C, this particular cycloaddition only proceeded in low yield, producing some of the dimers (**20**) and (**21**) as well as the adduct (**22**). Control experiments showed that the starting acetate (**18**) is in equilibrium with the ylide (**3**). Thus, in the absence of a dipolarophile and after treatment with triethylamine in dichloromethane for 24 h most of the acetate could be recovered on work-up; a slow degradation occurred after longer periods, presumably owing to self-condensations. Under the thermal conditions some formation of the dimers (**20**) and (**21**) occurred. As expected, no formation of dimers was observed of the type produced by pyrylium-3-olate[7] or as reported by Nilsen and Undheim.[5]

A systematic study of the reactivity of 2-benzopyrylium-4-olate with representative dipolarophiles was undertaken. Cyclo-

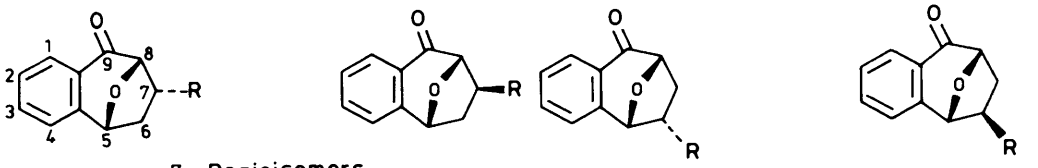


hexenone, an electron-deficient dipolarophile that reportedly fails to react with pyrylium-3-olate,[7] added in high yield to the benzo analogue (**3**) to give a mixture of three adducts, the *exo*-adduct (**23**), and the isomeric *exo*- and *endo*-adducts, (**24**) and (**25**), isolated in the ratio 2:5:3 respectively (see Table 1). The major regioisomer is that expected from frontier orbital considerations, (*see below*). The missing isomer is that which would arise from the transition state in which the carbonyl oxygen atoms of cyclohexenone and the olate would be adjacent; presumably bad dipole–dipole interactions occur in this process. Structural assignments were made mainly on the basis of coupling patterns derived from 400 MHz ^1H n.m.r. studies, supported by nuclear Overhauser enhancements. Thus, in the *exo*-isomer (**24**) the enhancement between protons at positions 4a and 5 is only 2% whereas in the *endo*-isomer (**25**) this is 7%, as expected from the closer approach of these protons in the latter isomer. Similar observations were utilised in the structural assignments made in the products from the following experiments. Acrolein, under thermal conditions, also gave a mixture of three adducts, (**26**)—(**28**), with 2-benzopyrylium-4-olate, comparable to those observed for cyclohexanone although, under base-catalysed conditions, the *exo*-adduct (**28**) was predominant.

Table 1. Summary of isomer composition of cycloadducts of 2-benzopyrylium-4-olate

Substrate	Conditions[a]	Yield (%)[b]	Adduct type, ratio (formula)[c]			
			endo-7	*exo*-7	*endo*-6	*exo*-6
Cyclohexenone	Base	77	—	21 (**23**)	51 (**25**)	27 (**24**)
	Thermal	77	—	21	46	33
Acrolein	Base	45	—	—	—	100
	Thermal	36	—	25 (**26**)	25 (**27**)	50 (**28**)
Styrene	Base	95	38 (**29**)	3 (**30**)	49 (**31**)	40 (**32**)
	Base	74	90 (**33**)	10 (**34**)	—	—
Ethyl vinyl ether	Thermal	73	57	19	17 (**35**)	7 (**36**)
Vinyl acetate	Base	99	51 (**37**)	3 (**38**)	36 (**39**)	9 (**30**)
	Thermal	93	41	5	41	13
			exo		*endo*	
Cyclopentene	Base	63	11 (**42**)		89 (**44**)	
Cyclohexene	Base	10	—		100 (**45**)	
	Thermal	93	14 (**43**)		86	
Norborna-2,5-diene	Base	75	100 (**41**)		—	

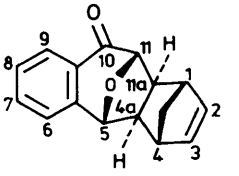
[a] Base: triethylamine in dichloromethane at room temperature thermal: heating at 160 °C in acetonitrile in a sealed tube. [b] Isolated yields; a dash indicates that the isomer was not detected: the limits of detection varied widely. [c] Series 7 indicates those regioisomers in which the dipolarophile substituent is adjacent to position 7 of the benzotropone nucleus, likewise series 6 indicates those adjacent to position 6.



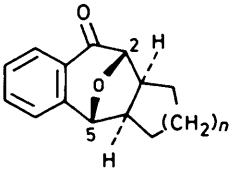
7 - Regioisomers

6 - Regioisomers

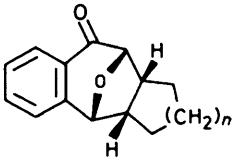
R = CHO	-	(**26**)	(**27**)	(**28**)
R = Ph	(**29**)	(**30**)	(**31**)	(**32**)
R = OEt	(**33**)	(**34**)	(**35**)	(**36**)
R = OAc	(**37**)	(**38**)	(**39**)	(**40**)



(**41**)



(**42**) *n* = 1
(**43**) *n* = 2



(**44**) *n* = 1
(**45**) *n* = 2

Styrene is a conjugated dipolarophile and although it reacts with pyrylium-3-olate to give a single adduct, a mixture of all four adducts was produced with the benzo analogue (see Table 1). The two *endo*-isomers (**29**) and (**31**) were recognised by the phenyl shielding of 1-H in the n.m.r. spectrum of the former and of 4-H in the latter. For the *exo*-isomers assignments could only be made by using [$^2H_6$]benzene as solvent.

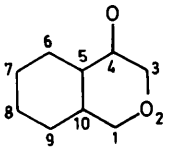
The electron-rich dipolarophile, ethyl vinyl ether added in good yield to the dipole (**3**). Under base-catalysed conditions a 9:1 mixture of the *endo*:*exo* isomers (**33**) and (**34**) formed (74% yield). Using thermal generation of the ylide (**3**), the selectivity of the addition was not so good, a 57:19:17:7 ratio of the adducts (**33**) to (**36**) were formed (80% yield). In both cases, however, the major regioisomer was that predicted by frontier molecular orbital theory and is the reverse of that obtained with the pyrylium-3-olate zwitterion. Vinyl acetate also reacts with 2-benzopyrylium-4-olate under both thermal and base-catalysed reaction conditions giving approximately equal mixtures of the two regioisomers; *endo*-addition is preferred to *exo*-addition (Table 1). Control experiments showed that the cycloadditions are not reversible under the reaction conditions.

Finally, attention was directed to the reaction of this title ylide with unactivated olefins. It was found that norborna-2,5-diene, reacts as an efficient dipolarophile [11] giving, in 75% yield, a single adduct, characterised by highfield ^1H n.m.r. spectroscopy as the *exo*, *exo*-isomer (**41**). With cyclopentene and cyclohexene yields of adducts were dependent on the reaction conditions employed. With cyclopentene, using triethylamine on the acetate (**18**) at room temperature, a 55% yield was obtained of the *exo*- and *endo*-adducts (**42**) and (**44**), ratio 1:8 respectively. For the *endo*-adduct (**44**), the bridgehead protons at positions 11 and 5 appear as doublets (J 9 and 8 Hz), whilst in the *exo*-adduct (**42**) this coupling is small and the signals appear as singlets. Under similar conditions cyclohexene gave only a 10% yield of cycloadducts after 2 days. However, using thermal conditions (160 °C, 16 h), a 93% yield of the *exo*- and *endo*-isomers (**43**) and (**45**) formed, ratio 1:6 respectively.

The regioselectivity observed in the above cycloaddition reactions was examined in the light of frontier molecular orbital (FMO) theory. Katritzky's studies on pyridinium-3-olate [12] and

Table 2. HOMO and LUMO energies and coefficients for 2-benzopyrylium-4-olate and pyrylium-3-olate

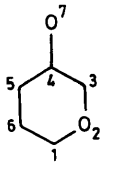
a 2-Benzopyrylium-4-olate:



HOMO energy −0.453 LUMO energy 0.336

Atom no.	1	2	3	4	5	6	7	8	9	10	11
HOMO coeff.	0.35	0.10	−0.56	−0.29	−0.09	0.23	0.19	−0.14	−0.26	0.03	0.54
LUMO coeff.	0.61	−0.33	0.34	0.19	−0.28	−0.16	0.34	0.05	−0.35	0.07	−0.14

b Pyrylium-3-olate



HOMO energy −0.566 LUMO energy 0.391

Atom no.	1	2	3	4	5	6	7
HOMO coeff.	0.37	0.06	−0.49	−0.29	−0.31	0.11	0.66
LUMO coeff.	0.49	−0.36	0.56	0.56	−0.54	0.12	−0.06

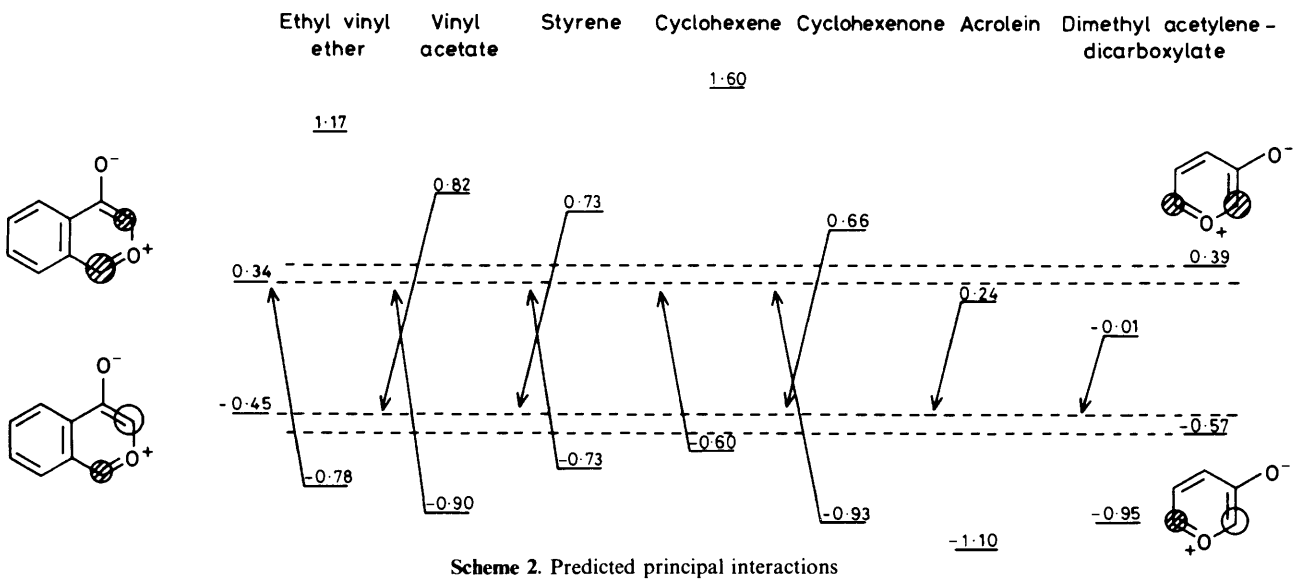
Table 3. HOMO and LUMO energies and coefficients for dipolarophiles

	HOMO			LUMO		
Dipolarophile	Energy	Coeff. 1	Coeff. 2	Energy	Coeff. 1	Coeff. 2
Cyclohexenone	−0.927	0.48	0.63	0.664	−0.63	0.09
Acrolein	−1.059	0.55	0.53	0.243	−0.58	0.13
Styrene	−0.734	0.56	0.37	0.734	0.56	−0.37
Ethyl vinyl ether	−0.776	0.69	0.49	1.172	0.67	−0.71
Vinyl acetate	−0.901	0.67	0.55	0.815	0.32	−0.24
Cyclohexene	−0.600	0.71	0.71	1.600	0.71	−0.71
Dimethyl acetylenedicarboxylate	−0.953	0.50	0.50	−0.011	0.41	−0.41

our own studies on pyrylium-3-olate[13] have shown that the regiochemistry of the cycloaddition reactions can be successfully predicted by FMO theory.[14] Of the three categories described by Sustmann[15] (type I: dominant HOMO of dipole with LUMO of dipolarophile; type III: dominant LUMO of dipole with HOMO of dipolarophile; type II: both interactions significant), type II is particularly common for carbonyl ylides since they have the smallest HOMO–LUMO energy gap of the common 1,3-dipoles.[16] For carbonyl ylides the HOMO of the dipole is dominant for reactions with electron-deficient dipolarophiles such as acrolein, whilst the LUMO becomes important for cycloaddition to electron-rich species such as ethyl vinyl ether. In this study the FMO's of 2-benzopyrylium-4-olate (**3**), the related pyrylium-3-olate (**13**) and the dipolarophiles were calculated using the Hückel approximation as implemented in the LHASA suite of programs.[17] Tables 2 and 3 list HOMO and LUMO energies and atomic coefficients of the 1,3-dipoles and the dipolarophiles respectively and Scheme 2 illustrates the anticipated MO interactions; energies are given in terms of β, the resonance integral for adjacent carbon p-orbitals.

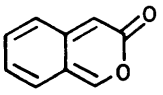
For acrolein the dominant interaction is between its LUMO and the 2-benzopyrylium-4-olate HOMO ($HOMO_B$), which predicts the 6-regioisomer, as observed. For ethyl vinyl ether (eve) the dominant interaction is $HOMO_{eve}$ – $LUMO_B$, which correctly predicts that the 7-regioisomer will predominate. Notably, the addition of ethyl vinyl ether to pyrylium-3-olate gives the reverse regioisomer but this can be explained by the reversal in the relative sizes of the coefficients of the reacting orbitals in the two systems; a similar effect is observed[13] by the substitution of a phenyl group at the 2-position of pyrylium-3-olate. For styrene (sty) the energy separations, $HOMO_{sty}$ – $LUMO_B$ and $HOMO_B$ – $LUMO_{sty}$, are similar and yet predict opposite regioselectivities, which is a possible explanation for the observed lack of regiocontrol in this case. For cyclohexenone the predicted regiochemistry favours the 6-regioisomer, as observed but the complete absence of the 7-*endo*-isomer can only be explained in terms of unfavourable dipole interactions.

The approximate nature of the Hückel treatment, which neglects secondary interactions, obviates its usefulness as a predictor of stereoselection during the cycloadditions. Note-



Scheme 2. Predicted principal interactions

worthy in the above cycloaddition reactions is the strong *endo*-selectivity observed during the cycloaddition of cyclopentene and cyclohexene to the flat ylide (**3**). Major secondary orbital interactions of the type normally involved[18] to explain such selectivity are not present in these reactions. A similar preference for *endo*-addition has been observed by Jones in the addition of cylopentene, as well as other dienophiles to the flat dienes of the *o*-quinodimethane type;[19] for example, the benzopyrone (**46**) gave a 6.5:1 ratio of *endo*:*exo* adducts with cyclopentene. Jones proposed an attractive secondary orbital



(**46**)

interaction between the diene and the allylic hydrogens on the alkene, a proposal supported by perturbation theory; such secondary interactions have recently been reviewed.[20]

An alternative explanation may be an interaction of the σ-framework with the π-orbitals, during cycloaddition, leading to considerable sp^3 character in the reacting alkene orbitals in the transition state which favours *endo*-addition to flat enophiles such as the ylide (**3**).[21]

The above results illustrate the versatility of 2-benzopyrylium-4-olate (**3**) as a reactive 1,3-dipole. Trapping of this intermediate leads to a wide range of substituted benzotropone derivatives.

Experimental

M.p.s were determined on a Kofler hot-stage apparatus and are uncorrected. Solvents were dried and distilled before use. Chromatography was carried out either by column chromatography using MN-Kieselgel 60 (230—400 Mesh) ex CAMLAB or using centrifugally assisted chromatography on a Chromatotron Model 7924T from Harrison Research. For the latter plates were coated with a 2 mm layer of silica gel PF-254 with $CaSO_4 \cdot 0.5\ H_2O$ type 60 ex Merck.

^1H N.m.r. spectroscopy was carried out on either a Jeol FX90Q (90 MHz) spectrometer or a Bruker WH400 (400 MHz) instrument using tetramethylsilane as internal reference and deuteriochloroform as solvent. I.r. spectra were recorded on a Perkin-Elmer 1420 or 297 machine using films (for oils) or solutions in chloroform (for solids). U.v. spectra were determined on solutions in ethanol using a Pye Unicam SP800 Spectrophotometer.

Mass spectra were recorded on a Kratos MS25 instrument and accurate mass measurements were carried out on an AEI-Kratos MS 9/50 machine.

Thermal cycloadditions were carried out in thick-walled Carius tubes. The solutions were degassed with freeze-thaw cycles at 1 mmHg pressure then sealed at this pressure and heated in a constant temperature oil-bath. Reactions were generally performed under an atmosphere of oxygen-free nitrogen. Light petroleum refers to the fraction of boiling range 40—60 °C.

8,8a-*Dihydro*-1-*methoxy*-1H-2-*benzopyran*-4(3H)-*one* (**16**).—6-Methoxy-2*H*-pyran-3(6*H*)-one (**14**) (49.1 g, 0.4 mol) and 1-acetoxybutadiene[22] (86 g, 0.77 mol) in benzene (80 ml) were heated for 16 h under reflux. The solvent was removed under reduced pressure (1 mmHg, 30 °C) and the residual adduct dissolved in dichloromethane (200 ml) and triethylamine (150 ml). After 2 h at room temperature the volatile fraction was removed and the residue crystallised from ether to give, as one anomer, the *title compound* (**16**) (30.5 g, 44%), m.p. 65—66 °C (from ether) (Found: C, 66.5; H, 6.7. $C_{10}H_{12}O_3$ requires C, 66.6; H, 6.7%); $\nu_{max.}$ 1 685, 1 620, and 1 550 cm^{-1}; $\lambda_{max.}$ 315 and 202 nm (ε 15 300 and 5 130); δ_H 2.8—3.1 (3 H, m), 3.52 (3 H, s, MeO), 4.43 and 4.11 (2 H, ABq, *J* 17 Hz, 3α- and 3β-H), 4.46 (1 H, d, *J* 7.5 Hz, 8a-H), 6.1—6.4 (2 H, m), and 7.1 (1 H, m). The mother liquors, purified by chromatography on SiO_2 [1% (v/v) ethyl acetate in dichloromethane] afforded, as a second crop a further fraction containing some of the isomeric anomer (23.8 g, 34%).

1-*Methoxy*-1H-2-*benzopyran*-4(3H)-*one* (**17**).—The diene (**16**) (29.8 g) in toluene (120 ml) was added to 5% palladium-on-charcoal (2 g) in refluxing toluene (150 ml) through which a rapid stream of nitrogen was passed. After a further 0.5 h the reaction mixture was cooled, filtered through Celite, and chromatographed through SiO_2 [1% (v/v) ethyl acetate in dichloromethane] to give the *title compound* (14.7 g, 50%), m.p. 34—36 °C (Found: M^+, 178.063 43. $C_{10}H_{10}O_3$ requires M^+, 178.062 99); $\nu_{max.}$ 1 695 and 1 600 cm^{-1}; δ_H 3.60 (3 H, s), 4.46 and 4.25 (2 H, ABq, *J* 17 Hz), 5.60 (1 H, s), and 7.2—7.6 (3 H, m). Also recovered from the chromatography was the tetrahydro compound, 1-methoxy-6,7,8,8a-tetrahydro-1*H*-2-benzopyran-4(3*H*)-one (**19**) (9.1 g, 30%) but this mixture of anomers was not fully characterised.

Attempted Hydrolysis of the Acetal (**17**).—The acetal (5 g) in water (20 ml), tetrahydrofuran (40 ml) and 2M-sulphuric acid (7 ml) was stirred at room temperature for 3 days. The product was extracted into dichloromethane, dried, and the solvent removed. The residue was chromatographed through SiO_2 (ether) to produce 1-*hydroxy*-1H-2-*benzopyran*-4(3H)-*one* (1.16 g, 25%), m.p. 121—122 °C (Found: C, 65.9; H, 4.9; $C_9H_8O_3$ requires C, 65.9; H, 4.9%); $\nu_{max.}$ 3 580, 3 374, 1 695, and 1 600 cm^{-1}; δ_H 3.45 (1 H, d, *J* 55 Hz, exchange with D_2O), 4.28 and 4.79 (ABq, *J* 17 Hz), 6.11 (1 H, d, *J* 5.5 Hz, collapses to a singlet with D_2O), 7.3—7.8 (3 H, m), and 8.0 (1 H, m). Also obtained were the *acetal dimers* (**20**) and (**21**) (*ca.* 2.3 g, 50%). Samples of these were re-chromatographed. One isomer showed m.p. 207—208 °C (from ether) (Found: C, 69.4; H, 4.7. $C_{18}H_{14}O_5$ requires C, 69.6; H, 4.6%). The other isomer showed m.p. 152—156 °C (from ether) (Found: C, 69.9; H, 4.5. $C_{18}H_{14}O_5$ requires C, 69.6; H, 4.6%.

1-*Acetoxy*-1H-2-*benzopyran*-4(3H)-*one* (**18**).—The methoxy acetal (**17**) (21.3 g) was heated in a mixture of acetic acid (130 ml) and acetic anhydride (130 ml) at reflux for 1 h. After removal of the solvents and chromatography of the residue through SiO_2, using ether–light petroleum (1:2) as solvent, the *title acetate* was obtained (15.5 g, 63%) as a viscous gum (Found: C, 64.2; H, 5.0. $C_{11}H_{10}O_4$ requires C, 64.1, H, 4.9%); $\nu_{max.}$ 1 745, 1 701, and 1 603 cm^{-1}; δ_H 2.13 (3 H, s), 4.35 and 4.74 (2 H, Abq, *J* 17.5 Hz), 7.10 (1 H, s), 7.3—7.8 (3 H, m), and 8.05 (1 H, m); *m/z* 206 (M^+, 0.5%), 176 (1.0), 164 (11.3, $M - CH_2O$), 147 (100, $M - CH_3CO_2$), 146 ($M - CH_3CO_2H$), 134 (68), 133 (36), 105 (27), and 91 (35).

Cycloadditions to 2-*Benzopyrylium*-4-*olate.**—(i) *Dimethyl acetylenedicarboxylate.* The acetate (**18**) (97 mg, 0.5 mmol), the acetylene (200 mg, 1.5 mmol), and triethylamine (0.2 ml) in dichloromethane (4 ml) were stirred at room temperature for 3 h. Removal of the volatiles and chromatography through SiO_2 [ether–light petroleum (1:1)] gave *dimethyl* 8,9-*dihydro*-9-*oxo*-5,8-*epoxy*-5H-*benzocycloheptene*-6,7-*dicarboxylate* (**22**) (119 mg, 88%) as colourless crystals, m.p. 88—89 °C (from ether) (Found: C, 62.4; H, 4.1. $C_{15}H_{12}O_6$ requires C, 62.5; H, 4.2%); $\nu_{max.}$ 1 750—1 715, 1 654, and 1 605 cm^{-1}; δ_H 3.8 (6 H, s), 5.33 (1 H, s), 5.81 (1 H, s), 7.2—7.5 (3 H, m), and 7.93 (1 H, m); *m/z* 288 (M^+, 44%), 260 (5%, $M - CO$), 229 (66, $M - CO_2Me$), 228 (58, $M - HCO_2Me$), 200 (12.7), and 170 (100).

(ii) *Cyclohexenone.* (*a*) Pyrolysis conditions. The acetate (**18**) (0.23 g, 1.1 mmol) and cyclohexenone (1 ml) in acetonitrile (7 ml) were heated in a sealed tube at 160 °C for 16 h. Removal of solvent and filtration through SiO_2 [ether–light petroleum (1:1)] afforded a mixture of adducts (0.21 g, 77%). Separation of the isomers was effected by t.l.c. [Chromatotron; ether–light petroleum (1:2)] to give a 21:46:33 ratio of (**23**), (**25**) and (**24**) respectively.

(*b*) Base catalysed conditions. The acetate (0.24 g, 1.2 mmol) in acetonitrile (10 ml) was treated with cyclohexenone (1.0 ml) and triethylamine (0.3 ml) at room temperature for 40 h before removal of the volatiles and chromatography through silica gel as above. The starting acetate (0.07 g) was recovered as well as a mixture of the adducts (0.15 g, 77% based on reacted acetate), separated by h.p.t.l.c. (Chromatotron) as above to give a 21:51:27 ratio of the adducts (**23**), (**25**), and (**24**) respectively. The *exo*-6-adduct, 2,3,4aα,5,11,11aα-*hexahydro*-5β,11β-*epoxydibenzo*[a,d]*cycloheptene*-4(1H),10-*dione* (**24**) had m.p. 123—124 °C (from ether) (Found: C, 74.3; H, 5.8. $C_{15}H_{14}O_3$ requires C, 74.3; H, 5.8%); $\nu_{max.}$ 1 700 cm^{-1}; δ_H(400 MHz) 1.62 (1 H, m), 1.86 (1 H, m), 2.00 (1 H, m), 2.22 (1 H, m), 2.45 (2 H, m), 2.82 (2 H, m), 4.49 (1 H, s), 5.80 (1 H, s), 7.35 (1 H, d *J* 7.6 Hz), 7.42 (1 H, dt, *J* 1.2, 7.6 Hz), 7.57 (1 H, dt, *J* 1.4, 7.5 Hz), and 8.00 (1 H, d, *J* 7.6 Hz). The *endo*-6-adduct, 2,3,4aβ,5,11,11aβ-*hexahydro*-5β,11β-*epoxydibenzo*[a,d]*cycloheptene*-4(1H),10-*dione* (**25**) had m.p. 101—102 °C (from ether) (Found: C, 74.3; H, 5.7. $C_{15}H_{14}O_3$ requires C, 74.3; H, 5.8%); $\nu_{max.}$ 1 700 cm^{-1}; δ_H(400 MHz), 0.91 (1 H, m), 1.42 (1 H, m), 1.6 (2 H, m), 1.98 (1 H, m), 2.23 (1 H, dddt, *J* 18.2, 1.6, 1.0, 4.5 Hz), 3.20 (1 H, ddt, *J* 7.5, 8.6, 11.0 Hz), 3.46 (1 H, dd, *J* 7.6, 11.5 Hz), 4.88 (1 H, d, *J* 8.5 Hz), 5.52 (1 H, d, *J* 7.5 Hz), 7.28 (1 H, ddt, *J* 7.6, 1.2, 0.6 Hz), 7.39 (1 H, dt, *J* 1.3, 7.5 Hz), 7.51 (1 H, dt, *J* 1.4, 7.5 Hz), and 7.97 (1 H, ddt, *J* 7.7, 1.4, 0.5 Hz). The *exo*-7-adduct, 2,3,4aα,5,11,11aα-*hexahydro*-5β,11β-*epoxydibenzo*[a,d]*cycloheptene*-1(4H),10-*dione* (**23**) had m.p. 135 °C (from ether) (Found: C, 74.4; H, 5.9. $C_{15}H_{14}O_3$ requires C, 74.3; H, 5.8%); $\nu_{max.}$ 1 710 cm^{-1}; δ_H(400 MHz) 1.55 (1 H, m), 1.84 (1 H, m), 2.07 (1 H, m), 2.22 (1 H, m), 2.41 (1 H, ddd, *J* 17.8, 9.0, 7 Hz), 2.51 (1 H, dddd, *J* 17.8, 8.0, 3.5, 1.2 Hz), 2.80 (1 H, m), 5.00 (1 H, s), 5.19 (1 H, s), 7.28 (1 H, d, *J* 7.7 Hz), 7.43 (1 H, dt, *J* 1.1, 7.7 Hz), 7.57 (1 H, dt, *J* 1.4, 7.5 Hz), and 8.00 (1 H, d, *J* 7.7 Hz).

(iii) *Acrolein.* (*a*) Base-catalysed. The acetate (0.11 g, 1.0 mmol), acrolein (0.25 g, 4.5 mmol), and triethylamine (0.2 g) in dichloromethane (4 ml) were left at room temperature for 5 h. After removal of volatiles chromatography through SiO_2 [ether–light petroleum (1:1)] gave 6β-*formyl*-6,7-*dihydro*-5β,8β-*epoxy*-5H-*benzocyclohepten*-9(8H)-*one* (**28**) as a colourless gum (51 mg, 45%) (Found: M^+, 202.062 79. $C_{12}H_{10}O_3$ requires M^+, 202.062 99); δ_H(400 MHz) 2.09 (1 H, dddd, *J* 13.5, 9.4, 1.8, 0.5 Hz), 2.79 (1 H, ddd, *J* 13.7, 8.4, 3.9 Hz), 3.02 (1 H, dddd, *J* 9.5, 3.9, 1.8, 0.7 Hz), 4.87 (1 H, dd, *J* 8.3, 1.7 Hz), 5.57 (1 H, s), 7.3—7.7 (3 H, m), 8.02 (1 H, d, *J* 7.5 Hz), 9.80 (1 H, d, *J* 1.8 Hz); *m/z* 202 (M^+, 30%), 173 (19), 160 (12), 145 (100) 131 (22), and 117 (46).

(*b*) Thermal conditions. The acetate (0.15 g, 1.5 mmol), acrolein (0.2 g, 3.6 mmol), and acetonitrile (3 ml) were heated at 140 °C for 19 h in a sealed tube. Removal of volatiles and chromatography [Chromatotron; ether–light-petroleum (1:2)] gave adducts (**26**), (**27**), and (**28**) in a 1:1:2 ratio (55 mg, 36%) as well as the dimers (**20**) and (**21**) (40 mg, 35%). The *exo*-7-adduct, 7β-formyl-6,7-dihydro-5β,8β-epoxy-5*H*-benzocyclohepten-9-(8*H*)-one (**26**) was isolated as a colourless gum, δ_H 2—3.2 (3 H, m), 4.97 (1 H, s), 5.45 (1 H, d, *J* 7 Hz), 7.4—7.6 (3 H, m), 7.95 (1 H, d, *J* 7.5 Hz), 9.80 (1 H, s).

The *endo*-6 adduct, 6α-formyl-6,7-dihydro-5β,8β-epoxy-5*H*-benzocyclohepten-9(8*H*)-one (**27**) had δ_H 2.23 (1 H, ddd, *J* 13.5, 7, 2 Hz), 2.67 (1 H, ddd, *J* 13.5, 11, 8.5 Hz), 3.58 (1 H, m), 4.85 (1 H, dd, *J* 8.5, 1.5 Hz), 7.2—7.7 (3 H, m), 8.0 (1 H, d, *J* 7.5 Hz), and 9.1 (1 H, d, *J* 2 Hz).

(iv) *Styrene.* The acetate (0.2 g, 1 mmol), styrene (0.95 g, 9 mmol) and triethylamine (0.4 ml) in dichloromethane (4 ml) were left at room temperature for 20 h. Removal of the volatiles and chromatography through SiO_2 [ether–light petroleum (1:1)] gave, in order of elution a 3:1 mixture of the two *exo*-isomers (25 mg, 10%) the *endo*-6-adduct (96 mg, 40%) and *endo*-7-adduct (76 mg, 31%), as well as recovered acetate (29 mg, 15%) (total yield of adducts 81%; 95% based on reacted starting material). The *exo*-isomers were separated by t.l.c. [Chromatotron, ether–light petroleum (1:4)].

The 7-*endo*-adduct, 6,7-*dihydro*-7α-*phenyl*-5β,8β-*epoxy*-5H-*benzocyclohepten*-9(8H)-*one* (**29**) was isolated as a colourless gum (Found: C, 81.3; H, 5.5. $C_{17}H_{14}O_2$ requires C, 81.6; H, 5.6%); $\nu_{max.}$ 1 700 and 1 600 cm^{-1}; $\nu_{max.}$ 287, 247, and 209 nm (ε 1 800, 10 300, and 16 000); δ_H(400 MHz) 2.16 (1 H, dd, *J* 12.9, 5.4 Hz), 2.99 (1 H, ddd, *J* 12.9, 11.3, 7.5 Hz), 4.09 (1 H, ddd, *J* 11.3, 8.4, 5.4 Hz), 4.88 (1 H, d, *J* 8.4 Hz), 5.43 (1 H, d, *J* 7.4 Hz) 6.82 (2 H, m), 7.15 (3 H, m), 7.35 (1 H, d, *J* 7.5 Hz), 7.41 (1 H, dt, *J* 1.1, 7.5 Hz), 7.61 (1 H, dt, *J* 1.2, 7.5 Hz), and 7.88 (1 H, d, *J* 7.5 Hz): *m/z*

* All adducts were obtained as racemates; the relative configuration is based on substituent orientation with respect to the (arbitrarily chosen) β-epoxide bridge.

250 (M^+, 35%), 146 (40 benzopyrylium), 131 (100), 118 (25), and 104 (42, styrene).

The 7-*exo*-adduct, 6,7-dihydro-7β-phenyl-5β,8β-epoxy-5*H*-benzocyclohepten-9(8*H*)-one (**30**), and δ_H(400 MHz) 2.00 (1 H, dd, *J* 12.5, 9.1 Hz), 2.14 (1 H, ddd, *J* 12.5, 6.9, 5.9 Hz), 3.18 (1 H, ddd, *J* 9.1, 5.9, 1.5 Hz), 4.99 (1 H, d, *J* 1.6 Hz), 5.12 (1 H, d, *J* 6.9 Hz), 6.70 (1 H, d, *J* 7.5 Hz), 7.0—7.3 (7 H, m), and 8.30 (1 H, d, *J* 7.5 Hz).

The 6-*endo*-adduct, 6,7-*dihydro*-6α-*phenyl*-5β,8β-*epoxy*-5H-*benzocycloheptene*-9(8H)-*one* (**31**) was obtained as a colourless gum (Found: C, 81.5; H, 5.6. $C_{17}H_{14}O_2$ requires C, 81.6; H, 5.6%), $\nu_{max.}$ 1 700 and 1 600 cm^{-1}; $\nu_{max.}$ 288, 249, and 209 (ε 1 900, 10 000, and 15 000); δ_H(400 MHz) 1.99 (1 H, ddd, *J* 13.9, 7.3, 2.0 Hz), 2.95 (1 H, ddd, *J* 13.9, 10.6, 8.9 Hz), 4.01 (1 H, dt, *J* 7.0, 10.5 Hz), 4.90 (1 H, dd, *J* 8.9, 2.0 Hz), 4.01 (1 H, dt, *J* 7.0, 10.5 Hz), 4.90 (1 H, dd, *J* 8.9, 2.0 Hz), 5.25 (1 H, d, *J* 6.6 Hz), 6.53 (1 H, d, *J* 7.5 Hz), 6.67—6.72 (2 H, m), 7.05—7.3 (3 H, m), 7.24 (1 H, dt, *J* 1.5, 7.5 Hz), 7.35 (1 H, dt, *J* 1.2, 7.5 Hz), and 8.07 (1 H, d, *J* 7.8 Hz); *m/z* 250 (M^+, 14%), 207 (5), 178 (11), 146 (40), 118 (26), and 104 (100).

The 6-*exo*-adduct, 6,7-dihydro-6β-phenyl-5β,8β-epoxy-5*H*-benzocyclohepten-9(8*H*)-one (**32**) was a colourless gum, δ_H 2.3—2.5 (2 H, m), 3.37 (1 H, m), 4.97 (1 H, m), 5.18 (1 H, s), 7.2—7.7 (8 H, m), and 8.02 (1 H, d, *J* 7.5 Hz).

(v) *Ethyl vinyl ether*. (*a*) Base-catalysed conditions. The acetate (0.32 g, 1.5 mmol), ethyl vinyl ether (1 ml), and triethylamine (0.5 ml) in acetonitrile (8 ml) were allowed to react at room temperature for 48 h. Removal of volatiles gave a mixture of the 7-*endo* and 7-*exo*-adducts (0.25 g, 74%) in a 10:1 ratio.

(*b*) Thermal conditions. The acetate (0.23 g, 1 mmol), ethyl vinyl ether (3 ml), and acetonitrile (6 ml) were heated in a sealed tube at 160 °C for 43 h. Removal of volatiles and chromatography of the residues though SiO_2 [ether–light petroleum (1:3)] followed by purification by t.l.c. [Chromatotron; ether–light petroleum (1:5)] gave a 57:19:17:7 ratio of the isomers (**33**)—(**36**) (total yield, 181 mg, 73%).

The 7-*endo*-adduct, 7α-*ethoxy*-6,7-*dihydro*-5β,8β-*epoxy*-5H-*benzocyclohepten*-9(8H)-*one* (**33**) was obtained as a colourless gum (Found: C, 71.3; H, 6.2. $C_{13}H_{14}O_3$ requires C, 71.5; H, 6.4%); $\nu_{max.}$ 1 706 and 1 605 cm^{-1}; $\lambda_{max.}$ 286, 246, and 208 nm (ε 1 300, 8 900, and 9 600); δ_H(400 MHz) 1.03 (3 H, t, *J* 7.0 Hz), 1.85 (1 H, dd, *J* 13.1, 2.6 Hz), 2.74 (1 H, ddd, *J* 13.1, 9.4, 7.4 Hz), 3.43 (1 H, dq, *J* 8.9, 7.0 Hz), 3.58 (1 H, dq, *J* 8.9, 7.0 Hz) 4.54 (1 H, ddd, *J* 9.5, 7.0, 2.6 Hz), 4.85 (1 H, d, *J* 7.0 Hz), 5.19 (1 H, d, *J* 7.4 Hz), 7.23 (1 H, d, *J* 7.5 Hz), 7.38 (1 H, dt, *J* 1.1, 7.5 Hz), 7.51 (1 H, dt, *J* 1.2, 7.2 Hz), and 8.01 (1 H, d, *J* 7.7 Hz).

The 7-*exo*-adduct, 7β-ethoxy-6,7-dihydro-5β,8β-epoxy-5*H*-benzocyclohepten-9(8*H*)-one (**34**) had δ_H(400 MHz, C_6D_6) 1.91 (1 H, dd, *J* 12.9, 7.5 Hz), 2.24 (1 H, ddd, *J* 12.9, 7.5, 3.5 Hz), 3.20 (1 H, dq, *J* 9.0, 7.0 Hz), 3.38 (1 H, dq, *J* 9.0, 7.0 Hz), 3.91 (1 H, dd, *J* 7.4, 3.5 Hz), 5.04 (1 H, s), 5.07 (1 H, d, *J* 7.4 Hz), 6.64 (1 H, ddd, *J* 7.5, 1.2, 0.5 Hz), 7.03 (1 H, dt, *J* 1.5, 7.5 Hz), 7.09 (1 H, dt, *J* 1.4, 7.2 Hz), and 8.19 (1 H, ddd, *J* 7.6, 1.5, 0.6 Hz).

The 6-*endo*-adduct, 6α-ethoxy-6,7-dihydro-5β,8β-epoxy-5*H*-benzocyclohepten-9(8*H*)-one (**35**), had δ_H(400 MHz) 101 (3 H, t, *J* 7.0 Hz), 1.62 (1 H, ddd, *J* 13.5, 4.7, 2.0 Hz), 2.79 (1 H, dt, *J* 13.5, 9.2 Hz), 3.4—3.65 (2 H, m), 4.48 (1 H, ddd, *J* 9.5, 6.0, 4.5 Hz), 4.63 (1 H, dd, *J* 9.0, 2.0 Hz), 5.23 (1 H, d, *J* 6.0 Hz), 7.28 (1 H, d, *J* 7.7 Hz), 7.43 (1 H, dt, *J* 1.1, 7.7 Hz), 7.55 (1 H, dt, *J* 1.3, 7.7 Hz), 8.04 (1 H, d, *J* 7.7 Hz), 7.56 (1 H, dt, *J* 1.5, 7.5 Hz), and 7.97 (1 H, d, *J* 7.7 Hz).

The 6-*exo*-adduct, 6β-ethoxy-6,7-dihydro-5β,8β-epoxy-5*H*-benzocyclohepten-9(8*H*)-one (**36**) δ_H(400 MHz) 1.28 (3 H, t, *J* 7.0 Hz), 2.20 (1 H, ddd, *J* 14.0, 7.0, 1.6 Hz), 2.38 (1 H, dddd, *J* 14.0, 8.9, 2.0, 1.0 Hz), 3.4—3.6 (2 H, m), 4.03 (1 H, dd, *J* 6.9, 2.1 Hz), 4.87 (1 H, dd, *J* 8.8, 1.5 Hz), 5.23 (1 H, s), 7.31 (1 H, d, *J* 7.5 Hz), and 7.41 (1 H, dt, *J* 1.1, 7.5 Hz).

(vi) *Vinyl acetate*. (*a*) Thermal conditions. The acetate (0.25 g, 1.2 mmol), vinyl acetate (2 ml), and acetonitrile (6 ml) were heated in a sealed tube at 160 °C for 16 h. After removal of volatiles the residue was separated by t.l.c. [Chromatotron; ether–light petroleum] to give two fractions. Fraction 1 (0.14 g, 50% had a melting range of 64—73 °C (Found: C, 67.2; H, 5.2. $C_{13}H_{12}O_4$ requires C, 67.2; H, 5.2%); $\nu_{max.}$ 1 739, 1 702, and 1 604 cm^{-1}. The ^{1}H n.m.r. (400 MHz) spectrum showed this to be a 3:1 mixture of the 6-*endo*:6-*exo* adducts. Fraction 2 (0.12 g, 43%) was obtained as a colourless gum (Found: C, 67.4, H, 5.0. $C_{13}H_{12}O_4$ requires C, 67.2; H, 5.2%), $\nu_{max.}$ 1 746, 1 705, and 1 604 cm^{-1}. The ^{1}H n.m.r. (400 MHz) spectrum showed this to be an 8:1 mixture of the 7-*endo*: 7-*exo* adducts.

(*b*) Base-catalysed conditions. The acetate (0.32 g, 1.5 mmol), vinyl acetate (2 ml), and triethylamine (0.4 ml) in acetonitrile (8 ml) were left at room temperature for 3 days before removal of the volatiles and chromatography of the residue through SiO_2 [Chromatotron; ether–light petroleum (1:2)] to give two fractions: the 6-adducts (**39**) and (**40**) (0.17 g, 46%) ratio 4:1 and the 7-adducts (**37**) and (**38**) (0.19 g, 53%) ratio 20:1. Samples of the individual isomers were separated for 400 MHz n.m.r. studies by further chromatography on the Chromatotron [ether–light petroleum (1:10)].

The 3-*endo*-adduct, 7α-*acetoxy*-6,7-*dihydro*-5β,8β-*epoxy*-5H-*benzocyclohept*-9(8H)-*one* (**37**) showed δ_H 1.88 (3 H, s), 1.91 (1 H, dd, *J* 3.5, 2.5 Hz), 2.87 (1 H, ddd, *J* 13.6, 9.6, 7.3 Hz), 4.92 (1 H, d, *J* 7.3 Hz), 5.26 (1 H, d, *J* 7.3 Hz), 5.65 (1 H, ddd, *J* 9.6, 7.3, 2.5 Hz), 7.27 (1 H, d, *J* 7.7 Hz), 7.42 (1 H, dt, *J* 1.2, 7.5 Hz), 7.56 (1 H, dt, *J* 1.3, 7.5 Hz), and 8.02 (1 H, d, *J* 7.7 Hz).

The 3-*exo*-adduct, 7β-*acetoxy*-6,7-*dihydro*-5β,8β-*epoxy*-5H-*benzocyclohept*-9(8H)-*one* (**38**) showed δ_H 2.11 (3 H, s), 2.34 (1 H, ddd, *J* 13.6, 7.4, 3.3 Hz), 2.53 (1 H, dd, *J* 13.6, 7.5 Hz), 4.75 (1 H, s), 5.27 (1 H, dd, *J* 7.0, 3.5 Hz), 5.43 (1 H, d, *J* 7.4 Hz), 7.22 (1 H, d, *J* 7.5 Hz), 7.40 (1 H, dt, *J* 1.2, 7.5 Hz), 7.54 (1 H, dt, *J* 1.5, 7.5 Hz), and 7.95 (1 H, d, *J* 7.7 Hz).

The 6-*endo*-adduct, 6α-*acetoxy*-6,7-*dihydro*-5β,8β-*epoxy*-5H-*benzocyclohept*-9(8H)-*one* (**39**) showed δ_H 1.74 (3 H, s), 1.82 (1 H, ddd, *J* 14.2, 3.7, 1.6 Hz), 2.88 (1 H, ddd, *J* 14.2, 9.6, 8.8 Hz), 4.68 (1 H, dd, *J* 8.8, 1.6 Hz), 5.41 (1 H, ddd, *J* 9.7, 6.1, 3.7 Hz), 5.50 (1 H, d, *J* 6.1 Hz), 7.18 (1 H, d, *J* 7.5 Hz), 7.46 (1 H, dt, *J* 1.2, 7.5 Hz), 7.53 (1 H, dt, *J* 1.4, 7.5 Hz), and 8.05 (1 H, d, *J* 7.5 Hz).

The 6-*exo*-adduct, 6β-acetoxy-6,7-dihydro-5β,8β-epoxy-5*H*-benzocyclohept-9(8*H*)-one (**40**) showed δ_H 2.15 (3 H, s), 2.33 (1 H, ddd, *J* 14.7, 7.3, 1.7 Hz), 2.47 (1 H, dddd, *J* 14.7, 8.8, 2.2, 1.0 Hz), 4.88 (1 H, dd, *J* 8.8, 1.6 Hz), 5.14 (1 H, dd, *J* 7.3, 2.2 Hz), 5.23 (1 H, s), 7.41 (1 H, d, *J* 7.5 Hz), 7.45 (1 H, dt, *J* 1.2, 7.5 Hz), 7.59 (1 H, dt, *J* 14, 7.5 Hz), and 7.98 (1 H, d, *J* 7.5 Hz).

(vii) *Norborna*-2,5-*diene*. The acetate (0.13 g, 0.6 mmol), norborna-2,5-diene (2 ml), and triethylamine (0.5 ml) were left at room temperature for 4 days before removal of the volatiles and chromatography of the residue through SiO_2 [ether–light petroleum (1:2)] to afford 1,4,4aα,11aα-*tetrahydro*-5β,11β-*epoxy*-1β,4β-*methano*-5H-*dibenzo*[a,d]*cyclohepten*-10(11H)-*one* (**41**) (0.11 g, 75%), m.p. 96—97 °C (from hexane) (Found: C, 80.7; H, 5.9. $C_{16}H_{14}O_2$ requires C, 80.7; H, 5.9%); $\nu_{max.}$ 1 702 cm^{-1}; $\lambda_{max.}$ 285, 295, 247, and 205 nm (ε 1 570, 1 570, 9 190, and 24 800); δ_H 1.35 (1 H, d, *J* 9 Hz), 2.15 (2 H, s), 2.26 (1 H, d, *J* 9 Hz), 2.95 (2 H, s), 4.41 (1 H, s), 4.90 (1 H, s), 6.15 (2 H, s), 7.1—7.6 (3 H, m), and 7.95 (1 H, d, *J* 8 Hz); *m/z* 238 (M^+, 13%), 209 (2.5), 172 (18), 145 (26), 144 (100), 116 (28), and 115 (47).

(viii) *Cyclohexene*. The acetate (0.09 g, 0.5 mmol) in cyclohexene (5 ml) was heated at 155 °C for 48 h in a sealed tube. Removal of solvent and chromatography through SiO_2 (ether–light petroleum (1:2)] gave the *exo*-adduct (**43**) (13 mg, 13%) followed by the *endo*-adduct (**45**) (82 mg, 80%). Under base-catalysed conditions only the *endo*-adduct (10 mg, 10%) was detected.

The *endo*-adduct, 1,2,3,4,4aβ,11aβ-*hexahydro*-5β,11β-*epoxy*-

5H-*dibenzo*[a,d]*cyclohepten*-10(11H)-*one* (**45**), was obtained as a viscous gum (Found: M^+, 228.114 53. $C_{15}H_{16}O_2$ requires M^+, 228.115 02); $\nu_{max.}$ 1 704 and 1 601 cm^{-1}; δ_H(400 MHz) 0.40 (1 H, m), 0.66 (1 H, m), 1.2—1.6 (6 H, m), 2.61 (2 H, m), 4.76 (1 H, d, *J* 8.4 Hz), 5.20 (1 H, d, *J* 6.9 Hz), 7.17 (1 H, d, *J* 7.5 Hz), 7.39 (1 H, dt, *J* 1.2, 7.6 Hz), 7.51 (1 H, dt, *J* 1.4, 7.5 Hz), 7.99 (1 H, d, *J* 7.5 Hz); *m/z* 228 (M^+, 19%), 199 (12), 182 (15), 158 (15), 157 (25), 147 (88), 146 (100), and 118 (47).

The *exo*-adduct, 1,2,3,4,4aα,11aα-*hexahydro*-5β,11β-*epoxy*-5H-*dibenzo*[a,d]*cyclohepten*-10(11H)-*one* (**43**), was obtained as an amorphous solid (Found: M^+, 228.114 29. $C_{15}H_{18}O_2$ requires M^+, 228.115 02); δ_H 1.3—2.2 (methylene envelope), 4.32 (1 H, s), 7.2—7.6 (3 H, m), 7.95 (1 H, d, *J* 7.5 Hz); *m/z* 228 (M^+, 25%), 199 (44), 182 (49), 158 (33), 157 (52), 147 (72), 146 (100), and 118 (75).

(ix) *Cyclopentene.* The acetate (0.11 g, 0.5 mmol) in cyclopentene (3 ml) containing triethylamine (1 ml) was left at room temperature for 2 days. After removal of the solvent, chromatography through SiO_2 [ether–light petroleum (1:2)] gave, besides recovered acetate (21 mg, 19%), 1,2,3,3aβ,4,10aβ-*hexahydro*-4β,10β-*epoxybenz*[f]*azulen*-9(10H)-*one* (**44**) (52 mg, 46%) as a viscous gum (Found: C, 78.3; H, 6.7. $C_{14}H_{14}O_2$ requires C, 78.5; H, 6.6%); δ_H(400 MHz) 0.50 (1 H, m), 1.06 (1 H, m), 1.36 (2 H, m), 1.50 (2 H, m), 3.25 (2 H, m), 4.78 (1 H, d, *J* 8.8 Hz), 5.14 (1 H, d, *J* 7.7 Hz), 7.20 (1 H, d, *J* 7.5 Hz), 7.37 (1 H, dt, *J* 1.3, 7.5 Hz), 7.52 (1 H, dt, *J* 1.3, 7.5 Hz), and 7.95 (1 H, d, *J* 7.5 Hz).

Also obtained was 1,2,3,3aα,4,10aα-*hexahydro*-4β,10β-*epoxybenz*[f]*azulen*-9(10H)-*one* (**42**) (6.3 mg, 5%) as a viscous gum (Found: M^+, 214.099 52. $C_{14}H_{14}O_2$ requires M^+, 214.099 37); δ_H 1.4—2.2 (6 H, m), 2.5—2.7 (2 H, m), 4.42 (1 H, s), 4.95 (1 H, s), 7.1—7.6 (3 H, m), and 8.0 (1 H, dd, *J* 1.8, 7 Hz).

Acknowledgements

We thank the University of Leeds for a research studentship (to R. J. W.).

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Received 10*th March* 1986; *Paper* 6/470