Benzoxepine formation by the 1,7 electrocyclisation of diene-conjugated carbonyl ylides: studies on relative rates of cyclisation *via* intramolecular competition reactions

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A series of reactions has been carried out using reactants of the type 11/12 in which carbonyl ylide cyclisation on to the substituent at the 6 position is in competition with cyclisation on to the unsubstituted phenyl group at the 2 position. The relative reactivity of the two groups, determined by measuring the product ratio 13 : 15 and 14 : 16, has been determined for a series of 6-substituted compounds. Alkenyl groups and the thiophene ring are found to be *ca.* 10–20 times more reactive than phenyl. In cases where the 6-substituent is a substituted aryl group it has been found that, unlike the analogous nitrile ylides, aromatic substituents have little effect on the reactivity of the ring. The selectivity is unaffected by the nature of the substituent on the terminal atom of the carbonyl ylide. Mechanistic studies using deuteriated reactants show that the cyclisation step is irreversible.

Introduction

This work is concerned with the electrocyclisation reactions of unsaturated 1,3-dipolar intermediates and in particular with the 1,7 cyclisation of diene-conjugated systems **1**, which provides a general route to unsaturated seven-membered heterocycles **2**.[1] It describes further work on our investigations into the structural factors which control the rates of these reactions. The initial work[2] was concerned with nitrile ylides and utilised intramolecular competition reactions in the system **3** to determine the reactivity of a series of substituents at position 6 relative to that of the unsubstituted phenyl group at position 2. The results, summarised in Table 8, showed that: (i) the reactivity was strongly dependent on the 'double bond character' of the bond under attack, as would be expected; and (ii) the reactivity of the phenyl groups was enhanced by *both* electron withdrawing and electron donating aromatic substituents, particularly when at the *meta* position. The latter effect was unexpected and contrasts with the behaviour of nitrile ylides (Sustmann type I dipoles) in cycloaddition reactions, where the reactivity of the dipolarophile is increased by electron withdrawing groups but diminished by electron donating groups. The next objective was to find out if the same pattern of reactivity was general to all 1,3-dipolar intermediates or, as for cycloaddition reactions, it varied in a systematic way with the nature of the 1,3-dipole.

This paper reports a study of carbonyl ylide cyclisation reactions which almost exactly parallels the earlier work on nitrile ylides. Carbonyl ylides were selected for several reasons: (i) extensive earlier work on the synthetic and mechanistic aspects of their 1,7 electrocyclisation reactions, largely from Eberbach's group, had shown that they cyclise effectively in systems where both unsaturated elements of the conjugated diene system are aromatic[3] (*e.g.* **6** → **8**) or heteroaromatic,[4] and that the cyclisation definitely proceeds *via* a formally conrotatory 1,7 electrocyclisation mechanism;[3] and (ii) their use would extend the reactivity studies to dipoles of the allyl type in contrast to the nitrile ylides studied earlier which are of the propargyl–allenyl type.

Results and discussion

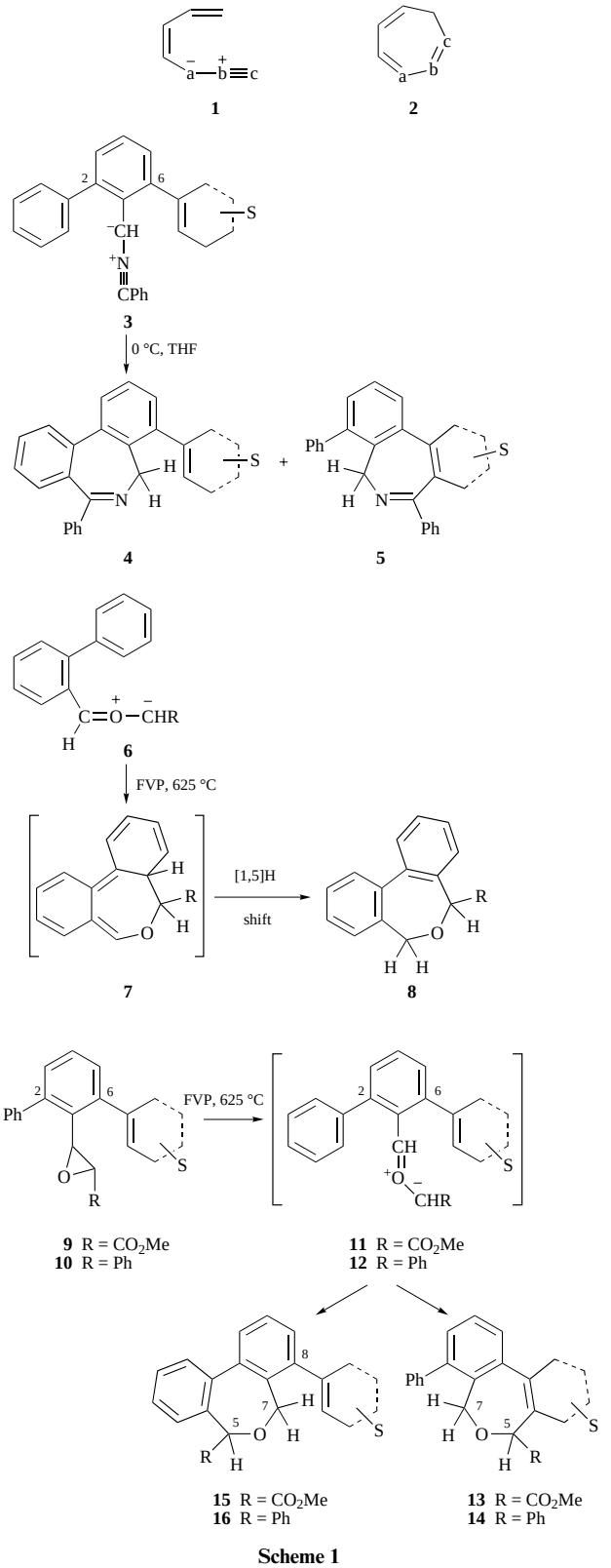
The relative reactivity data was determined *via* the internal competition reaction shown in Scheme 1, in which the carbonyl ylides **11**, **12** were generated by the flash vacuum pyrolysis (FVP) of the oxiranes **9**, **10** at 625 °C. The background and mechanistic assumptions implicit in this method were discussed in the earlier work[2] and, as there, the reactivity of a range of unsaturated substituents (Table 1) incorporated at the 6 position, relative to that of the phenyl group at the 2 position, has been determined by measuring the ratio of the products **13** : **15** and **14** : **16**. In each case the identity of one of the cyclisation products, **15** or **16**, was established by comparison with an 'authentic' sample.

Table 1 Identification of 6-substituent in componds **9**–**12**, **19**, **22**, and 8-substituent in **15**, **16**

Compd.	Substituent
a	Phenyl
b	(*E*)-2-Phenylethenyl
c	2-Thienyl
d	3-Thienyl
e	3,5-Dichlorophenyl
f	3,5-Bis(trifluoromethyl)phenyl
g	3,5-Dimethylphenyl
h	3-Nitrophenyl
i	4-Fluorophenyl
j	4-Methylphenyl
k	4-Chlorophenyl
l	4-Methoxyphenyl
m	4-(Trifluoromethyl)phenyl

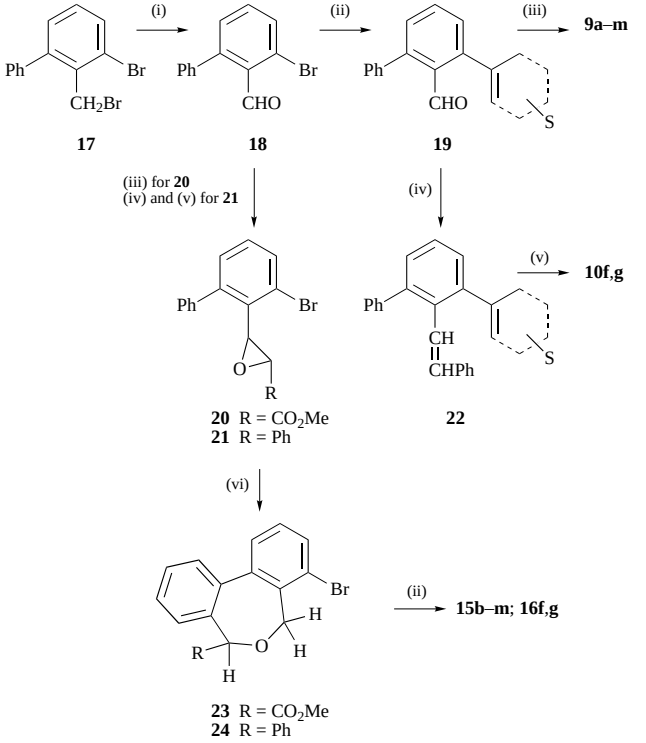
Synthesis of the 3-[(2-phenyl-6-substituted)phenyl]oxiranes 9a–m, 10f,g as carbonyl ylide precursors and the 'authentic' dibenzoxepines 15a–m, 16f,g

Two series of oxiranes were studied, the major series **9a**–**m** (Scheme 1) had an ester as the R substituent while the minor series **10f**,**g** had a phenyl substituent. The unsaturated groups incorporated at the 6 position, whose relative reactivity was to be measured, are identified in Table 1. The preparative routes are shown in Scheme 2. The key intermediate for the synthesis of both series and for the 'authentic' dibenzoxepines **15a**–**m** and **16f**,**g** was 2-bromo-6-phenylbenzaldehyde **18**. This was prepared in good yield by the Bender and Hass method[5] from the known[2] benzyl bromide **17**. The ester-substituted compounds **9a**–**m** were then prepared by two further steps, Suzuki coupling with the appropriate aryl, heteroaryl or vinyl boronic acid to give the substituted benzaldehydes **19a**–**m** (Tables 2 and 3)



Scheme 1

and finally a Darzens reaction to give **9a**–**m** (Tables 4 and 5). The phenyl substituted analogues **10f**,**g** were synthesised from **18** *via* Suzuki coupling to give **19**, Wadsworth–Emmons olefination to give **22**, and finally oxidation with *m*-chloroperbenzoic acid. The 'authentic' dibenzoxepines **15b**–**m** and **16f**,**g**, required for identification of the products of the competition reactions, were prepared by FVP of the appropriate bromo-substituted oxirane **20**, **21** to give the 4-bromooxepines **23**, **24** which were then converted into the target compounds (Tables 6 and 7) by Suzuki coupling.



Scheme 2 *Reagents and conditions* (i) NaOEt–$CH_3CH(NO_2)CH_3$; (ii) $ArB(OH)_2$ or vinyl$B(OH)_2$–Pd^0; (iii) $ClCH_2CO_2Me$–NaOMe; (iv) $(EtO)_2P(O)CH_2Ph$–NaOEt; (v) MCPBA; (vi) FVP, 625 °C

Competitive cyclisation reactions of the carbonyl ylides 11a–m and 12f,g

The overall course of the competition reactions is shown in Scheme 1. The methods used are discussed in (1) below and in more detail in the Experimental section. The results and the mechanism of the reaction are discussed in (2) below.

(1) Experimental method. In a typical flash vacuum pyrolysis experiment the oxirane **9** or **10** (*ca*. 0.5 mmol) was distilled (150–180 °C) into an unpacked pyrolysis tube (625 °C) and the products were collected in a cold trap at the exit. Preliminary work had shown that the reactants could be distilled under high vacuum without decomposition. The whole product mixture was then dissolved in deuteriochloroform and analysed for the **13**:**15** or **14**:**16** ratio by ^{1}H NMR spectroscopy and by HPLC. The reaction mixtures were very clean and contained only the expected products with, in some cases, a little residual oxirane. They were then worked up and the dibenzoxepines were isolated as a mixture by dry column flash chromatography. The yields and product ratios are shown in Table 8. In the NMR analyses the spectra were run at either 200 or 360 MHz at a temperature of 328 K. The elevated temperature was required because, in spectra obtained at 298 K, some of the peaks were broadened due to ring inversion of the oxepine ring. The spectra all showed a set of characteristic peaks (Table 9) for each of the two isomers, with a singlet due to the proton on C-5 and a pair of doublets due to the methylene group at C-7. In each mixture the peaks due to the 8-substituted isomer (**15** or **16**) were identified from the NMR spectrum of the 'authentic' sample prepared as discussed above, using peak enhancement where necessary. The product ratio (Table 8) was determined from the integrals of the 5-H absorptions and also measured using HPLC. Control experiments showed that the isomer ratio was not changed when the product mixture was passed through the pyrolysis tube under the reaction conditions and also that the isolated single isomers **15** were not isomerised into **13**.

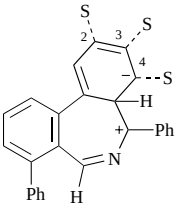
(2) The relative reaction rates and the mechanism of the cyclisation. The results are shown in Table 8 alongside those for the analogous nitrile ylide cyclisations.[2] In comparing the two sets of data it is important to be aware of the major differences

Table 2 Yields and physical data for the 2-phenyl-6-arylbenzaldehydes **19a**–**m**[a]

Compd.	Reaction time/h	Yield (%)	Cryst. solvent[b]	Mp/°C	Molecular formula	Found (calc.) (%) C	H	N	M^+
19a	3	81	H	77–78	$C_{19}H_{14}O$	88.7 (88.4)	5.7 (5.4)		258.106 53 (258.10 477)
19b	3	90	H	92–93	$C_{21}H_{16}O$	88.6 (88.7)	5.5 (5.6)		284.119 34 (284.120 12)
19c	3	87		oil	$C_{17}H_{12}OS$	77.0 (77.2)	4.65 (4.55)		264.059 90 (264.060 89)
19d	5	93	H–E	76–77	$C_{17}H_{12}OS$	76.9 (77.2)	4.5 (4.8)		264.059 14 (264.060 89)
19e	3	85	H–E	123–124	$C_{19}H_{12}Cl_2O$	69.6 (69.75)	3.8 (3.65)		326.024 62 (326.026 52)
19f	3	81	H	131–132	$C_{21}H_{12}F_6O$	64.25 (63.95)	2.95 (3.05)		394.077 88 (394.079 23)
19g	4	91	H	109–110	$C_{21}H_{18}O$	88.5 (88.1)	6.25 (6.3)		286.135 80 (286.135 77)
19h	4	85	H–E	124–125	$C_{19}H_{13}NO_3$	75.3 (75.2)	4.5 (4.3)	4.8 (4.6)	303.088 86 (303.089 54)
19i	3	83	H	112–113	$C_{19}H_{13}FO$				276.092 78 (276.095 04)
19j	3	85	H	87–88	$C_{20}H_{16}O$	88.45 (88.2)	6.0 (5.85)		272.120 92 (272.120 12)
19k	2	80	H	97–98	$C_{19}H_{13}ClO$	77.8 (77.9)	4.5 (4.44)		292.065 91 (292.065 49)
19l	5	84	H–E	85–86	$C_{20}H_{16}O_2$	83.55 (83.3)	5.85 (5.55)		288.114 54 (288.115 03)
19m	5	82	H–E	87–88	$C_{20}H_{13}F_3O$	73.4 (73.6)	4.1 (4.0)		326.093 08 (326.091 85)

[a] Compounds identified in Table 1. [b] H = hexane; E = diethyl ether.

in the reaction conditions; the nitrile ylide cyclisations were carried out in a relatively polar solvent (THF) at 0 °C whereas the carbonyl ylides were cyclised in the gas phase at 625 °C. The results are similar in two respects but show one major difference. The first similarity is in the effect of the 'double bond character' of the bond on to which cyclisation occurs [cases (**b**), (**c**) and (**d**), Table 8]; in both cyclisations the order of reactivity is as expected, *i.e.* olefin > thiophene > benzene. The differences, however, are much smaller for the carbonyl ylide cyclisations, but this may simply reflect the lower selectivity expected at the higher reaction temperature. The results for the *para*-substituted aryl rings [cases (**i**)–(**m**)] are also similar for the two cyclisations in that all the substituents have a slight activating effect. The striking difference is in the results for the *meta* substituted aryl rings [cases (**e**)–(**h**)]. In the nitrile ylide cyclisations all the *meta* substituents exerted a substantial activating effect [8 to > 100 for cases (**f**)–(**h**)], whereas in the carbonyl ylide reactions a small activation (1.3–1.5) was produced in two cases [(**e**) 3,5-dichloro- and (**h**) 3-nitro-] and a slight deactivation (0.7–0.8) in the other two cases [(**g**) 3,5-dimethyl- and (**f**) 3,5-bis(trifluoromethyl)-].



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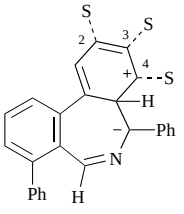

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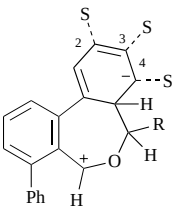

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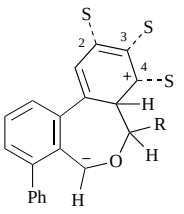

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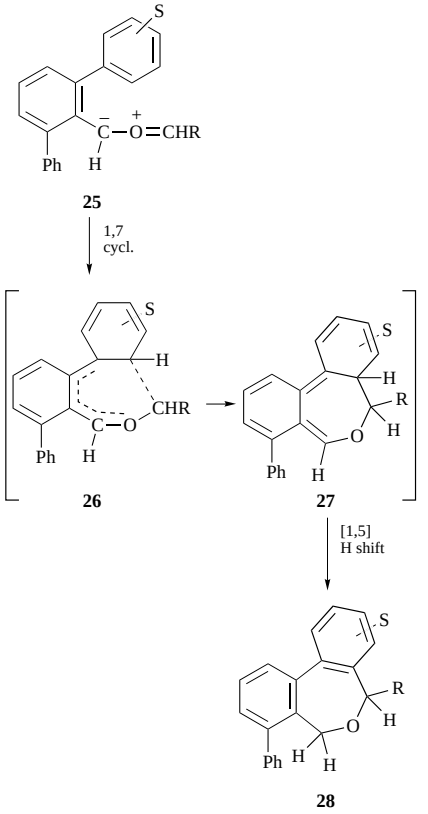


Scheme 3

The difference in the effect of *meta* substituents for the two dipoles is not easy to explain using the model suggested for rationalising the nitrile ylide results.[2] The course of the carbonyl ylide cyclisation is shown in Scheme 3; it is a two step process in which the 1,7 cyclisation proceeds through the transition state **26** to the intermediate **27** which then undergoes a [1,5] hydrogen shift to give the product. It is known[3] that the 1,7 cyclisation step is formally conrotatory and it has been sug-

Table 3 NMR and IR spectroscopic data for the aldehydes **19a**–**m**[a]

Compd.	δ_H	δ_C	ν_{max}/cm^{-1} (C=O)
19a	7.35–7.65 (13 H, m, aromatic), 10.0 (1 H, s, CHO)	193.5 (CHO), 144.1 (C-1), 139.4 (C-2), 132.9 (C-1, phenyl), 131.4, 130.2, 129.4, 128.0, 127.5 (aromatic CH signals)	1695
19b	7.12 (1 H, d, *J* 16.2, ethenyl CH), 7.25–7.79 (13 H, m, aromatic), 8.1 (1 H, d, ethenyl CH), 10.03 (1 H, s, CHO)	194.1 (CHO), 146.7 (C-1), 138.5 (C-2), 138.3 (C-6), 137.0 [C-1, (ethenyl phenyl)], 131,1 [C-1, (C-2 phenyl)], 132.3, 132.1, 129.8, 129.7, 128.4, 128.1 127.8, 127.7, 126.9, 126.8, 126.1 (remaining CH signals)	1693
19c	7.1–7.7 (11 H, m, aromatic), 10.05 (1 H, s, CHO)	192.1 (C=O), 140.3 (C-1), 139.1 (C-6), 138.2 (C-2, thiophene), 134.9 (C-2), 133.2 [C-1, (C-2 phenyl)], 131.2, 130.0, 129.8, 129.5, 128.4, 128.1, 127.6, 127.5, 127.0 (aromatic CH signals)	1692
19d	7.14 (1 H, dd, *J* 5.3, 1.0, aromatic), 7.25–7.48 (9 H, m, aromatic), 7.54–7.69 (1 H, m, aromatic), 10.00 (1 H, s, CHO)	193.5 (CHO), 144.0 (C-1), 139.5 (C-6), 139.4 (C-2), 138.4 [C-3, (C-6 thiophene)], 133.2 [C-1, (C-2 phenyl)], 131.4, 130.2, 130.0, 129.4, 129.2, 128.0, 127.5, 125.3, 124.2 (aromatic CH signals)	1693
19e	7.20–7.28 (2 H, m, aromatic), 7.32–7.50 (7 H, m, aromatic), 7.57–7.65 (2 H, m, aromatic), 9.92 (1 H, s, CHO)	192.6 (CHO), 145.5 (C-1), 143.2 (C-6), 140.4 (C-2), 138.3 [C-1, (C-6 $Cl_2C_6H_3$)], 134.3 [C-3, (C-6 $Cl_2C_6H_3$)], 132.4 [C-1, (C-2 phenyl)], 131.8, 130.9, 130.1, 129.6, 128.2, 128.0, 127.5, 127.3 (aromatic CH signals)	1691
19f	7.3–7.9 (11 H, m, aromatic), 9.9 (1 H, s, CHO)	192.4 (CHO), 146.5 (C-1), 142.6 (C-6), 139.8 (C-2), 137.8 {C-1, [C-6 3,5-$(CF_3)_2C_6H_3$]}, 131.9 [C-1, (C-2 phenyl)], 125.9 (CF_3), 120.5 {C-3, [C-6 3,5-$(CF_3)_2C_6H_3$]}, 132.1, 131.2, 130.5, 129.8, 129.3, 128.4, 128.2, 121.0 (remaining CH aromatic signals)	1690
19g	2.4 (6 H, s, CH_3), 7.0–7.5 (11 H, m, aromatic), 10.0 (1 H, s, CHO)	193.6 (CHO), 144.7 (C-1), 143.6 (C-6), 139.7 (C-2), 139.2 {C-3 [3,5-$(CH_3)_2C_6H_3$]}, 137.5 {C-1 [3,5-$(CH_3)_2C_6H_3$]}, 132.9 [C-1, (C-2 phenyl], 21.1 (CH_3), 131.2, 130.0, 129.3, 129.2, 128.7, 127.3 [remaining CH aromatic signals, (overlap of 2 CH signals)]	1692
19h	7.32–7.73 (10 H, m, aromatic), 8.20–8.27 (2 H, m, aromatic), 9.92 (1 H, s, CHO)	192.6 (CHO), 147.6 [C-3, (C-6 3-$NO_2C_6H_4$)], 146.1 (C-1), 142.1 (C-6), 140.4 (C-2), 138.0 [C-1, (C-6 3-$NO_2C_6H_4$)], 132.2 [C-1, (C-2 phenyl)], 135.2, 132.0, 131.0, 130.4, 130.1, 129.7, 128.6, 128.3, 128.1, 123.9, 122.7 (CH aromatic signals)	1695
19i	7.07–7.14 (2 H, m, aromatic), 7.24–7.46 (9 H, m, aromatic), 7.55–7.61 (1 H, m, aromatic), 9.92 (1 H, s, CHO)		1698
19j	2.47 (3 H, s, CH_3), 7.3–7.65 (12 H, m, aromatic), 10.04 (1 H, s, CHO)	193.4 (CHO), 144.1 (C-1), 143.9 (C-6), 139.5 (C-2), 137.2 [C-4 (4-$CH_3C_6H_4$)], 136.3 [C-1 (4-$CH_3C_6H_4$)], 132.9 [C-1, (C-2 phenyl)], 21.0 (CH_3), 131.2, 130.1, 129.9, 129.3, 128.7, 127.9, 127.3 [remaining CH aromatic signals, (overlap of one CH signal)]	1694
19k	7.28–7.64 (12 H, m, aromatic), 9.95 (1 H, s, CHO)	193.1 (CHO), 144.8 (C-1), 142.4 (C-6), 138.9 (C-2), 138.3 [C-4 (4-ClC_6H_4)], 133.5 [C-1 (4-ClC_6H_4)], 132.8 [C-1, (C-2 phenyl)], 131.5, 130.6, 130.4, 130.2, 129.5, 128.1, 127.7 (aromatic CH signals, overlap of one CH signal)	1695
19l	3.86 (3 H, s, OCH_3), 6.95–7.02 (2 H, m, aromatic), 7.29–7.62 (10 H, m, aromatic), 9.98 (1 H, s, CHO)	193.5 (CHO), 159.1 [C-4 (4-$CH_3OC_6H_4$)], 143.9 (C-1), 143.8 (C-6), 139.6 (C-2), 132.9 [C-1, (C-2 phenyl)], 131.4 [C-1 (4-$CH_3OC_6H_4$)], 113.5 [C-3 (4-$CH_3OC_6H_4$)], 55.1 (OCH_3), 131.3, 130.6, 130.2, 129.8, 129.3, 127.9, 127.3 (remaining aromatic CH signals)	1696
19m	7.32–7.49 (8 H, m, aromatic), 7.59–7.70 (4 H, m, aromatic), 9.94 (1 H, s, CHO)	192.9 (CHO), 145.2 (C-1), 143.9 (C-6), 141.9 (C-2), 138.5 [C-4 (C-6 4-FC_6H_4)], 132.6 [C-1, (C-2 phenyl)], 129.1 [C-1, (C-6 4-FC_6H_4)], 124.8 (CF_3), 131.7, 130.7, 130.3, 129.6, 129.5, 128.2, 127.9 (aromatic CH signals)	1692

[a] Compounds identified in Table 1

gested that it, like the analogous nitrile ylide reaction, goes through a helical transition state. However it is not known whether the transition state is early or late. In the analogous nitrile ylide cyclisations[2] it was suggested that the transition state was late and that the intermediate corresponding to **27** could therefore be taken as a model of the transition state and that the latter would therefore be subject to similar stabilising/destabilising effects by the substituents. It was suggested that the canonical forms **29**, **30** would make a significant contribution to the resonance stabilisation of the intermediate since both contain an intact benzene ring and that these structures would be further stabilised by aromatic substituents in the upper ring with, respectively, electron withdrawing or donating properties. The substituents would similarly serve to stabilise the transition state for the cyclisation, assuming it is 'product'-like, and so enhance the reactivity of the ring. Such substituents would have a maximum effect when conjugated with the charge to be delocalised, *i.e.* in the 2 or 4 positions (as in the cyclisation of the *meta*-substituted cases) and a lesser effect when in the 3 position (as in the cyclisation of the *para*-substituted cases). The closest analogues to **29**, **30** for the intermediate **27** in the carbonyl ylide cyclisation are shown in structures **31**, **32**. Of these, **31** would be expected to be the more stable because of electron donation by the oxygen atom adjacent to the carbon bearing the positive charge. By the same argument used in the nitrile ylide case it would be predicted that electron withdrawing substituents at the 2 and/or 4 positions would stabilise **31** and electron donating groups at these positions would stabilise **32**, and in both cases thus enhance the reactivity of the ring. Experimentally this is found not to be true. The failure of this

Table 4 Yields and physical data for the 2-methoxycarbonyl-3-[(2-phenyl-6-substituted)phenyl]oxiranes **9a**–**m**[a]

Compd.	Reaction time/h	Yield (%)	Cryst. solvent[b]	Mp/°C	Molecular formula	Found (calc.) (%) C	H	N	M^+
9a	5	85	H–E	153–154	$C_{22}H_{18}O_3$				330.1257 (330.1256)
9b	3	81	H	103–104	$C_{24}H_{20}O_3$	80.6 (80.9)	5.4 (5.6)		356.1422 (356.1412)
9c	3	78	H–E	131–132	$C_{20}H_{16}O_3S$	71.3 (71.45)	4.9 (4.75)		336.0812 (336.0820)
9d	12	76	H–E	141–142	$C_{20}H_{16}O_3S$	71.7 (71.45)	5.1 (4.75)		336.0823 (336.0820)
9e	5	82	H–E	121–122	$C_{22}H_{16}Cl_2O_3$	66.2 (66.3)	4.0 (4.0)		398.0509 (398.0477)
9f	4	89	H–E	112–113	$C_{24}H_{16}F_6O_3$	62.2 (61.8)	3.7 (3.4)		466.1012 (466.1004)
9g	6	84	H–E	68–70	$C_{24}H_{22}O_3$				358.1539 (358.1569)
9h	4	74	H–E	124–125	$C_{22}H_{17}NO_5$	70.25 (70.4)	4.5 (4.5)	4.0 (3.75)	375.1095 (375.1107)
9i	2	81	H–E	137–138	$C_{22}H_{17}FO_3$	75.45 (75.85)	4.6 (4.85)		348.1156 (348.1161)
9j	24	76	H–E	127–128	$C_{23}H_{20}O_3$	80.1 (80.2)	5.85 (5.8)		344.1410 (344.1412)
9k	2	78	H–E	156–157	$C_{22}H_{17}ClO_3$	72.3 (72.4)	4.9 (4.65)		364.0870 (364.0866)
9l	10	77	H–E	180–181	$C_{23}H_{20}O_4$	76.3 (76.65)	5.55 (5.55)		360.1377 (360.1362)
9m	6	83	H–E	176–177	$C_{23}H_{17}F_3O_3$	69.1 (69.35)	4.35 (4.25)		398.1095 (398.1130)

[a] Compounds identified in Table 1. [b] H = hexane; E = diethyl ether.

prediction for carbonyl ylides may be because the rationalisation of substituent effects is wholly wrong in the nitrile ylide case, or it may be due to the difference in the nature of the 1,3-dipoles or in the reaction conditions. Several possible explanations in the latter category are discussed below.

Effect of the nature of the substituent on the terminal carbon of the carbonyl ylide.—One plausible possibility was that the presence of the electron withdrawing ester group on the attacking carbon of the carbonyl ylide was affecting or negating the predicted substituent effect. This was tested by cyclising the two compounds **12f** and **12g**, which had a phenyl substituent in place of the ester in the main series. These examples had respectively 3,5-bis(trifluoromethyl) and 3,5-dimethyl substituents in the aromatic ring, both of which had a moderate activating effect on the nitrile ylide cyclisation and a mild deactivating effect on the cyclisation of **11f**,**g**. The relative reactivities (Table 8) were found to be unaffected by the change of substituent and this explanation was therefore discarded.

Reaction mechanism.—Another, more fundamental, possibility was that the mechanisms of the two reactions may differ in the identity of the rate (and hence product ratio) determining step. As discussed above these cyclisation reactions, *e.g.* **25** ⟶ **28**, involve two steps; 1,7 electrocyclisation, followed by a [1,5] sigmatropic hydrogen migration which leads to the product. Mechanistic study of the analogous nitrile ylide cyclisation has shown that the cyclisation step is irreversible[1c] and hence that the selectivity is exerted in this step. In this work on carbonyl ylide cyclisation it has been shown by control reactions that the *overall* process is irreversible, *i.e.* the isomers **13** and **15** do not interconvert under the cyclisation conditions. However this does not rule out the possibility that the first step might be reversible in this case due to the high temperature of the reaction, and thus that the product ratio would be affected by the rate constants of *both* steps. This has been investigated by one of the methods developed in earlier work using the deuteriated reactant **33** (Scheme 4).[6] This was generated in the usual way from the appropriate deuteriated oxirane (98% monodeuteriated). As discussed earlier[5] the application of the steady state approximation to **34** and **36** leads to Eqn. (1) for the product

$$\mathbf{35/37} = (xk_{-1} + k_H)/(k_{-1} + k_H) \quad (1)$$

ratio, where $x = k_H/k_D$. Thus the ratio will be 1 if $k_{-1} = 0$ and will tend to x as $k_{-1} \gg k_H$.

Cyclisation of the carbonyl ylide **33** was carried out under the usual conditions and the mixture of isomers **35** and **37** was isolated by flash column chromatography. Mass spectroscopy of this mixture showed that no deuterium had been lost in either the reaction or work-up. The ^{2}H NMR spectrum showed that the deuterium in the product mixture was located only on C-7 (δ_D 4.37) (compound **37**) and in the aromatic ring (δ_D 7.58) (compound **35**). The integral ratio of these peaks and hence the product ratio was 0.99 ± 0.02 (average from three cyclisations). Thus the cyclisation step is also irreversible in this reaction and the difference in the substituent effects must be due to some other cause.

Since neither of the above hypotheses provide an explanation, then it may be that the difference in substituent effects is simply due to the difference in reaction conditions, *i.e.* the absence of solvation in the carbonyl ylide reaction. This could in principle be investigated experimentally by generating the carbonyl ylides in solution *via* an alternative route. The choice of such a route, however, is not straightforward but it is hoped to do this in future work. More interestingly, it is possible that the difference is due to the intrinsic difference in unsaturation between the two types of 1,3-dipole. This affects the extent of charge delocalisation in the intermediate, *i.e.* **31/32** for the allyl type dipole (*cf.* **29**, **30** for the propargyl–allenyl dipole). Again, assuming a late transition state, the absence of charge delocalisation on to the 'attacking' terminal carbon of the 1,3-dipole of the carbonyl ylide would diminish the effect of any coulombic assistance[2] to cyclisation produced by the polarising effect of the substituents.

The main practical conclusion which can be drawn is that the rate of the 1,7 carbonyl ylide cyclisations is little affected by either the olefinic/aromatic character of the γ,δ bond or whether it is electron rich or electron poor. This fact, combined with the use of the Suzuki coupling to provide an easy route to

Table 5 NMR and IR spectroscopic data for the 2-methoxycarbonyl-3-[(2-phenyl-6-substituted)phenyl]oxiranes **9a**–**m**[a]

Compd.	δ_H	δ_C	ν_{max}/cm^{-1} (C=O)
9a	2.72 (1 H, d, *J* 2.0, 2-H), 3.49 (3 H, s, OCH_3), 4.43 (1 H, d, *J* 2.0, 3-H), 7.32–7.51 (13 H, m, aromatic)	168.5 (CO), 143.1 (q), 140.4 (q), 130.6 (q), 57.7 (C-3), 55.7 (C-2), 51.9 (OCH_3), 129.0, 128.8, 128.3, 128.2, 127.2 (aromatic CH signals)	1695
9b	2.98 (1 H, d, *J* 2.0, 2-H), 3.60 (3 H, s, OCH_3), 4.38 (1 H, d, *J* 2.0, 3-H), 7.08 (1 H, d, *J* 16.1, ethenyl CH), 7.21–7.66 (13 H, m, aromatic), 7.70 (1 H, d, *J* 16.1, ethenyl CH)	168.8 (CO), 142.6 (q), 140.3 (q), 138.2 (q), 137.0 (q), 130.0 (q), 57.1 (C-3), 55.2 (C-2), 52.1 (OCH_3), 131.4, 128.8, 128.6, 128.5, 128.3, 127.8, 127.1, 126.7, 125.6, 124.7 (remaining CH signals), (overlap of one CH signal)	1740
9c	2.8 (1 H, d, *J* 2.0, 2-H), 3.55 (3 H, s, OCH_3), 4.48 (1 H, d, *J* 2.0, 3-H), 7.09–7.24 (3 H, m, aromatic), 7.30–7.49 (8 H, m, aromatic)	168.6 (CO), 143.3 (q), 141.2 (q), 140.3 (q), 135.5 (q), 131.0 (q), 57.4 (C-3), 56.0 (C-2), 52.0 (OCH_3), 129.6, 128.7, 128.4, 128.3, 127.3, 127.0, 125.9 (aromatic CH signals, overlap of 2 CH signals)	1739
9d	2.78 (1 H, d, *J* 2.0, 2-H), 3.55 (3 H, s, OCH_3), 4.43 (1 H, d, *J* 2.0, 3-H), 7.23–7.25 (1 H, m, aromatic), 7.30–7.46 (10 H, m, aromatic)	168.6 (C=O), 143.1 (q), 140.5 (q), 140.4 (q), 137.7 (q), 130.5 (q), 57.4 (C-3), 55.6 (C-2), 52.0 (OCH_3), 129.1, 128.8, 128.7, 128.4, 128.3, 128.2, 127.1, 125.4, 123.1 (aromatic CH signals)	1740
9e	2.74 (1 H, d, *J* 1.9, 2-H), 3.54 (3 H, s, OCH_3), 4.34 (1 H, d, *J* 1.9, 3-H), 7.29–7.50 (11 H, m, aromatic)	168.2 (C=O), 143.5 (q), 143.4 (q), 140.3 (q), 140.0 (q), 134.7 (q), 130.5 (q), 57.1 (C-3), 55.5 (C-2), 52.1 (OCH_3), 129.8, 128.8, 128.7, 128.5, 128.3, 127.4, 127.3 (aromatic CH signals), (overlap of one CH signal)	1740
9f	2.72 (1 H, d, *J* 2.0, 2-H), 3.5 (3 H, s, OCH_3), 4.32 (1 H, d, *J* 2.0, 3 H), 7.29–7.55 (8 H, m, aromatic), 7.88–7.91 (3 H, m, aromatic)	168.0 (C=O), 147.2 (q), 143.6 (q), 142.7 (q), 139.9 (q), 139.8 (q), 130.7 (q), 121.1 (CF_3), 56.9 (C-3), 55.5 (C-2), 52.0 (OCH_3), 130.2, 129.1, 128.9, 128.7, 128.4, 127.6, 125.3 (aromatic CH signals), (overlap of one CH signal)	1745
9g	2.46 [6 H, s, $(CH_3)_2C_6H_3$], 2.82 (1 H, d, *J* 2.0, 2-H), 3.57 (3 H, s, OCH_3), 4.55 (1 H, d, *J* 2.0, 3-H), 7.13 (3 H, br s, aromatic), 7.36–7.54 (8 H, m, aromatic)	168.4 (C=O), 143.1 (q), 142.8 (q), 140.4 (q), 140.2 (q), 137.4 (q), 130.3 (q), 57.5 (C-3), 55.5 (C-2), 51.6 (OCH_3), 21.0 (CH_3), 129.1, 128.7, 128.6, 128.1, 127.7, 127.2, 126.9, 126.4 (aromatic CH signals)	1743
9h	2.72 (1 H, d, *J* 2.0, 2-H), 3.47 (3 H, s, OCH_3), 4.37 (1 H, d, *J* 2.0, 3-H), 7.30–7.80 (10 H, m, aromatic), 8.21–8.30 (2 H, m, aromatic)	168.1 (C=O), 147.9 (q), 143.4 (q), 142.2 (q), 140.4 (q), 139.8 (q), 132.9 (q), 57.1 (C-3), 55.6 (C-2), 52.0 (OCH_3), 134.8, 130.6, 129.7, 129.1, 128.7, 128.6, 128.3, 127.5, 123.6, 122.1 (aromatic CH signals)	1742
9i	2.71 (1 H, d, *J* 2.0, 2-H), 3.50 (3 H, s, OCH_3), 4.36 (1 H, d, *J* 2.0, 3-H), 7.09–7.20 (4 H, m, aromatic), 7.24–7.50 (8 H, m, aromatic)	168.5 (C=O), 164.1 (q), 143.1 (q), 142.0 (q), 140.3 (q), 136.5 (q), 130.5 (q), 115.0 (q), 57.5 (C-3), 55.7 (C-2), 51.9 (OCH_3), 130.4, 130.3, 129.1, 128.7, 128.4, 128.2, 127.3 (remaining aromatic CH signals)	1739
9j	2.42 (3 H, s, 4-$CH_3C_6H_4$), 2.71 (1 H, d, *J* 2.0, 2-H), 3.48 (3 H, s, OCH_3), 4.42 (1 H, d, *J* 2.0, 3 H), 7.24–7.46 (12 H, m, aromatic)	168.5 (C=O), 143.1 (q), 143.0 (q), 140.5 (q), 137.5 (q), 136.8 (q), 130.5 (q), 57.7 (C-3), 55.6 (C-2), 51.7 (OCH_3), 20.9 (CH_3), 129.0, 128.8, 128.7, 128.6, 128.2, 128.1, 127.1 (aromatic CH signals), (overlap of one signal)	1736
9k	2.71 (1 H, d, *J* 2.0, 2-H), 3.51 (3 H, s, OCH_3), 4.38 (1 H, d, *J* 2.0, 3-H), 7.28–7.50 (12 H, m, aromatic)	168.4 (C=O), 143.1 (q), 141.8 (q), 140.2 (q), 138.9 (q), 133.3 (q), 130.5 (q), 57.5 (C-3), 55.6 (C-2), 52.0 (OCH_3), 130.1, 129.2, 128.9, 128.7, 128.4,128.3, 128.2, 127.3 (aromatic CH signals)	1738
9l	2.7 (1 H, d, *J* 2.0, 2-H), 3.50 (3 H, s, OCH_3), 3.86 (3 H, s, 4-$CH_3OC_6H_4$), 4.42 (1 H, d, *J* 2.0, 3-H), 6.98 (2 H, d, *J* 8.8, aromatic), 7.30–7.48 (10 H, m, aromatic)	168.6 (C=O), 158.8 (q), 143.0 (q), 142.8 (q), 140.5 (q), 132.8 (q), 130.6 (q), 57.7 (C-3), 55.7 (C-2), 55.0 (4-$CH_3OC_6H_4$), 51.8 (OCH_3), 129.8, 129.0, 128.7, 128.6, 128.3, 128.2, 127.1, 113.6 (aromatic CH signals)	1743
9m	2.71 (1 H, d, *J* 2.0, 2-H), 3.48 (3 H, s, OCH_3), 4.38 (1 H, d, *J* 2.0, 3-H), 7.30–7.57 (10 H, m, aromatic), 7.70–7.73 (2 H, m, aromatic)	168.4 (C=O), 144.2 (q), 143.3 (q), 141.5 (q), 140.1 (q), 136.6 (q), 125.2 (CF_3), 57.4 (C-3), 55.5 (C-2), 52.0 (OCH_3), 129.6, 129.1, 128.9, 128.7, 128.5, 128.3, 127.4 (aromatic CH signals)	1740

[a] Compounds identified in Table 1.

the reactants, makes this a wide ranging and effective synthetic route to fused oxepines.

Experimental

NMR spectra were run as solutions in deuteriochloroform at 298 K unless otherwise stated. Chemical shifts are recorded as δ values and *J* values are given in Hz. In the ^{13}C spectra, carbon multiplicity was established by DEPT. Mass spectra were obtained using electron ionisation at 70 eV. Preparative chromatography was carried out by the 'dry column flash' technique[7] using silica gel (15 μm, Fluka Kieselgel GF254) and eluting solvents based on hexane admixed with diethyl ether. Ether refers to diethyl ether. Evaporation of solvents indicates evaporation under reduced pressure using a rotary evaporator. All drying of solutions was done with anhydrous magnesium sulfate.

Solvents, reagents and starting materials

Tetrahydrofuran (THF) was distilled under nitrogen from sodium diphenyl ketyl immediately before use. 1,2-Dimethoxyethane (DMF) was passed through a column of activated alumina immediately before use. The arylboronic acids used in the coupling reactions were all obtained from either Aldrich Chemical Company or Lancaster Synthesis.

General method for flash vacuum pyrolysis (FVP)

The appropriate oxirane was distilled (150–180 °C) at 1×10^{-4} mmHg through a furnace tube (35 × 2.5 cm) which was maintained at 625 °C. The product was collected in a U-tube which was cooled by liquid nitrogen and situated at the exit of the furnace.

Preparation of the 2-phenyl-6-substituted-benzaldehydes 19a–m

2-Bromo-6-phenylbenzaldehyde 18. Sodium (0.74 g, 0.032 mol) was dissolved in absolute ethanol (100 cm^3), 2-nitropropane (3.36 g, 0.037 mol) was added and the solution was stirred for 1 h. 2-Bromo-6-phenylbenzylbromide[2] **17** (3.82 g, 0.012 mol) was added and stirring continued for 72 h. The

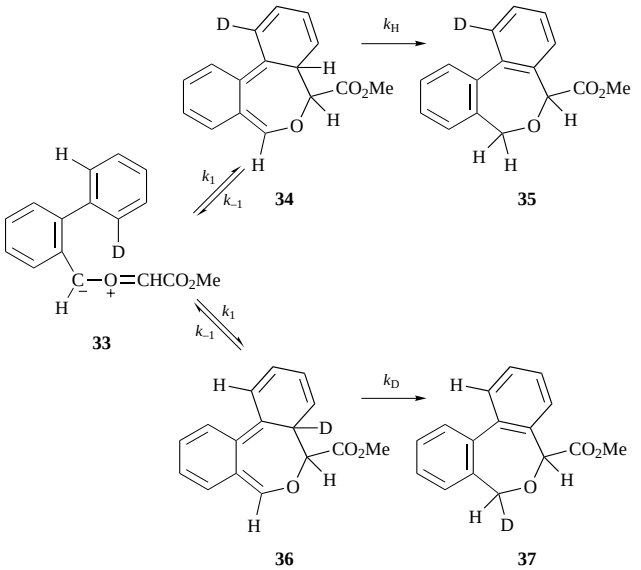
Table 6 Yields and physical data for the 5-methoxycarbonyl-8-substituted-5,7-dihydrodibenzo[*c*,*e*]oxepines **15b**–**m**[a]

Compd.	Reaction time/h	Yield (%)	Cryst. solvent[b]	Mp/°C	Molecular formula	Found (calc.) (%) C	H	M^+
15b	24	86	H	135–136	$C_{24}H_{20}O_3$	81.1 (80.9)	5.9 (5.6)	356.1436 (356.1412)
15c	24	80	H–E	117–118	$C_{20}H_{16}O_3S$	71.1 (71.4)	4.5 (4.75)	336.0806 (336.0820)
15d	24	76		oil	$C_{20}H_{16}O_3S$			336.0806 (336.0820)
15e	8	84	H–E	87–90	$C_{22}H_{16}Cl_2O_3$	66.6 (66.2)	4.05 (4.0)	398.0480 (398.0477)
15f	4	65		oil	$C_{24}H_{16}F_6O_3$	62.1 (61.8)	3.3 (3.4)	446.1027 (446.1004)
15g	8	74		oil	$C_{24}H_{22}O_3$			358.1568 (358.1569)
15h	8	77	H–E	115–116	$C_{22}H_{17}NO_5$			375.1084 (375.1107)
15i	4	67	H	119–120	$C_{22}H_{17}FO_3$			348.1160 (348.1162)
15j	2	80	H	169–170	$C_{23}H_{20}O_3$	79.9 (80.2)	6.0 (5.8)	344.1410 (344.1413)
15k	3	62	H	155–156	$C_{22}H_{17}ClO_3$	72.55 (72.5)	4.9 (4.65)	364.0888 (364.0866)
15l	2	80	H–E	138–139	$C_{23}H_{20}O_4$	76.3 (76.65)	5.6 (5.55)	360.1355 (360.1362)
15m	4	91	H–EA	139–140	$C_{23}H_{17}F_3O_3$			398.1130 (398.1130)

[a] Compounds identified in Table 1. [b] H = hexane; E = diethyl ether; EA = ethyl acetate.

ethanol was evaporated and the residue was dissolved in ether (50 cm^3). The solution was washed with water (2 × 50 cm^3), dried and the solvent was evaporated. Dry flash chromatography (silica, hexane–ether, 80:20) of the residue gave 6-bromo-2-phenylbenzaldehyde as a yellow oil (2.3 g, 82%) which solidified on standing, mp 51–52 °C (Found: C, 60.2; H, 3.5. $C_{13}H_9BrO$ requires C, 60.0; H, 3.45%) (HRMS: found M^+, 259.9814. $C_{13}H_9{}^{79}BrO$ requires *M*, 259.9837); δ_H 7.23–7.48 (6 H, m, aromatic), 7.54–7.70 (2 H, m, aromatic) and 9.97 (1 H, s, CHO); δ_C 191.8 (CHO), 146.4 (q, C-1), 137.7 (q, C-2), 122.5 (q, C-6), 128.6 (q, C-1, phenyl), 133.2, 132.5, 130.0, 129.3, 128.2 and 128.0 (remaining CH aromatics); ν_{max}(Nujol)/cm^{-1} 1706 (C=O).

Compounds **19a**–**m** were prepared from the 2-bromo-6-phenylbenzaldehyde **18** using the general method given in detail for 2,6-diphenylbenzaldehyde **19a**. Reaction times, yields and the physical properties of the products are given in Table 2 and their spectroscopic properties in Table 3.



Scheme 4

2,6-Diphenylbenzaldehyde 19a. 2-Bromo-6-phenylbenzaldehyde **18** (1.5 g, 5.75 mmol) and tetrakis(triphenylphosphine)-palladium (0.2 g, 3%) in 1,2-dimethoxyethane (DME) (15 cm^3) were stirred for 20 min. A solution of phenylboronic acid (0.73 g, 6.0 mmol) and sodium carbonate (0.63 g, 6 mmol) in water (10 cm^3) was added and the mixture heated at reflux for 3 h. After evaporation of the DME, dichloromethane (50 cm^3) was added and the organic layer was separated, dried and filtered through a pad of activated alumina. The solvent was evaporated and the residue was crystallised from hexane to give 2,6-diphenylbenzaldehyde (1.2 g, 81%).

Preparation of the 2-(methoxycarbonyl)-3-[(2-phenyl-6-substituted)phenyl]oxiranes 9a–m

Compounds **9a**–**m** were prepared from the corresponding 2-phenyl-6-substituted-benzaldehydes **19a**–**m** using the general method given in detail for 2-(methoxycarbonyl)-3-[(2,6-diphenyl)phenyl]oxirane **9a**. Reaction times, yields and the physical properties of the products are given in Table 4 and their spectroscopic properties in Table 5.

2-(Methoxycarbonyl)-3-[(2,6-diphenyl)phenyl]oxirane 9a. A solution of 2,6-diphenylbenzaldehyde **19a** (0.75 g, 2.90 mmol) and methyl chloroacetate (0.94 g, 8.66 mmol) in dry THF (25 cm^3), under dry nitrogen, was treated with sodium methoxide (0.40 g, 7.40 mmol) and heated under reflux for 5 h. The THF was evaporated and the residue was dissolved in dichloromethane (50 cm^3) and washed with water (2 × 20 cm^3). The dichloromethane solution was dried and passed through a pad of activated alumina. Evaporation of the solvent and crystallisation of the residue from hexane–ether gave the product **9a** as a white crystalline solid (0.82 g, 85%).

Preparation of the 5-methoxycarbonyl-8-substituted-5,7-dihydrodibenz[*c*,*e*]oxepines 15b–m

Compounds **15b**–**m** were prepared by the route shown in Scheme 2. The general method used for the final step is given in detail for the first example **15b**. Reaction times, yields and the physical properties of the products **15b**–**m** are given in Table 6, and their spectroscopic properties in Table 7.

2-Methoxycarbonyl-3-[(2-bromo-6-phenyl)phenyl]oxirane 20. This compound was prepared from 2-bromo-6-phenyl-

Table 7 NMR and IR spectroscopic data for the 5-methoxycarbonyl-8-substituted-5,7-dihydrobenzoxepines **15b**–**m**[a]

Compd.	δ_H[b]	δ_C[c]	ν_{max}/cm^{-1} (C=O)
15b	3.50 (3 H, s, OCH_3), 4.62 (2 H, br s, 7-$H_{ax,eq}$), 5.09 (1 H, s, 5-H), 7.11 (1 H, d, *J* 16.1, ethenyl CH), 7.22–7.68 (13 H, m, aromatic); ([$^2H_6$]DMSO) 3.20 (3 H, s, CH_3), 4.28 (1 H, d, *J* 12.2, 7-H_{ax}), 4.75 (1 H, d, 7-H_{eq}), 5.22 (1 H, s, 5-H), 6.77–7.69 (14 H, m, aromatic/phenyl ethenyl CH)	172.0 (C=O), 141.3 (q), 141.0 (q, broad), 137.5 (q), 137.1 (q), 136.9 (q), 132.9 (CH), 132.6 (CH), 132.0 (q, broad), 129.4, 129.0, 128.9, 128.5, 128.4, 127.9, 127.8, 127.3, 126.6, 126.2 (CH), 62.6 (C-7), 51.9 (OCH_3);[d] ([$^2H_6$]DMSO) 171.5 (C=O), 141.3 (q), 140.0 (q), 137.1 (q), 133.7 (q), 132.7 (CH), 132.3 (CH), 132.1 (q), 129.6, 129.4, 129.0, 128.8, 128.0, 127.0, 126.9, 126.4, 126.2, 125.5 (CH), 76.2 (C-5), 61.7 (C-7), 51.5 (OCH_3)	1732
15c	3.43 (3 H, s, OCH_3), 4.40 (1 H, d, *J* 11.5, 7-H_{ax}), 4.51 (1 H, d, 7-H_{eq}), 5.17 (1 H, s, 5-H), 7.12–7.16 (1 H, m, aromatic), 7.36–7.61 (9 H, m, aromatic)	172.0 (C=O, br), 141.7 (q), 141.1 (q), 135.3 (q), 133.7 (q, br), 132.5 (q), 131.8 (q, Br), 130.3, 129.5, 128.7, 128.6, 128.0, 127.8, 127.6, 127.0, 125.7 (overlap of one aromatic CH signal), 64.1 (C-7), 51.9 (OCH_3)[d]	1729
15d	3.41 (3 H, s, OCH_3), 4.35 (1 H, d, *J* 12.0, 7-H_{ax}), 4.56 (1 H, d, 7-H_{eq}), 5.17 (1 H, s, 5-H), 7.29–7.79 (10 H, m, aromatic)	172.1 (C=O, br), 141.6 (q), 140.6 (q), 137.4 (q), 137.0 (q), 133.7 (q), 133.4 (q), 129.4, 128.9, 128.7, 128.4, 128.0, 126.5, 126.1, 125.9, 123.6, 119.6 (CH), 64.2 (C-7), 51.8 (OCH_3)[d]	1731
15e	3.39 (3 H, s, OCH_3), 4.23 (1 H, d, *J* 11.9, 7-H_{ax}), 4.45 (1 H, d, H_{eq}), 5.18 (1 H, s, 5-H), 7.31–7.60 (10 H, m, aromatic)	171.9 (C=O, br), 143.1 (q), 141.5 (q), 139.8 (q), 134.8 (q), 134.7 (q), 132.6 (q, br), (one quaternary signal not seen), 129.6, 129.5, 128.9, 128.7, 128.2, 127.8, 127.7, 127.5, 127.4 (CH), 77.1 (C-5), 63.6 (C-7), 51.9 (OCH_3)	1733
15f	3.36 (3 H, s, OCH_3), 4.20 (1 H, d, *J* 12.0, 7-H_{ax}), 4.51 (1 H, d, 7-H_{eq}), 5.24 (1 H, s, 5-H), 7.38–7.62 (8 H, m, aromatic), 7.94 (1 H, br s, aromatic), 8.28 (1 H, br s, aromatic)	171.9 (C=O, br), 142.3 (q), 141.8 (q), 139.4 (q), 139.2 (q), 133.7 (q, br), 132.5 (q), 131.8 (q), 129.7, 129.6, 129.1, 128.8, 128.2, 127.9, 127.0 (overlap of two aromatic CH peaks) 121.1 (CF_3), 63.6 (C-7), 51.8 (OCH_3)[d] ([$^2H_6$]DMSO) 172.2 (C=O), 142.6 (q), 141.6 (q), 139.3 (q), 138.9 (q), 134.1 (q), 132.4 (q), 131.3 (q), 130.3, 130.1, 130.0, 129.9, 121.2 (CF_3), 129.8, 129.5, 129.0, 128.3, 128.1 (CH), 76.8 (C-5), 63.4 (C-7), 51.6 (OCH_3)	1736
15g	2.42 (6 H, s, CH_3), 3.48 (3 H, s, OCH_3), 4.35 (1 H, d, *J* 11.6, 7-H_{ax}), 4.50 (1 H, d, 7-H_{eq}), 5.19 (1 H, s, 5-H), 7.36–7.61 (10 H, m, aromatic)	171.9 (C=O, br), 142.8 (q), 141.1 (q), 140.1 (q), 137.9 (q), 137.6 (q), 133.4 (q, br), 132.0 (q, br), 129.9, 129.3, 128.8, 128.4, 128.3, 128.1, 127.2, 126.5, 124.9, 63.9 (C-7), 51.8 (OCH_3), 21.3 (CH_3)[d]	1730
15h	3.49 (3 H, s, CH_3), 4.23 (1 H, d, *J* 11, 7-H_{ax}), 4.41 (1 H, d, 7-H_{eq}), 5.21 (1 H, s, 5-H), 7.25–7.71 (9 H, m, aromatic), 8.17–8.27 (2 H, m, aromatic)		1733
15i	3.42 (3 H, s, CH_3), 4.26 (1 H, d, *J* 11.8, 7-H_{ax}), 4.45 (1 H, d, 7-H_{eq}), 5.18 (1 H, s, 5-H), 7.20–7.69 (11 H, m, aromatic)		1738
15j	2.43 (3 H, s, CH_3), 3.45 (3 H, s, OCH_3), 4.33 (1 H, d, *J* 11.7, 7-H_{ax}), 4.49 (1 H, d, 7-H_{eq}), 5.18 (1 H, s, 5-H), 7.30–7.60 (11 H, m, aromatic)	172.0 (C=O, br), 142.5 (q), 141.3 (q), 140.5 (q, br), 137.3 (q), 136.9 (q), 133.4 (q, br), 132.0 (q, br), 129.9, 129.4, 129.3, 128.9, 128.7, 128.6, 128.4, 128.1, 126.5, 77.1 (C-5, br), 64.1 (C-7), 51.8 (OCH_3), 21.1 (CH_3)	1735
15k	3.41 (3 H, s, OCH_3), 4.25 (1 H, d, *J* 11.7, 7-H_{ax}), 4.44 (1 H, d, 7-H_{eq}), 5.18 (1 H, s, 5-H), 7.35–7.65 (11 H, m, aromatic)	172.0 (C=O, br), 141.4 (q), 141.3 (q), 141.0 (q, br), 138.6 (q), 133.4 (q), 132.3 (q, br), 130.7, 129.7, 129.5, 128.8, 128.5, 128.4, 128.2, 126.9, (overlap of one aromatic CH signal), 63.9 (C-7), 51.9 (OCH_3)[d]	1744
15l	3.44 (3 H, s, OCH_3), 3.86 (3 H, s, $ArOCH_3$), 4.31 (1 H, d, *J* 11.6, 7-H_{ax}), 4.47 (1 H, d, 7-H_{eq}), 5.18 (1 H, s, 5-H), 7.0–7.62 (11 H, m, aromatic)	172.1 (C=O, br), 158.9 (q), 142.2 (q), 141.3 (q), 132.6 (q), (remaining quaterenary carbons were not seen due to being too broad), 130.5, 129.9, 129.4, 128.6, 128.4, 128.1, 126.3, 113.6, 64.2 (C-7), 55.1 (OCH_3), 51.9 (OCH_3)[d]	1733
15m	3.42 (3 H, s, OCH_3), 4.25 (1 H, d, *J* 11.9, 7-H_{ax}), 4.44 (1 H, d, *J* 11.9, 7-H_{eq}), 5.20 (1 H, s, 5-H), 7.25–7.84 (11 H, m, aromatic)		

[a] Compounds identified in Table 1. [b] At 328 K and in $CDCl_3$ unless otherwise stated. [c] At 298 K and in $CDCl_3$ unless otherwise stated. [d] C-5 peak broad and obscured by $CDCl_3$ peaks.

benzaldehyde **18** (1.8 g, 6.9 mmol), methyl chloroacetate (2.6 g, 24.1 mmol) and sodium methoxide (1.11 g, 20.55 mmol) by the method given above for **9a**, with a reaction time of 6 h. The product **20** was crystallised from hexane–ether (80:20) as a white solid (1.75 g, 76%), mp 107–108 °C, from hexane–ether (90:10) (Found: C, 57.8; H, 3.95%; M^+, 332.0036. $C_{16}H_{13}BrO_3$ requires C, 57.65; H, 3.9%; *M*, 332.0048); δ_H 3.0 (1 H, d, *J* 2.0, 2-H), 3.67 (3 H, s, OCH_3), 4.32 (1 H, d, *J* 2.0, 3-H) and 7.29–7.61 (8 H, m, aromatic); δ_C 168.4 (C=O), 144.0 (q), 139.6 (q), 132.1 (q), 124.7 (q), 131.6, 129.5, 129.2, 128.4, 128.2, 127.5 (CH), 57.9 (C-3), 55.8 (C-2) and 52.2 (OCH_3); ν_{max}(Nujol)/cm^{-1} 1730 (C=O).

4-Bromo-7-methoxycarbonyl-5,7-dihydrodibenz[*c*,*e*]oxepine 23. The oxirane **20** (0.25 g, 0.75 mmol) on FVP (distillation temperature 130–160 °C, time 1 h) followed by dry flash chromatography (silica, hexane–ether, 90:10) gave compound **23** as a white solid (0.16 g, 64%) mp 141–142 °C (Found: C, 57.4; H, 3.6%; M^+, 332.0057. $C_{16}H_{13}BrO_3$ requires C, 57.65; H, 3.9%; *M*, 332.0057); δ_H(328 K) 3.48 (3 H, s, CH_3), 4.62 (1 H, d, *J* 12, 7-H_{ax}), 4.76 (1 H, d, *J* 12, 7-H_{eq}), 5.05 (1 H, s, 5-H), 7.23–7.66 (7 H, m, aromatic); δ_C 171.3 (C=O), 142.6 (q), 139.6 (q), 133.8 (q), 133.1 (q), 125.1 (q), 132.5, 130.0, 129.5, 128.9, 127.8, 126.9 (CH), (overlap of one CH signal), 76.6 (C-5), 65.9 (C-7) and 52.0 (CH_3); ν_{max}(Nujol)/cm^{-1} 1723 (C=O).

(*E*)-5-Methoxycarbonyl-8-(phenylethenyl)-5,7-dihydrodibenz-[*c*,*e*]oxepine 15b. 4-Bromo-7-methoxycarbonyl-5,7-dihydrodibenz[*c*,*e*]oxepine **23** (0.25 g, 0.75 mmol) and (*E*)-2-phenylethenylboronic acid[8] (0.32 g, 2.16 mmol) were coupled using the method given above for **19a**, with a reaction time of 24 h. The product **15b** (0.23 g, 86%) was crystallised from hexane.

Table 8 Product ratios from the pyrolysis of the oxiranes **9b–m** and **10f,g**

Substituent	Oxiranes **9**		Oxiranes **10**		Nitrile ylide product ratio **5**:**4**[2]
	Prod. ratio **13**:**15**	Yield (%)	Prod. ratio **14**:**16**	Yield (%)	
b (*E*)-2-Phenylethenyl	20	65			>100
c 2-Thienyl	9	70			>100
d 3-Thienyl	8	75			
e 3,5-Dichlorophenyl	1.5	75			
f 3,5-Bis(trifluoromethyl)phenyl	0.7	70	(f) 0.7	75	32.0
g 3,5-Dimethyphenyl	0.8	70	(g) 0.9	75	8.3
h 3-Nitrophenyl	1.3 (2′/6′ = 3.7)	70			>100
i 4-Fluorophenyl	1.2	70			1.2
j 4-Methylphenyl	1.3	75			1.5
k 4-Chlorophenyl	1.2	70			2.2
l 4-Methoxyphenyl	1.2	75			1.6
m 4-Trifluoromethylphenyl	1.3	80			2.8

Table 9 ^{1}H NMR spectral data on the products of the pyrolysis of the oxiranes **9b–m** and **10f,g**

Reactant	^{1}H NMR data [δ (*J* Hz)] at 328 K		
	Product(s)	5-H (s)	7-H, 7′-H
9b	**15b**	5.09	4.62 (br)
	13b	5.37	4.65, 4.85 (d, *J* 12.5)
9c	**15c**	5.17	4.40, 4.51 (d, *J* 11.5)
	13c	5.48	4.60, 4.71 (d, *J* 12.9)
9d	**15d**	5.17	4.38 (br), 4.55 (br)
	13d	5.48	superimposed on **15d**
9e	**15e**	5.18	4.23, 4.45 (d, *J* 11.9)
	13e	6.00	4.03, 4.73 (d, *J* 12.9)
9f	**15f**	5.24	4.20, 4.50 (d, *J* 12.0)
	13f	5.80	4.00, 4.82 (d, *J* 12.0)
9g	**15g**	5.22	4.35, 4.50 (d, *J* 11.6)
	13g	5.68	4.10, 4.73 (d, *J* 11.6)
9h	**15h**	5.22	4.28, 4.45 (d, *J* 11.7)
	(2-NO_2)	5.20	4.23, 4.56 (d, *J* 12.0)
	13h		
	(4-NO_2)	5.26	obscured
9i	**15i**	5.19	4.27, 4.48 (d, *J* 11.8)
	13i	5.14	4.31, 4.46 (d, *J* 11.6)
9j	**15j**	5.20	4.33, 4.49 (d, *J* 11.7)
	13j	5.17	superimposed on **15j**
9k	**15k**	5.19	4.27, 4.47 (d, *J* 11.7)
	13k	5.15	4.28, 4.52 (d, *J* 11.6)
9l	**15l**	5.20	4.31, 4.47 (d, *J* 11.6)
	13l	5.17	superimposed on **15l**
9m	**15m**	5.21	4.26, 4.46 (d, *J* 11.9)
	13m	5.25	3.94, 4.56 (d, *J* 12.0)
10f	**16f**	5.55	4.16, 4.62 (d, *J* 11.9)
	14f	6.55	4.17, 5.02 (d, *J* 12.0)
10g	**16g**	5.63	4.21, 4.87 (d, *J* 11.5)
	14g	6.37	4.34, 4.86 (d, *J* 12.0)

Preparation of 2-phenyl-3-[2-phenyl-6-(substituted)phenyl]-oxiranes 10f,g

These were prepared by the route shown in Scheme 2.

(*E*)-1-Phenyl-2-{2-phenyl-6-[3,5-bis(trifluoromethyl)phenyl]}-ethene 22f. 2-Phenyl-6-[3,5-bis(trifluoromethyl)phenyl]benzaldehyde **19f** (0.8 g, 2.03 mmol), in DME (10 cm^3) was added over 1 h to a solution of diethyl benzylphosphonate (0.55 g, 2.41 mmol) and sodium hydride (0.1 g; 60% in oil). The solution was stirred at room temp. for 12 h. Evaporation of the solvent and dry flash chromatography (silica, hexane–ether, 70:30) of the residue gave the product (0.93 g, 97%) as a colourless oil (HRMS: found M$^+$, 468.1311. $C_{28}H_{18}F_6$ requires *M*, 468.1313); HPLC analysis showed the *E*:*Z* ratio to be >98:1; δ_H 6.0 (1 H, d, *J* 16.3, ethenyl CH), 6.78 (1 H, d, *J* 16.3, ethenyl CH) and 6.9–7.9 (16 H, m, aromatic).

(*E*)-1-Phenyl-2-[2-phenyl-6-(3,5-dimethylphenyl)phenyl]-ethene 22g. 2-Phenyl-6-(3,5-dimethylphenyl)benzaldehyde **19g** (0.4 g, 1.4 mmol), in DMF (10 cm^3) was added over 10 min to a solution of diethyl benzylphosphonate (0.35 g, 1.53 mmol) and sodium ethoxide (0.1 g, 1.47 mmol) in DMF (15 cm^3), under nitrogen. The solution was stirred at room temperature for 2 h and worked up as for **22f** to give the product as a yellow oil (0.4 g, 79%) (HRMS: found M$^+$, 360.1878. $C_{28}H_{24}$ requires *M*, 360.1871); δ_H 2.39 (s, 6 H, 2 × CH_3), 6.06 (1 H, d, *J* 16.7, ethenyl CH), 6.88 (1 H, d, *J* 16.7, ethenyl CH), 7.02–7.47 (16 H, m, aromatic).

2-Phenyl-3-{2-phenyl-6-[3,5-bis(trifluoromethyl)phenyl]-phenyl}oxirane 10f. A solution of (*E*)-1-phenyl-2-{2-phenyl-6-[3,5-bis(trifluoromethyl)phenyl]}ethene **22f** (0.5 g, 1.06 mmol) and *m*-chloroperbenzoic acid (80%; 0.7 g, 3.24 mmol) in dichloromethane was stirred at room temperature for 48 h. The solution was washed with aqueous sodium carbonate (5% w/v; 2 × 30 cm^3), dried and the solvent was evaporated to give the product as a colourless oil which was crystallised to give a white solid (0.3 g, 82%, mp 57–58 °C from hexane) (Found: C, 69.35; H, 3.75%; M$^+$, 484.1266. $C_{28}H_{18}F_6O$ requires C, 69.4; H, 3.7%; *M*, 484.1262); δ_H 3.15 (1 H, d, *J* 2.1, 2-H), 4.10 (1 H, d, *J* 2.1, 3-H), 6.51–6.56 (2 H, m, aromatic), 7.11–7.57 (10 H, m, aromatic) and 8.0–8.08 (4 H, m, aromatic); δ_C 143.4 (q), 143.3 (q), 140.4 (q), 140.3 (q), 135.8 (q), 132.8 (q), 131.2 (q), 130.2, 129.4, 129.0, 128.9, 128.5, 128.4, 127.9, 127.8, 127.7, 127.4, 124.7, 120.9 (CF_3), 61.6 (C-3) and 61.4 (C-2). The ^{1}H NMR spectrum also showed the presence of a small quantity of a second isomer with absorptions at δ_H 4.52 (1 H, d, *J* 2.5, 2-H) and 4.87 (1 H, d, *J* 2.5, 3-H).

2-Phenyl-3-[2-phenyl-6-(3,5-dimethylphenyl)phenyl]oxirane 10g. A solution of (*E*)-1-phenyl-2-[2-phenyl-6-(3,5-dimethylphenyl)phenyl]ethene **22g** (0.35 g, 0.97 mmol) and *m*-chloroperbenzoic acid (80%; 0.34 g, 1.67 mmol) in dry dichloromethane (30 cm^3) was stirred at room temperature for 48 h. The solution was washed with aqueous sodium carbonate (5% w/v; 2 × 30 cm^3), dried and the solvent was evaporated to give the product as a yellow oil (0.3 g, 82%) (HRMS: found M$^+$, 376.1830. $C_{28}H_{24}O$ requires *M*, 376.1827); δ_H 2.3 (6 H, s, 2 × CH_3), 3.21 (1 H, d, *J* 2.1, 2-H), 4.18 (1 H, d, *J* 2.1, 3-H), 6.57–6.62 (2 H, m, aromatic) and 7.1–7.56 (14 H, m, aromatic); δ_C 143.4 (q), 143.3 (q), 141.4 (q), 141.0 (q), 137.7 (q), 136.6 (q), 132.4 (q), 129.0, 128.9, 128.6, 128.2, 127.9, 127.5, 127.0, 126.4, 125.0, 62.3 (C-3), 61.2 (C-2) and 21.1 (CH_3).

Preparation of the 5-phenyl-8-substituted-5,7-dihydrodibenz-[*c*,*e*]oxepines 16f,g

These compounds were prepared by the route shown in Scheme 2.

(*E*)-2-Bromo-6-phenylstilbene. 2-Bromo-6-phenylbenzaldehyde **18** (1.0 g, 3.86 mmol), in DMF (5 cm^3) was added over 10 min to a solution of diethyl benzylphosphonate (1.22 g, 5.34 mmol) and sodium methoxide (0.29 g, 5.37 mmol) in DMF (50 cm^3). The solution was stirred at room temperature for 2 h. Evaporation of the solvent, dry flash chromatography (silica, hexane–ether, 70:30) of the residue and crystallisation from hexane gave the product (1.1 g, 85%) as a white solid, mp 74.5–75.5 °C (HRMS: found M$^+$, 334.0364, 336.0333. $C_{20}H_{15}Br$ requires *M*, 334.0357, 336.0338); δ_H 6.37 (1 H, d, *J* 16.5), 7.02 (1

H, d, *J* 16.5), 7.2–7.4 (12 H, m, aromatic) and 7.63 (1 H, dd, *J* 8.1, 1.2, aromatic).

2-Phenyl-3-[(2-bromo-6-phenyl)phenyl]oxirane 21. Reaction of (*E*)-2-bromo-6-phenylstilbene (2.5 g, 7.46 mmol) and *m*-chloroperbenzoic acid (80%; 6.4 g, 11.92 mmol) using the method described for **22f** gave **21** as a colourless oil (0.3 g, 82%) bp 180–190 °C/0.5 mmHg (Found: C, 68.15; H, 4.45%; M^+, 350.0336. $C_{20}H_{15}BrO$ requires C, 68.4; H, 4.25%; *M*, 350.0306); δ_H 3.40 (1 H, d, *J* 2.1, 2-H), 4.05 (1 H, d, *J* 2.1, 3-H), 4.57 (1 H, d, *J* 2.3, 2-H), 5.47 (1 H, d, *J* 2.3, 3-H), (mixture of isomers, ratio *ca*. 1:5 respectively) and 6.89–7.93 (13 H, m, aromatic).

4-Bromo-7-phenyl-5,7-dihydrodibenz[*c*,*e*]oxepine 24. The oxirane **21** (0.25 g, 0.71 mmol) on FVP (distillation temperature 150–180 °C, time 1 h) followed by dry flash chromatography (silica, hexane–ether, 90:10) gave compound **24** (0.15 g, 75%) as a white solid, mp 141–142 °C (Found: C, 68.5; H, 4.6%; M^+, 350.0303. $C_{20}H_{15}BrO$ requires C, 68.4; H, 4.3%; *M*, 350.0306); δ_H(297 K) 4.33 (1 H, d, *J* 11.7, 7-H_{ax}), 5.21 (1 H, d, *J* 11.7, 7-H_{eq}), 5.39 (1 H, s, 5-H), 6.86 (1 H, m, aromatic), 7.28–7.53 (10 H, m, aromatic) and 7.64–7.67 (1 H, m, aromatic); δ_C 143.3 (q), 140.2 (q), 139.6 (q), 137.8 (q), 133.9 (q), 124.6 (q), 132.3, 129.7, 129.4, 128.7, 128.4, 128.3, 127.9, 127.5, 127.3, 126.8 (CH), 77.1 (C-5) and 66.3 (C-7).

5-Phenyl-8-[3,5-bis(trifluoromethyl)phenyl]-5,7-dihydrodibenz[*c*,*e*]oxepine 16f. 4-Bromo-7-phenyl-5,7-dihydrodibenz-[*c*,*e*]oxepine **24** (0.1 g, 0.28 mmol) and 3,5-bis(trifluoromethyl)benzeneboronic acid (0.1 g, 0.36 mmol) were coupled using the method described for **19a** with a reaction time of 10 h to give **16f** (0.11 g, 80%) as an oil (HRMS: found M^+, 484.12602. $C_{28}H_{18}F_6O$ requires *M*, 484.12618); δ_H(297 K) 4.18 (1 H, d, *J* 11.9, 7-H_{ax}), 4.64 (1 H, d, *J* 11.9, 7-H_{eq}), 5.55 (1 H, s, 5-H), 6.89 (1 H, d, aromatic) and 7.34–8.04 (14 H, m, aromatic); δ_C 142.7 (q), 142.3 (q), 140.6 (q), 139.7 (q), 139.2 (q), 137.9 (q), 132.3 (q), 131.2 (q), 129.7, 129.5, 129.4, 129.1, 129.0, 128.8, 128.4, 128.0, 127.9, 127.7, 127.3, 127.2 (CH), 121.1 (CF_3), 77.1 (C-5) and 63.7 (C-7).

5-Phenyl-8-(3,5-dimethylphenyl)-5,7-dihydrodibenz[*c*,*e*]-oxepine 16g. 4-Bromo-7-phenyl-5,7-dihydrodibenz[*c*,*e*]oxepine **24** (0.1 g, 0.28 mmol) and 3,5-dimethylphenylboronic acid (0.08 g, 0.56 mmol) were coupled using the method described for **19a** with a reaction time of 10 h to give **16g** (0.09 g, 85%) as an oil (HRMS: found M^+, 376.1835. $C_{28}H_{24}O$ requires *M*, 376.1827); δ_H(297 K) 2.42 (6 H, s, 2 × CH_3), 4.21 (1 H, d, *J* 11.5, 7-H_{ax}), 4.87 (1 H, d, *J* 11.5, 7-H_{eq}), 5.63 (1 H, s, 5-H) and 6.64–7.74 (15 H, m, aromatic).

Intramolecular competition reactions of the carbonyl ylides 11b–m and 12f,g *via* FVP of the oxiranes 9b–m and 10f,g

General method. Using the general FVP method specified earlier, the reactant (*ca*. 0.2 g) was distilled into the furnace tube (625 °C) over 1 h using an inlet temperature of 150–180 °C. The ratio of the cyclised products (**13**:**15** and **14**:**16**, Table 8), was measured from the crude product mixture by two methods; (i) ^{1}H NMR spectroscopy (200 or 360 MHz) at 328 K *via* comparative integration of the 5-H absorptions, and (ii) HPLC using a 5 μm silica column (250 × 4.6 mm), eluting with hexane for the products from **10f**,**g**, or with hexane–ether (80:20 to 90:10 as appropriate) for the products from **9b**–**m**. One of the products in each case was identified by comparison with the appropriate 'authentic' sample, **15b**–**m** or **16f**,**g** *via* peak enhancement where appropriate. The products were then separated out as a mixture by dry column flash chromatography (silica, hexane–ether, 60:40 to 80:20 as appropriate), the yields are given in Table 8 and their ^{1}H NMR spectra in Table 9.

Preparation and FVP of 2-methoxycarbonyl-3-(2-[2-^{2}H]phenylphenyl)oxirane

2-[2-^{2}H]Phenylbenzaldehyde. Bromo[2-^{2}H]benzene[6] (0.58 g, 3.68 mmol) and tetrakis(triphenylphosphine)palladium (0.11 g, 0.095 mmol) in 1,2-dimethoxyethane (DME) (20 cm^3) were stirred for 20 min. A solution of 2-formylphenylboronic acid (0.5 g, 3.3 mmol) and sodium carbonate (0.35 g, 3.3 mmol) in water (5 cm^3) was added and the mixture was heated under reflux for 12 h. The usual work-up followed by Kugelrohr distillation gave the product (0.44 g, 66%) as a colourless oil,[3] Kugelrohr oven temperature 170–180 °C at 0.05 mmHg; shown by mass spectroscopy to be 98% monodeuteriated; δ_H 7.19–7.58 (7 H, m), 7.96 (1 H, dd, *J* 7.7, 1.1) and 9.92 (1 H, s, CHO).

2-Methoxycarbonyl-3-(2-[2-^{2}H]phenylphenyl)oxirane. Sodium methoxide (0.47 g, 8.6 mmol) was added to a solution of 2-[2-^{2}H]phenylbenzaldehyde (0.52 g, 2.84 mmol) and methyl chloroacetate (0.99 g, 9.1 mmol) in THF (25 cm^3) and the mixture was heated under reflux for 5 h. The usual work-up followed by Kugelrohr distillation gave the product (0.55 g, 76%) as a pale yellow oil,[3] Kugelrohr oven temperature 190–220 °C at 0.01 mmHg; shown by mass spectroscopy to be 98% monodeuteriated (HRMS: found M^+, 255.1001. $C_{16}H_{13}{}^2HO_3$ requires *M*, 255.1006); δ_H 3.44 (1 H, br s, 3-H), 3.69 (3 H, s, CH_3), 3.92 (1 H, br s, 2-H) and 7.2–7.4 (8 H, m, aromatic); *m*/*z* (EI) 255 (9%), 196 (28), 195 (23), 183 (34), 182 (47), 181 (12), 168 (21), 167 (61), 166 (100), 165 (38), 154 (17), 153 (27), 152 (13) and 77 (10).

FVP of 2-Methoxycarbonyl-3-(2-[2-^{2}H]phenylphenyl)oxirane. Using the general FVP method, the reactant (0.044 g) was distilled into the furnace tube using an inlet temperature of 120–140 °C. Dry flash chromatography (silica, ether–hexane, 3:1) of the product gave a mixture of 5-methoxycarbonyl-5,7-dihydro-[1-^{2}H]- and -[7-^{2}H]-dibenz[*c*,*e*]oxepines **35** and **37** (0.017 g, 39%) shown by mass spectrometry to be 98% monodeuteriated (HRMS: found M^+, 255.1008. $C_{16}H_{13}{}^2HO_3$ requires *M*, 255.1006); δ_H 3.43 (3 H, s, CH_3), 4.45 (*ca*. 1.5 H, br s, 7-H), 4.99 (1 H, s, 5-H) and 7.2–7.5 (*ca*. 7.5 H, m, aromatic); $\delta_{2_H}(CHCl_3)$ 4.47 (br) and 7.58 (br) integral ratio (1:1.02); *m*/*z* (EI) 255 (21%), 197 (22), 196 (100), 195 (22), 169 (17), 168 (85), 167 (28), 166 (55), 165 (22), 153 (18), 152 (11) and 83 (11). Two further experiments gave yields of 38 and 35% and ^{2}H NMR integral ratios of 0.99 and 0.97 (average = 0.99 ± 0.02).

Non-deuteriated samples of 2-methoxycarbonyl-3-(2-phenylphenyl)oxirane[3] and 5-methoxycarbonyl-5,7-dihydrodibenz[*c*,*e*]oxepine[3] were prepared by the same routes as the deuteriated samples for comparison of their NMR and mass spectra.

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