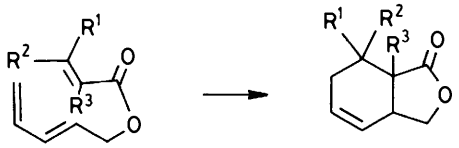
The Use of Dichloromaleic and Bromomaleic Anhydrides in the Synthesis of Lactones by the Intramolecular Diels–Alder Reaction

Mark J. Batchelor and John M. Mellor *
Department of Chemistry, the University, Southampton, SO9 5NH

Reaction of (*E*)-penta-2, 4-dien-1-ol with dichloromaleic anhydride gives an unstable triene, which on heating undergoes an intramolecular Diels–Alder cyclisation to give a bicyclic acid, which on dechlorodecarboxylation affords an unsaturated bicyclic lactone. Reaction of (*E*)-penta-2, 4-dien-1-ol with half-esters derived from dichloromaleic anhydride permits similar cyclisation to afford bicyclic esters. Elaborations of these adducts *via* reduction and dehydrochlorination reactions are described. Similar adducts are prepared from bromomaleic anhydride and are further elaborated. From 3-vinylcyclohex-2-enol *via* the intermediacy of triene precursors derived from dichloromaleic anhydride, bromomaleic anhydride, and half-esters of maleic and fumaric acid tricyclic adducts are obtained in certain cases. These cyclisations and the subsequent elaborations are discussed with respect to their synthetic potential and their relation to related recently reported examples.

Cyclic lactones[1] can be prepared by the intramolecular Diels–Alder (IMDA) reaction of a triene precursor composed of a diene unit linked through an ester unit to an acrylate moiety. With simple acrylates (Scheme; $R^1 = R^2 = R^3 = H$) such cyclisations[2] are inefficient and typically require long reaction times and high temperatures. Cyclisation[3–5] is more efficient for those acrylate esters which are further activated by suitably placed functional groups. Thus fumarate esters[3] (Scheme; $R^1 = R^3 = H$, $R^2 = CO_2R$) and maleate esters[3] (Scheme; $R^1 = CO_2R$, $R^2 = R^3 = H$), and also esters derived from malonic acids[5] (Scheme; $R^1 = R^2 = H$, $R^3 = CO_2R$), require less vigorous conditions.



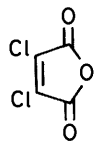
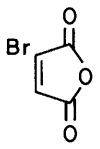
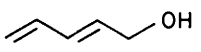
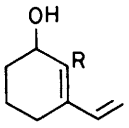
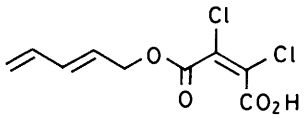
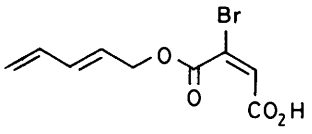
Scheme.

In such successful cyclisations, subsequent elaboration of the adducts may be constrained by the difficulty of introducing further functionality. This problem has been recognised,[4] and one solution is to introduce such functionality before cyclisation into the diene moiety. The recent use[4] of 5-acyloxypenta-2,4-dien-1-ols in intramolecular Diels–Alder reactions illustrates this strategy. An alternative possibility is the use of a dienophilic moiety incorporating additional functionality. There are few examples of this second strategy although Corey *et al.*[6] have employed a β-chloroacrylate ester in the synthesis of a gibberellic acid, and Yates and Auksi[7] have used β-bromoacrylates to give Diels–Alder adducts, which could be subsequently elaborated using the bromine functionality. In view of the ready availability of dichloromaleic anhydride and bromomaleic anhydride we decided to study the intramolecular Diels–Alder reaction of a series of triene precursors readily derived from these anhydrides. In this paper we report the formation of a series of Diels–Alder adducts and their subsequent elaboration, which exemplify the utility of these anhydrides in the construction of functionalised bicyclic and tricyclic lactones. In the following paper[8] we report a similar study of syntheses of bicyclic amides from amido triene precursors.

The major section of this paper is concerned with the synthesis and subsequent chemistry of trienes derived from (*E*)-penta-2, 4-dien-1-ol. Following the account of this, the simplest of acyclic hydroxy dienes, we describe studies based on the two cyclic alcohols (**1**) and (**2**). Direct reaction of these alcohols with dichloromaleic anhydride or bromomaleic anhydride affords triene acids. Thus (*E*)-penta-2, 4-dien-1-ol with the respective anhydrides gives the acids (**3**) and (**4**), which are reasonably stable under the conditions of their formation. The alternative methodology of formation of a half-ester of the appropriate acid followed by subsequent reaction of this half-ester with a hydroxy diene to afford a triene ester was particularly studied. Reaction of dichloromaleic anhydride with different alcohols gave the half-esters (**5**)—(**8**), from which by further esterification the triene esters (**9**)—(**12**) were prepared from the hydroxy diene. Similarly the trienes (**13**) and (**14**) were prepared from the methyl ester (**5**) and the cyclic hydroxy dienes (**1**) and (**2**) respectively. For the second esterification a variety of methods was used. As indicated in the Experimental section the appropriate half-ester could be treated with oxalyl chloride or thionyl chloride to give the intermediate acid chloride, which was then esterified with a hydroxy diene. Alternatively, direct coupling of acid and alcohol using dicyclohexylcarbodi-imide (DCC), or Mitsunobu conditions, was possible.

In the case of bromomaleic anhydride the first esterification might lead to two different half-esters. In all cases we find that only a single ester is formed, corresponding to attack α to the bromo group. This selectivity has previously been recognised in metal hydride reductions[9] of monosubstituted maleic anhydrides. Hence reaction of bromomaleic anhydride with a hydroxy diene gives the triene acid (**4**), and reaction first with methanol, followed by coupling of the intermediate acid (**15**) with the appropriate hydroxy dienes, gives specifically the respective triene esters (**16**) and (**17**).

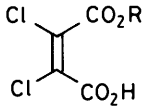
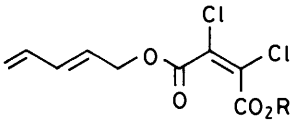
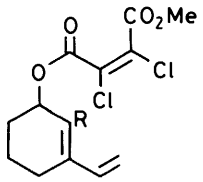
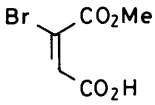
For purposes of comparison the esters (**18**)—(**20**) were prepared by similar reaction of esters of maleic or fumaric acid with hydroxy dienes. In the case of these esters and those esters derived from dichloromaleic anhydride the only possible structural ambiguity concerning the trienes is the question of geometrical isomerisation but in no case have we observed significant isomerisation. In the case of trienes derived from bromomaleic anhydride an added complication concerns the regioselectivity of the esterifications. The structural assignment to those trienes based on bromomaleic anhydride was initially made by reference to the literature precedents,[9] but was fully confirmed by the nature of those cyclisation products derived from the trienes (*vide infra*).

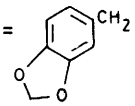







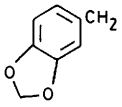
(1) R = H
(2) R = Me

(3)

(4)

(5) R = Me
(6) R = PhCH$_2$
(7) R = 
(8) R = Me$_3$SiCH$_2$CH$_2$

(9) R = Me
(10) R = PhCH$_2$
(11) R = 
(12) R = Me$_3$SiCH$_2$CH$_2$

(13) R = H
(14) R = Me

(15)

The products of cyclisation of the trienes derived from (*E*)-penta-2, 4-dien-1-ol are described in Table 1. The acid (**3**) on heating in xylene gave a single adduct, the acid (**26**); the other possible adduct (**21**) was not observed. The ester (**9**) under similar conditions gave a single adduct, the ester (**22**); again the alternative adduct (**27**) was not observed. In contrast the esters (**10**) and (**12**) gave, in addition to the major products (**23**) and (**25**), low yields of the minor adducts (**28**) and (**30**). In the case of the ester (**11**) only the adduct (**24**) was isolated; again the second isomer (**29**) was not observed. Although the bromo acid (**4**) failed to give, other than in trace amounts, the expected bicyclic adducts the related bromo ester (**16**) gave the adducts (**31**) and (**32**) in better yield. Finally in Table 1, for comparison purposes, we describe the formation of the adducts (**33**) and (**34**) from the fumarate ester (**20**).

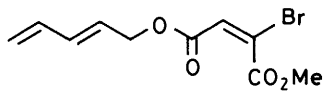
Structures could be assigned to the adducts on the basis of spectroscopic observations. The two main distinctive features were in the i.r. spectra ($\nu_{max.}^{trans}$ 1 805 cm^{-1} and $\nu_{max.}^{cis}$ 1 780—1 790 cm^{-1}) and in the ^{1}H n.m.r. spectra ($J_{6,7\alpha}^{trans}$ 7.5 Hz, $J_{6,7\beta}^{trans}$ 10 Hz and $J_{6,7\alpha}^{cis}$ 5.5 Hz, $J_{6,7\beta}^{cis}$ 1.0 Hz). In the case of the bromo esters (**31**) and (**32**) observation of $J_{1,6}$ provided a further structural guide. In the ester (**31**) the value of $J_{1,6}$ (13.5 Hz) was indicative of the *trans* ring junction whereas in the ester (**32**) the value of $J_{1,6}$ (7.0 Hz) indicated a *cis* ring junction. Similar observations permitted the relative assignments of ring fusion in the esters (**33**) and (**34**). These assignments concerning the stereochemistry about the ring junction are in good agreement with the literature precedents.[3,4,10]

Alongside the problem of the structural assignment of the ring junction in each set of adducts there is also the question of the stereochemistry of the ester functionality. This is determined by the initial stereochemistry in the triene unless geometrical isomerisation occurs as a competing process, or unless epimerisation occurs following cyclisation. The structural assignments shown in Table 1 are based on (i) related examples from the literature[3,4,10] where in similar cyclisations isomerisation is not observed, (ii) further spectroscopic analysis of the adducts, and (iii) certain features of the chemistry of the adducts (*vide infra*), which confirm the conclusions. Both our own inability to promote the isomerisation of derivatives of dichloromaleic acid to derivatives of dichlorofumaric acid, and the evidence from the literature[11] to the effect that indirect routes to derivatives of dichlorofumaric acid are preferable, suggest that even in this case, where ^{1}H n.m.r. spectroscopic analysis of the acyclic precursors is more difficult, isomerisation can be excluded. In other examples in Table 1 the homogeneity of triene precursors was checked (^{1}H n.m.r.) and prior isomerisation could be excluded.

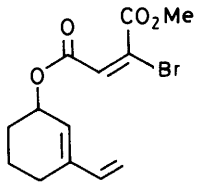
Table 1. Cyclisation of trienes derived from (*E*)-penta-2,4-dien-1-ol

Triene	Conditions	Products and yields: *trans*-Adducts		*cis*-Adducts	
(3)	xylene, reflux, 18 h	(21)	0%	(26)	20%
(9)	xylene, reflux, 48 h	(22)	68%	(27)	0%
(10)	xylene, reflux, 24 h	(23)	51%	(28)	6%
(11)	xylene, reflux, 18 h	(24)	33%	(29)	0%
(12)	xylene, reflux, 36 h	(25)	38%	(30)	15%
(16)	xylene, reflux, 18 h	(31)	66%	(32)	14%
(20)	xylene, reflux, 18 h	(33)	32%	(34)	16%

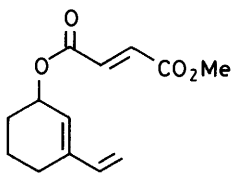
Although the absence of isomerisation under the IMDA conditions is to be expected,[3,4,10] in the case of bromo adducts (**31**) and (**32**) spectroscopic evidence confirmed the expectation. In the *trans*-ester (**31**) the resonance for 1-H is observed at δ 2.83, whereas in the *cis*-isomer (**32**) 1-H is observed at δ 3.79.



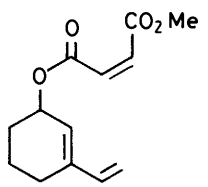
(16)



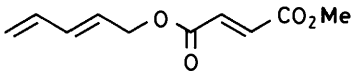
(17)



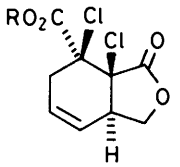
(18)



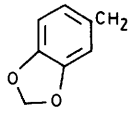
(19)



(20)

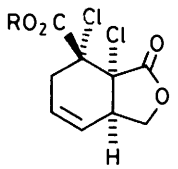


(21) R = H
(22) R = Me
(23) R = $PhCH_2$

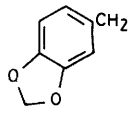


(24) R =

(25) R = $Me_3SiCH_2CH_2$

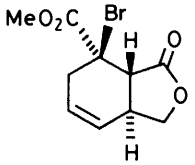


(26) R = H
(27) R = Me
(28) R = $PhCH_2$

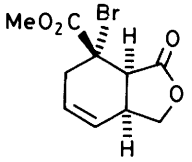


(29) R =

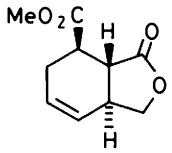
(30) R = $Me_3SiCH_2CH_2$



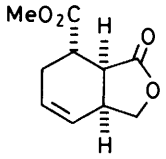
(31)



(32)



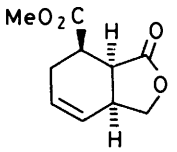
(33)



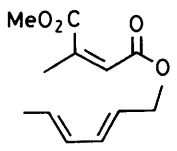
(34)

The relative deshielding of 1-H in the *cis*-isomer can be attributed to the closer proximity of the ester functionality, and is of similar magnitude to that observed in related adducts.[3] Further evidence confirming these structural assignments is provided below.

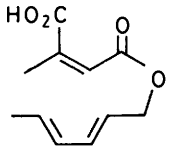
It is concluded from the results in Table 1 that esters of dichloromaleic and bromomaleic acid cyclise efficiently to give predominantly *trans*-adducts. In contrast the acids (**3**) and (**4**) cyclise much less efficiently, but, interestingly, in the case of the acid (**3**) the only adduct isolated is the *cis* adduct (**26**). Both the preferential formation of the *trans*-esters, and the formation of a *cis*-acid, have good precedent. Although there are a number of reports of cyclisation of triene esters to give *trans*-fused products the closest parallel to our observations is in the work of White and Sheldon.[3] They observed that the ester (**36**) cyclised to give the *trans*-ester (**38**), whereas the acid (**37**) gave the *cis*-acid (**39**). The apparent anomaly was explained by White and Sheldon on the basis of a kinetically controlled closure *via* an *anti* transition state to give the ester (**38**), but a thermodynamic control in formation of (**39**). It was suggested that intramolecular protonation of the lactone carbonyl group by the carboxylic acid might facilitate the reverse of the Diels–Alder cyclisation. Such a ring opening might establish reversibility of the IMDA reaction and hence lead, *via* the alternative kinetically less favoured *syn* transition state, to the thermodynamically more stable *cis*-adduct (**39**). In addition to our observation of isolation of the *cis*-fused (**26**), other examples[3,4] of preferential formation of *cis*-fused products by IMDA reaction of maleate half-esters are known. In view of the considerable structural variations within these examples it seems



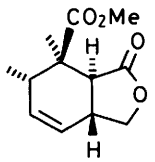
(35)



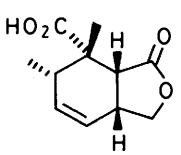
(36)



(37)



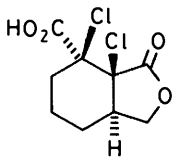
(38)



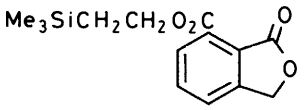
(39)

unlikely that the White and Sheldon explanation[3] of formation of the *cis*-adducts by thermodynamic control is applicable. Alternatively the formation of *cis*-adducts may reflect a kinetic control. Internal protonation of the ester carbonyl group permits a catalysed IMDA process with possible facilitation of the *syn* transition state.

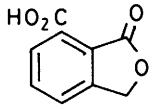
Attempts to prepare acid (**21**), the possible product from an *anti* transition state, were unsatisfactory. Hydrolysis of the ester (**22**) failed. Reduction of the benzyl ester (**23**) gave only the saturated acid (**40**) in 87% yield. Although the adduct (**24**) was isolated as sole product—no adduct (**29**) formed—attempted deprotection[12] failed. Adducts (**25**) and (**30**) could be prepared and separated but failed to provide a route to the acid (**21**). Instead reaction of ester (**25**) with 2 equivalents of tetrabutylammonium fluoride[13] gave the aromatic ester (**41**) in quantitative yield. In this reaction the fluoride ion is preferentially acting as a base, and due to the *trans*-ring junction the elemination of hydrogen chloride from a *trans* antiperiplanar relationship is particularly favoured. Further treatment of the ester (**41**) with tetrabutylammonium fluoride gave the known[14] acid (**42**). In marked contrast the ester (**30**) under similar conditions gave the chloro diene (**44**). In the ester (**30**) the *cis* ring fusion makes dehydrochlorination less favourable. However, in loss of the protecting group generation of a carboxylate anion then permits dechlorodecarboxylation from a favoured antiperiplanar relationship. Such dechlorodecarboxylations are discussed further below and in the following paper.[8] Hence we were unable to investigate the possible isomerisation of the acid (**21**) to the acid (**26**) under the IMDA conditions, and it is not possible to discriminate between the possible explanations for the sole formation of acid (**26**). Such explanations are the White and Sheldon view[3] of a reversible Diels–Alder reaction, a kinetic preference for a *syn* transition state, or the subsequent decomposition of the acid (**21**), which we consider to be unlikely, but cannot exclude.



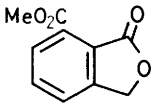
(**40**)



(**41**)



(**42**)



(**43**)

Three aspects of the chemistry of the adducts shown in Table 1 have been studied, *viz.* selective reduction, dehydrochlorination, and dechlorodecarboxylation. Reduction of the ester (**22**) with zinc in acetic acid gave in quantitative yield a mixture (7:3) of the esters (**35**) and (**34**). The latter ester (**34**) is the major product obtained by cyclisation of the triene (**20**) (see Table 1).

In Table 2 are reported results of the catalytic hydrogenations of the ester (**22**) under various conditions. The structures of the products (**46**) and (**48**) were established from their spectra (see Experimental section). Further hydrogenation of the ester (**46**) affords the second product (**48**). With 10% palladium on charcoal as catalyst and ethyl acetate as solvent the saturated ester (**46**) can be isolated as sole product, whereas in methanol with Adam's catalyst only the ester (**48**) is obtained. Previously

Table 2. Hydrogenation of ester (**22**)

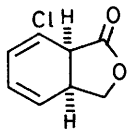
Catalyst	Ratio catalyst (mg)/ substrate (mmol)	Solvent	Products[a] ratio (**46**):(**48**)
PtO_2	26	MeOH	2:3
PtO_2	79	EtOAc	2.5:1
PtO_2	76	AcOH	2.5:1
PtO_2	185	MeOH	<1:100
10% Pd/C	132	EtOAc	2.5:1
10% Pd/C	21	EtOAc	6:1
10% Pd/C	11	EtOAc	>100:1

[a] Ratios determined by ^1H n.m.r. spectroscopy.

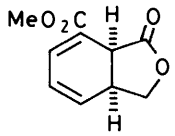
Table 3. Dehydrohalogenation of adducts and their reduction products

Starting compound	Reagents	Products	Yield (%)
(**22**)	Et_3N, THF	(**43**)	76
(**46**)	Et_3N, THF	(**49**) and (**50**)	35 and 28
(**31**)	NaOMe, MeOH	(**45**)	90
(**31**)	Et_3N, THF	recovery of (**31**)	
(**32**)	Et_3N, THF	(**45**)	85
(**47**)	Et_3N, THF	complex mixture	

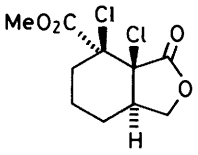
it has been recognised[15] in the hydrogenolysis of chloro compounds that the presence of hydrogen chloride tends to suppress hydrogenolysis, but that hydrogenolysis is facilitated[16] by the use of methanol as solvent. In the case of the bromo ester (**31**) reduction in ethyl acetate over 10% palladium on charcoal gave the saturated bromo ester (**47**). Although an ester (**41**) of the aromatic acid (**42**) was prepared by a dehydrochlorination using fluoride ion as a base, other esters could be obtained by use of the more normal amine bases. Thus the adduct (**22**) with triethylamine gave the methyl ester (**43**). Under similar conditions the saturated ester (**46**) gave a separable mixture of the esters (**49**) and (**50**) (see Table 3). However, control experiments establish that under the conditions of their formation the pure ester (**49**) slowly isomerises to give the ester (**50**). It seems likely that the ester (**50**) is formed *via* the intermediacy of the ester (**49**),



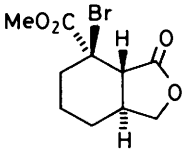
(**44**)



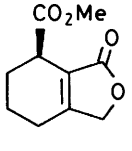
(**45**)



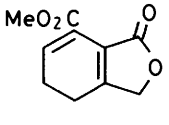
(**46**)



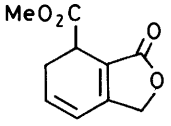
(**47**)



(**48**)



(**49**)



(**50**)

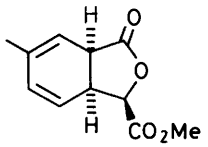
and that the greater thermodynamic stability of the latter can be attributed to the absence of the adverse steric interaction between the ester functionality and the carbonyl group of the lactone in this isomer.

With triethylamine as base the bromo adduct (**32**) readily underwent elimination to give the diene (**45**), whereas under similar reaction conditions the *trans*-fused adduct (**31**) was recovered unchanged. In the case of the *trans*-adduct (**31**) the rigid structure locking the bromine atom in an equatorial position prevents antiperiplanar elimination of hydrogen bromide. In contrast the *cis*-adduct (**32**) can readily adopt a conformation from which such an elimination is possible. These observations confirm our earlier conclusions of the absence of isomerisation of maleate esters to fumarate esters before cyclisation in the formation of the adducts (**31**) and (**32**). Such an isomerisation would have permitted dehydrobromination from a *trans*-fused lactone. Under more severe reaction conditions using sodium methoxide, it was possible to convert the ester (**31**) into the *cis*-fused diene (**45**) *via* dehydrobromination, and isomerisation from a less stable *trans*-lactone to the more thermodynamically stable *cis*-lactone (**45**). Although the spectroscopic data for the lactone (**45**) are consistent with the assigned structure, further support for the structural assignment is obtained by comparison with the data for the lactone (**51**) prepared by Yates and Auksi.[7] In the lactones (**45**) and (**51**) the lactone carbonyl absorptions are observed at 1 785 cm^{-1} and 1 795 cm^{-1}.

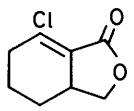
In the *cis*-fused acid (**26**) and the saturated *trans*-fused acid (**40**) there is a *trans* relationship between a vicinal chlorine substituent and a carboxylic acid group, so that dechlorodecarboxylation might be expected to occur readily. Reaction of the *cis*-fused acid (**26**) with triethylamine gave the diene (**44**), and the *trans*-fused acid (**40**) similarly gave the lactone (**52**). These reactions both confirm the relative stereochemistry in the adducts (**26**) and (**40**) and hence the absence of geometrical isomerisation at a stage before cyclisation, and afford interesting unsaturated lactones. It is probable that the diene (**44**) is formed *via* the intermediacy of the nonconjugated diene (**53**). In such an isomerisation the preference for formation of the *cis*-fused diene (**44**) is again noteworthy. By hydrogenation of this diene (**44**) the unsaturated lactone (**54**) could be isolated but under conditions of attempted isomerisation [triethylamine in tetrahydrofuran (THF), or hydrochloric acid in dioxane] this lactone was recovered unchanged. These results establish the greater stability of the *cis*-fused lactones over the possible *trans*-fused lactones. They also suggest that formation of the chloride (**44**) from the acid (**26**) can be attributed to a combination of kinetic and thermodynamic factors. As even the diene (**44**) is a stable compound showing little tendency to aromatise this procedure of dechlorodecarboxylation provides a novel route to unsaturated lactones. The dehydrochlorination, dehydrobromination, and dechlorodecarboxylation reactions, in combination with reductive steps, establish that the Diels–Alder adducts derived from dichloromaleic and bromomaleic anhydrides can be elaborated in a variety of interesting procedures.

An obvious extension of these procedures was the synthesis of tricyclic lactones from cyclic diene precursors. In particular, in view of the recent interest [17–20] in the elaboration of the esters of the alcohol (**55**) by IMDA reactions in an approach to the synthesis of forskolin, or analogues, and in the elaboration of the dienes (**56**) [21] and (**1**) [22] in an approach to nagilactones, we chose to study IMDA reactions of esters of the simpler cyclic alcohols (**1**) and (**2**).

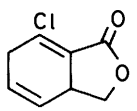
Reaction of the alcohol (**1**) with the appropriate acid chloride gave the triene precursor (**13**). However, attempted IMDA reaction of the triene (**13**) under a variety of conditions failed. Either the triene (**13**) was recovered unchanged or a complex and inseparable mixture of products was obtained. Similarly the ester



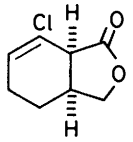
(**51**)



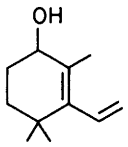
(**52**)



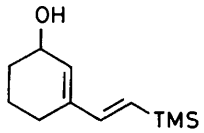
(**53**)



(**54**)



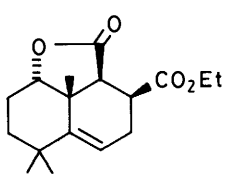
(**55**)



(**56**)

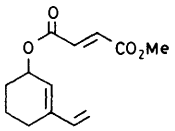
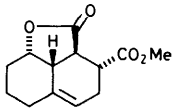
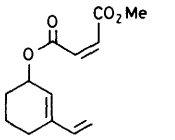
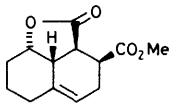
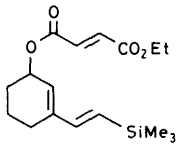
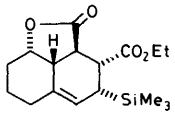
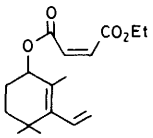
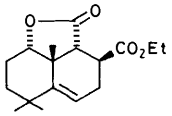
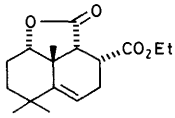
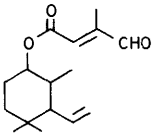
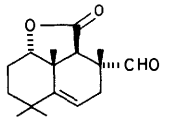
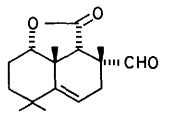
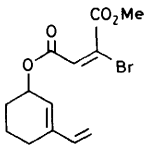
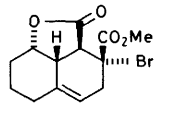
(**14**) failed to give any IMDA adducts. We speculated that trace quantities of hydrogen chloride might be responsible for acid-catalysed decomposition of the esters (**13**) and (**14**) under these conditions. Although the addition of an acid scavenger such as propylene oxide did not prevent the unwanted side reactions, support for this explanation of the failure of these IMDA reactions was found in the comparison of the behaviour of the esters (**18**) and (**19**). In these control experiments the fumarate ester (**18**) and the maleate ester (**19**) smoothly afforded the respective adducts (**57**) and (**58**). In Table 4 these results are shown alongside appropriate examples which have recently been reported elsewhere.[18,19,21] Structures can be assigned to compounds (**57**) and (**58**) by comparison with the data for other compounds shown in Table 4. In particular, comparison with the ester (**59**) [21] is helpful [for ester (**57**) $J_{8a,8b}$ 8, $J_{2a,8b}$ 13, $J_{2a,3}$ 11.5, and $J_{3,4}$ 8.5 and 8.5 Hz; for ester (**58**) $J_{8a,8b}$ 8.5, $J_{2a,8b}$ 13.5, $J_{2a,3}$ 4.5, $J_{3,4}$ 2.5 and 8.5 Hz; for ester (**59**) $J_{8b,8b}$ 8, $J_{2a,8b}$ 14.6, $J_{2a,3}$ 11.2, and $J_{3,4}$ 8.3 Hz]. The large value for the $J_{2a,8b}$ coupling constant indicates a *trans* relationship for these protons. The distinction between protons having a *trans* relationship, as in esters (**57**) and (**59**), and a *cis*-relationship, as in ester (**58**), is possible based on the magnitude of $J_{2a,3}$.

Two interesting conclusions stem from the formation of the esters (**57**) and (**58**). First it seems clear from the results in Table 4 that the inability to obtain IMDA adducts from the esters (**13**) and (**14**) may be attributed to the acid-catalysed decomposition of the reactants or the adducts. Secondly, and a point which underlines the possible ease of elimination of hydrogen chloride from the adducts, whilst the adducts formed from (**18**) and (**19**) retain their stereochemical integrity, in other examples [18,19] reported in Table 4 the initially formed IMDA adducts undergo isomerisation. This isomerisation involves an epimerisation, which has previously been recognised,[18] and shown to proceed *via* enolic intermediates. Thus the initially formed ester (**62**) undergoes epimerisation [18] to give the thermodynamically favoured (**60**), where 1,3-interaction between the alkoxycarbonyl and methyl substituents is avoided. The recent analysis [18] implicating this 1,3-interaction as the driving force for epimerisation is confirmed by our observations. In the adduct (**58**),



(**62**)

Table 4. Intramolecular Diels–Alder reactions of some monocyclic dienes

Reactant	Conditions	Product and yield (%)
 (18)	xylene, 18 h	 (58) 66
 (19)	xylene, 18 h	 (57) 52
	benzene, 120 °C, 90 h	 (59) 82
	benzene, 150 °C	 (60) 42
		 14
	benzene, 120 °C, 85 h	 47
		 7
 (17)	xylene, 18 h	 (61) 63

lacking the methyl substituents, there is no serious 1,3-interaction. Hence the adduct (**58**) is stable under the IMDA conditions. However, in adducts from dichloromaleic anhydride derivatives adverse strain could be alleviated by loss of hydrogen chloride. The fragility of esters of the alcohols (**1**) and (**2**) has previously been noted.[22] Hence the loss of reactants and products under IMDA conditions with the esters (**13**) and (**14**) is explicable.

In contrast, cyclisation of the triene (**17**) afforded the adduct (**61**) in 63% yield. The structure can be assigned to the adduct by comparison with spectral data of the adducts (**57**) and (**58**). The structural assignment is confirmed by attempted reaction of the adduct (**61**) with triethylamine in hot THF. No reaction is observed. This result indicates that the bromine occupies a pseudo-equatorial position from which elimination is difficult.

These results indicate that by use of the esters of bromomaleic acid, IMDA reactions are applicable to the synthesis of tricyclic systems. However, the use of esters of dichloromaleic acid appears to be restricted to the synthesis of bicyclic systems. In such cases many novel unsaturated lactones are accessible.

Experimental

M.p.s were determined in a capillary tube and are uncorrected. I.r. spectra were obtained using a Perkin-Elmer 1579 grating spectrometer. ^1H and ^{13}C N.m.r. spectra were obtained at 360 and 90.6 MHz respectively using a Bruker WH-360 spectrometer. Tetramethylsilane was used as an internal standard and deuteriochloroform was used as the solvent unless otherwise stated. Mass spectra were obtained at 70 eV using a Kratos MS-30 spectrometer equipped with a DS 505 Data System. Elemental analyses were performed at University College, London. Organic solutions were dried over anhydrous magnesium sulphate and solvent evaporation was carried out at at reduced pressure using a rotary evaporator. Flash chromatography was carried out on Macherey Nagel silica gel 60 (230—400 mesh) except where stated otherwise. Light petroleum refers to the fraction boiling in the range 40—60 °C.

Synthesis of Hydroxy Dienes.—3-Vinylcyclohex-2-enol (**1**) was prepared by reduction of 3-vinylcyclohex-2-enone with lithium aluminium hydride in 98% yield. 2-Methyl-3-vinylcyclohex-2-enol (**2**) was similarly prepared in 89% yield. (*E*)-Penta-2,4-dien-1-ol was prepared by reduction of (*E*)-methyl penta-2,4-dienoate with lithium aluminium hydride at −15 °C in 85% yield.

Synthesis of Dienophiles.—Methyl hydrogen dichloromaleate (**5**). Dichloromaleic anhydride (1.0 g, 6.0 mmol) was dissolved in methanol (20 ml) and the solution was kept at room temperature for 36 h. The solvent was removed at reduced pressure to give *methyl hydrogen dichloromaleate* (**5**) as a viscous liquid (1.2 g, 100%) [Found: M^+, 197.9481 (8.5%), *m/z* 167 (M^+ − OMe, 48.6), and 87 (100). $C_5H_4{}^{35}Cl_2O_4$ requires *M*, 197.9486]; δ_H 9.20 (1 H, s, CO_2H) and 3.85 (3 H, s, CO_2Me); $\nu_{max.}$(film) 3 500—2 500, 1 740, and 1 600 cm^{-1}.

Benzyl hydrogen dichloromaleate (**6**). A mixture of dichloromaleic anhydride (6.3 g, 37.7 mmol) and benzyl alcohol (4.0 g, 37.0 mmol) in dichloromethane (10 ml) was kept at room temperature for 72 h. The resulting solution was concentrated under reduced pressure to afford a white solid, which was recrystallised from light petroleum–ether (9:1) to give *benzyl hydrogen dichloromaleate* (**6**) as crystals (8.9 g, 86%), m.p. 84—86 °C [Found: *m/z* 229.9932 (M^+ − CO_2H, 0.4%) and 91 (100). $C_{10}H_7{}^{35}Cl_2O_2$ requires *m/z*, 229.9901 (M^+ − CO_2H)]; δ_H 10.14 (1 H, s, CO_2H), 7.36 (5 H, s, ArH), and 5.27 (2 H, s, $PhCH_2$); $\nu_{max.}$(Nujol) 3 300—2 500, 1 755, 1 705, and 1 595 cm^{-1}.

(E)-3-*Bromo*-3-*methoxycarbonylacrylic acid* (**15**). Bromomaleic anhydride (0.76 g, 4.3 mmol) was dissolved in methanol (15 ml) and the resulting solution was kept at room temperature

for 18 h. The solvent was then removed under reduced pressure to give a white solid (0.92 g), which was recrystallised from light petroleum–ether (8:1) to afford (E)-3-*bromo*-3-*methoxycarbonylacrylic acid* (**15**) as needles (0.77 g, 86%), m.p. 89—90 °C [Found: *m/z*, 209.9336 (M^+, 2.9%) and 85 ($M^+ - Br - CO_2$, 100). $C_5H_5{}^{81}BrO_4$ requires *M*, 209.9352]; δ_H 10.20 (1 H, s, CO_2H), 6.54 (1 H, s, 2-H), and 3.90 (3 H, s, CO_2Me); $\nu_{max.}$($CHCl_3$) 3 500—2 700, 1 750, 1 710, and 1 630 cm^{-1}.

3,4-*Methylenedioxybenzyl hydrogen dichloromaleate* (**7**). A mixture of dichloromaleic anhydride (2.73 g, 19.7 mmol) and 3,4-methylenedioxybenzyl alcohol (3.30 g, 19.7 mmol) in dichloromethane (30 ml) was kept at room temperature for 48 h. The resulting solution was concentrated under reduced pressure to afford the monoester (**7**) as an off-white solid, which was recrystallised from ether (5.50 g, 91%), m.p. 98 °C (decomp.); δ_H[$(CD_3)_2SO$] 11.6 (1 H, s, CO_2H), 6.8 (3 H, complex, ArH), 5.9 (2 H, s, OCH_2O), and 5.1 (2 H, s, OCH_2); $\nu_{max.}$(Nujol) 3 500—2 500, 1 725, and 1 610 cm^{-1}.

2-(*Trimethylsilyl*)*ethyl hydrogen dichloromaleate* (**8**). A mixture of dichloromaleic anhydride (0.71 g, 4.2 mmol) and 2-(trimethylsilyl)ethanol (0.50 g, 4.2 mmol) in dichloromethane (15 ml was kept at room temperature for 48 h. The resulting solution was concentrated under reduced pressure to afford the monoester (**8**) as a clear liquid (1.21 g, 100%), δ_H 11.06 (1 H, s, CO_2H), 4.37 (2 H, m, CH_2O), 1.07 (2 H, m, Me_3SiCH_2), and 0.08 (9 H, s, Me_3Si); $\nu_{max.}$(film) 3 600—2 700, 1 745, 1 725, and 1 600 cm^{-1}.

Synthesis of Triene Precursors—Preparation of Triene Acids.—(E)-*Penta*-2,4-*dienyl hydrogen dichloromaleate* (**3**). A mixture of dichloromaleic anhydride (2.0 g, 12.0 mmol) and (*E*)-penta-2,4-dien-1-ol (1.26 g, 15.0 mmol) in dichloromethane (10 ml) was kept at room temperature for 18 h. The resulting solution was concentrated under reduced pressure to afford the crude monoester (**3**) as an oil (2.15 g, 71%), δ_H 9.54 (1 H, s, CO_2H), 6.60—5.00 (5 H, complex, olefinic), and 4.80 (2 H, d, *J* 6.0 Hz, CH_2O); $\nu_{max.}$($CHCl_3$) 3 300—2 500, 1 740, and 1 720 cm^{-1}.

(E)-3-*Bromo*-3-[(E)-*penta*-2,4-*dienyloxycarbonyl*]*acrylic acid* (**4**). A mixture of bromomaleic anhydride (90 mg, 0.51 mmol) and (*E*)-penta-2,4-dien-1-ol (40 mg, 0.47 mmol) in dichloromethane (0.5 ml) was kept at room temperature for 36 h. The resulting solution was concentrated under reduced pressure to afford the crude acid (**4**) as an oil (100 mg, 75%), δ_H 9.60 (1 H, s, 2-H), 6.60—5.10 (5 H, complex, olefinic), and 4.79 (2 H, d, *J* 6.0 Hz, CH_2O); $\nu_{max.}$(film) 3 700—2 500, 1 730, and 1 630 cm^{-1}.

Preparation of Triene Esters.—Method A: typical procedure. Methyl (*E*)-*penta*-2,4-*dienyl dichloromaleate* (**9**). Methyl hydrogen dichloromaleate (**5**) (14.0 g, 70 mmol) and oxalyl chloride (60 ml, 148 mmol) were stirred in benzene (50 ml) at room temperature for 30 min and then at 50 °C for 1 h. The excess of oxalyl chloride and benzene were removed by evaporation to afford a clear yellow liquid, which was dissolved in benzene (40 ml) and then added to a stirred, ice-cold solution of (*E*)-penta-2,4-dien-1-ol (4.6 g, 55 mmol) and pyridine (4.4 g, 56 mmol) in benzene (80 ml). The resulting mixture was kept at room temperature for 18 h and was then diluted with ether (100 ml) and washed sequentially with saturated aqueous copper sulphate (2 × 100 ml), dil. sulphuric acid (100 ml), water (100 ml), saturated aqueous sodium hydrogen carbonate (100 ml), and saturated brine (100 ml). The organic phase was dried and concentrated under reduced pressure to afford *methyl* (*E*)-*penta*-2,4-*dienyl dichloromaleate* (**9**) as a pale yellow liquid (14.0 g, 96%) [Found: (chemical ionisation using NH_3) *m/z*, 265.0080 (M^+ + 1.0%) and 67 ($C_5H_7{}^+$, 100). $C_{10}H_{11}{}^{35}Cl_2O_4$ requires *m/z*, 265.0034 (M^+ + 1)]; δ_H 6.54—5.00 (5 H, complex, olefinic), 4.78 (2 H, d, *J* 6.0 Hz, CH_2O), and 3.88 (3 H, s, CO_2Me); $\nu_{max.}$($CHCl_3$) 1 745 and 1 600 cm^{-1}.

The following triene esters were also prepared by Method A.

Benzyl (E)-*penta*-2,4-*dienyl dichloromaleate* (**10**), obtained as an oil in 75% yield from benzyl hydrogen dichloromaleate (**6**) and (*E*)-penta-2,4-dien-1-ol [Found: (chemical ionisation using CH_4) *m/z*, 341.0356 (M^+ + 1, 0.2%) and 91 (100). $C_{16}H_{15}{}^{35}Cl_2O_4$ requires *m/z*, 341.0347 (M^+ + 1)]; δ_H 7.38 (5 H, complex, Ph), 6.50—5.10 (5 H, complex, olefinic), 5.25 (2 H, s, OCH_2Ph), and 4.75 (2 H, d, *J* 6.0 Hz, OCH_2); $\nu_{max.}$(film) 1 745 and 1 600 cm^{-1}.

Methyl 2-methyl-3-vinylcyclohex-2-enyl dichloromaleate (**14**), obtained as an oil in 35% yield from 2-methyl-3-vinylcyclohex-2-enol (**2**) and methyl hydrogen dichloromaleate (**5**), δ_H 6.82 (1 H, dd, *J* 11.0 and 17.0 Hz, $CH{=}CH_2$), 5.44 (1 H, m, 1-H), 5.30 (1 H, d, J_{trans} 17.0 Hz, CH=CH*H*), 5.18 (1 H, d, J_{cis} 11.0 Hz, CH=C*H*H), 3.85 (3 H, s, CO_2Me), and 2.50—1.60 (9 H, complex, 4-, 5-, and 6-H_2 and Me); $\nu_{max.}$(film) 1 740, 1 650, and 1 600 cm^{-1}.

Methyl 3-vinylcyclohex-2-enyl dichloromaleate (**13**), obtained as an oil in 84% yield from 3-vinylcyclohex-2-enol (**1**) and methyl hydrogen dichloromaleate (**5**), δ_H 6.33 (1 H, dd, *J* 11.0 and 18.0 Hz, $CH{=}CH_2$), 5.75 (1 H, m, 2-H), 5.50 (1 H, m, 1-H), 5.24 (1 H, d, J_{trans} 17.0 Hz, CH=CH*H*), 5.12 (1 H, d, J_{cis} 11.0 Hz, CH=C*H*H), 3.84 (3 H, s, CO_2Me), and 2.30—1.60 (6 H, complex, 4-, 5-, and 6-H_2); $\nu_{max.}$(film) 1 745 and 1 600 cm^{-1}.

(*E*)-Methyl 2-bromo-3-(3-vinylcyclohex-2-enyloxycarbonyl)-acrylate (**17**), obtained as an oil in 40% yield from 3-vinylcyclohex-2-enol (**1**) and (*E*)-3-bromo-3-methoxycarbonylacrylic acid (**15**), δ_H 6.51 (1 H, s, CH=CBr), 6.35 (1 H, dd, *J* 10.0 and 17.0 Hz, $CH{=}CH_2$), 5.73 (1 H, m, OCHC*H*=), 5.44 (1 H, m, OCH), 5.28 (1 H, d, J_{trans} 17.0 Hz, $CH{=}CHH$), 5.11 (1 H, d, J_{cis} 10.0 Hz, CH=C*H*H), 3.86 (3 H, s, CO_2Me), and 2.30—1.60 (6 H, complex, 3 × CH_2); $\nu_{max.}$($CHCl_3$) 1 745, 1 725, 1 625, and 1 610 cm^{-1}.

Method B: typical procedure. (E)-*Methyl* 2-*bromo*-3-[(E)-*penta*-2,4-*dienyloxycarbonyl*]*acrylate* (**16**). To a stirred solution of (*E*)-3-bromo-3-methoxycarbonylacrylic acid (**15**) (0.66 g, 3.2 mmol), (*E*)-penta-2,4-dien-1-ol (0.29 g, 3.5 mmol), and pyridine (0.25 g, 3.2 mmol) in ether (15 ml) at 0 °C was added a solution of DCC (0.65 g, 3.2 mmol) in ether (10 ml). The resulting mixture was stirred at room temperature for 18 h and then filtered. The filtrate was washed sequentially with saturated aqueous copper sulphate (2 × 30 ml) and brine (30 ml), dried, and concentrated under reduced pressure to give a viscous oil (0.88 g). Purification by flash column chromatography (eluant ether–light petroleum, 1:4) afforded (*E*)-methyl 2-bromo-3-[(*E*)-penta-2,4-dienyloxycarbonyl]acrylate (**16**) as an oil (0.46 g, 53%), δ_H 6.52 (1 H, CH=CBr), 6.45—5.10 (5 H, complex, olefinic), 4.68 (2 H, d, *J* 7.0 Hz, CH_2O), and 3.87 (3 H, s, CO_2Me); $\nu_{max.}$($CHCl_3$) 1 745, 1 730, 1 630, and 1 610 cm^{-1}.

The following triene esters were also prepared by Method B.

3,4-Methylenedioxybenzyl (*E*)-penta-2,4-dienyl dichloromaleate (**11**), obtained as an oil in 64% yield from (*E*)-penta-2,4-dien-1-ol and 3,4-methylenedioxybenzyl hydrogen dichloromaleate (**7**), δ_H 6.8 (3 H, complex, ArH), 6.5—5.1 (5 H, complex, olefinic), 5.9 (2 H, s, OCH_2O), 5.1 (2 H, s, $ArCH_2O$), and 4.6 (2 H, d, *J* 6.0 Hz, CH_2O); $\nu_{max.}$(film) 1 740, 1 725, 1 650, and 1 600 cm^{-1}.

(*E*)-Penta-2,4-dienyl 2-(trimethylsilyl)ethyl dichlormaleate (**12**), obtained as an oil in 87% yield from (*E*)-penta-2,4-dien-1-ol and 2-(trimethylsilyl)ethyl hydrogen dichloromaleate (**8**), δ_H 6.45—5.06 (5 H, complex, olefinic), 4.74 (2 H, d, *J* 6.0 Hz, $C_5H_7CH_2O$), 4.25 (2 H, m, CH_2O), 1.00 (2 H, complex, CH_2SiMe_3), and 0.00 (9 H, s, $SiMe_3$); $\nu_{max.}$($CHCl_3$) 1 740, 1 725, 1 650, and 1 600 cm^{-1}.

Method C: typical procedure. Methyl (E)-*penta*-2,4-*dienyl fumarate* (**20**). (*E*)-3-Methoxycarbonylacryloyl chloride (4.2 g, 28 mmol) was dissolved in dichloromethane (30 ml) and the solution was filtered. To the stirred filtrate at 0 °C was added

dropwise a solution of (*E*)-penta-2,4-dien-1-ol (1.5 g, 17.8 mmol), triethylamine (3.0 g, 30 mmol), and 4-dimethylaminopyridine (0.3 g, 2.6 mmol) in dichloromethane (50 ml). The mixture was stirred for 1 h at 0 °C and then the mixture was poured into water (100 ml) and extracted with chloroform (2 × 100 ml). The extract was washed with dil. aqueous sodium hydrogen carbonate (100 ml), dried, and concentrated under reduced pressure to afford a crude oil (4.0 g). This material was purified by flash chromatography (alumina; eluant ether–light petroleum, 2:3) to give *methyl* (E)-*penta*-2,4-*dienyl fumarate* (**20**) as an oil (3.47 g, 98%) [Found: *m/z*, 196.0737 (M^+, 7.1%) and 113 ($C_5H_7O^+$, 100). $C_{10}H_{12}O_4$ requires *M*, 196.0735]; δ_H 6.88 (2 H, s, COCH=CHCO), 6.55—4.90 (5 H, complex, olefinic), 4.73 (2 H, d, *J* 6.0 Hz, CH_2O), and 3.82 (3 H, s, CO_2Me); $\nu_{max.}(CHCl_3)$ 1 725, 1 645, and 1 605 cm^{-1}.

The following ester was also prepared by method C.

Methyl 3-vinylcyclohex-2-enyl fumarate (**18**), obtained as an oil in 66% yield from 3-vinylcyclohex-2-enol (**1**) and (*E*)-3-methoxycarbonylacryloyl chloride, δ_H 6.87 (2 H, s, COCH=CHCO), 6.36 (1 H, dd, *J* 11.0 and 17.0 Hz, C*H*=CH_2), 5.76 (1 H, m, OCHCH=), 5.47 (1 H, m, OCH), 5.28 (1 H, d, J_{trans} 17.0 Hz, CH=CH*H*), 5.10 (1 H, d, J_{cis} 11.0 Hz, CH=C*H*H), 3.83 (3 H, s, CO_2Me), and 2.30—1.60 (6 H, complex, 4-, 5-, and 6-H); $\nu_{max.}(CHCl_3)$ 1 720, 1 645, and 1 605 cm^{-1}.

Method D. Methyl 3-*vinylcyclohex*-2-*enyl maleate* (**19**). A solution of diethyl azodicarboxylate (1.4 g, 8.0 mmol) in THF (20 ml) was added dropwise to a stirred solution of 3-vinylcyclohex-2-enol (**1**) (0.5 g, 4.0 mmol), methyl hydrogen maleate (0.5 g, 4.0 mmol), and triphenylphosphine (2.1 g, 8.1 mmol) in THF (20 ml), and the resulting mixture was stirred for 1.5 h. The solvent was removed and the residue was redissolved in ether (30 ml). The precipitated triphenylphosphine oxide was filtered off and the filtrate was concentrated under reduced pressure to give an oily residue, which was purified by flash column chromatography (eluant ether–light petroleum, 3:7) to afford methyl 3-vinylcyclohex-2-enyl maleate (**19**) as an oil (0.25 g, 26%) and unconsumed 3-vinylcyclohex-2-ol (**1**) (0.08 g recovery); the title product showed δ_H 6.36 (1 H, dd, *J* 11.0 and 17.0 Hz, C*H*=CH_2), 6.26 (2 H, s, COCH=CHCO), 5.77 (1 H, m, OCHCH=), 5.48 (1 H, m, OCH), 5.26 (1 H, d, J_{trans} 17.0 Hz, CH=CH*H*), 5.10 (1 H, d, J_{cis} 11.0 Hz, CH=C*H*H), 3.77 (3 H, s, CO_2Me), and 2.50—1.60 (6 H, complex, 3 × CH_2); $\nu_{max.}(CHCl_3)$ 1 730, 1 645, and 1 605 cm^{-1}.

Cyclisation Reactions.—Typical procedure. (1RS,2SR,6RS)-*Methyl* 1,2-*Dichloro*-9-*oxo*-8-*oxabicyclo*[4.3.0]*non*-4-*ene*-2-*carboxylate* (**22**). Methyl (*E*)-penta-2,4-dienyl dichloromaleate (**9**) (2.25 g, 8.5 mmol) and 2,6-di-t-butyl-*p*-cresol (50 mg) were heated under reflux in xylene (100 ml) for 48 h. The xylene was removed under reduced pressure and the residue was washed with ether–light petroleum (1:1) to afford the *title compound* (**22**) as white crystals (1.54 g, 68%). Recrystallisation from chloroform–pentane gave an analytical sample, m.p. 123.5—125 °C (Found: C, 45.2; H, 3.7; Cl, 26.6. $C_{10}H_{10}Cl_2O_4$ requires C, 45.3; H, 3.8; Cl, 26.7%); δ_H 5.78 (1 H, dd, *J* 8.0 and 3.0 Hz, 4- or 5-H), 5.65 (1 H, dd, *J* 8.0 and 2.0 Hz, 5- or 4-H), 4.51 (1 H, dd, *J* 8.0 and 7.5 Hz, 7-H_α), 4.33 (1 H, dd, *J* 8.0 and 10.0 Hz, 7-H_β), 3.85 (3 H, s, CO_2Me), 3.43 (2 H, complex, 3- and 6-H), and 2.95 (1 H, m, 3-H); δ_C 167.76, 167.40 (C-9 and CO_2Me), 128.37, 119.82 (C-4 and C-5), 69.66 (C-1 or C-2), 67.64 (C-7), 66.87 (C-2 or C-1), 54.16 (OMe), 44.31 (C-6), and 39.83 (C-3); $\nu_{max.}(CHCl_3)$ 1 805 and 1 740 cm^{-1} [Found: (chemical ionisation using NH_3) *m/z* 264.9980 (M^+ + 1.0%), 229 (M^+ − ^{35}Cl, 57.0), and 149 (100). $C_{10}H_{11}{}^{35}Cl_2O_4$ requires *m/z*, 265.0034 (M^+ + 1)].

The following intramolecular Diels–Alder adducts were similarly obtained.

(1RS,2SR,6SR)-1,2-*Dichloro*-9-*oxo*-8-*oxabicyclo*[4.3.0]*non*-4-*ene*-2-*carboxylic acid* (**26**), as an oil in 20% yield from (*E*)-penta-2,4-dienyl hydrogen dichloromaleate (**3**), by heating for 18 h [Found: (chemical ionisation using NH_3) *m/z*, 268.0088 (M^+ + NH_3 + 1, 16.3%) and 188 (100). $C_9H_{12}{}^{35}Cl_2NO_4$ requires *m/z*, 268.0143 (M^+ + NH_3 + 1)]; δ_H 9.47 (1 H, br s, CO_2H), 6.10—5.60 (2 H, complex, 4- and 5-H), 4.84 (1 H, dd, *J* 8.5 and 6.0 Hz, 7-H_α), 4.28 (1 H, dd, *J* 8.5 and 1.0 Hz, 7-H_β), and 4.00—3.00 (3 H, complex, 3-H_2 and 6-H); $\nu_{max.}(CHCl_3)$ 3 300—2 700, 1 790, and 1 740 cm^{-1}.

(1RS,2SR,6RS)-*Benzyl* 1,2-*dichloro*-9-*oxo*-8-*oxabicyclo*-[4.3.0]*non*-4-*ene*-2-*carboxylate* (**23**), as an oil in 51% yield, and (1RS,2SR,6SR)-*benzyl* 1,2-*dichloro*-9-*oxo*-8-*oxabicyclo*[4.3.0]-*non*-4-*ene*-2-*carboxylate* (**28**), as an oil in 6% yield from benzyl (*E*)-penta-2,4-dienyl dichloromaleate (**10**), by heating for 24 h.

For compound (**23**) [Found: *m/z*, 342.0239 (M^+, 0.1%) and 91 (100). $C_{16}H_{14}{}^{35}Cl^{37}ClO_4$ requires *M*, 342.0240]; δ_H 7.36 (5 H, complex, Ph), 5.73 (1 H, m, 5- or 4-H), 5.53 (1 H, m, 4- or 5-H), 5.32 (1 H, d, *J* 12.0 Hz, PhC*H*H), 5.17 (1 H, d, *J* 12.0 Hz, PhCH*H*), 4.29 (1 H, dd, *J* 8.0 and 7.5 Hz, 7-H_α), 4.23 (1 H, dd, *J* 8.0 and 10.0 Hz, 7-H_β), 3.44 (1 H, m, 3-H), 3.18 (1 H, m, 6-H), and 2.91 (1 H, m, 3-H); δ_C 167.15, 166.85 (C-9 and CO_2Bn), 128.90, 128.77, 128.59, 128.52 (ArC), 128.47, 119.45 (C-4 and -5), 69.60 (C-1 or -2), 68.91 (CH_2Ph), 67.50 (C-7), 66.90 (C-2 or - 1), 44.16 (C-6), and 39.88 (C-3); $\nu_{max.}(CHCl_3)$ 1 805 and 1 740 cm^{-1}.

For compound (**28**) [Found: *m/z*, 340.0151 (M^+, 0.8%) and 91 (100). $C_{16}H_{14}{}^{35}Cl_2O_4$ requires *M*, 340.0268]; δ_H 7.38 (5 H, complex, Ph), 5.82 (1 H, m, 4- or 5-H), 5.65 (1 H, m, 5- or 4-H), 5.30 (2 H, s, PhCH_2), 4.75 (1 H, dd, *J* 9.0 and 5.5 Hz, 7-H_α), 4.12 (1 H, dd, *J* 9.0 and 1.0 Hz, 7-H_β), 3.44 (1 H, m, 6-H), 3.07 (1 H, m, 3-H), and 2.97 (1 H, m, 3-H); δ_C 164.04, 163.54 (C-9 and CO_2Bn), 126.09, 125.96, 125.77, 125.42 (ArC), 122.64, 121.47 (C-4 and -5), 68.21, 65.71 (PhCH_2 and C-7), 64.58, 64.16 (C-1 and -2), 45.84 (C-6), and 32.96 (C-3); $\nu_{max.}(CHCl_3)$ 1 790 and 1 740 cm^{-1}.

(1RS,2SR,6RS)-*Methyl* 2-*bromo*-9-*oxo*-8-*oxabicyclo*-[4.3.0]-*non*-4-*ene*-2-*carboxylate* (**31**), as a white crystalline solid, m.p. 152—154 °C (from chloroform–pentane), in 66% yield, and (1RS,2SR,6SR)-*Methyl* 2-*bromo*-9-*oxo*-8-*oxabicyclo*[4.3.0]*non*-4-*ene*-2-*carboxylate* (**32**), as a white crystalline solid, m.p. 124—126 °C (from chloroform–pentane), in 14% yield from (*E*)-methyl 2-bromo-3-[(*E*)-penta-2,4-dienyloxycarbonyl]acrylate (**16**) by heating for 18 h.

For compound (**31**) (Found: C, 43.6; H, 4.1. $C_{10}H_{11}BrO_4$ requires C, 43.7; H, 4.0%); δ_H 5.83 (1 H, m, 4- or 5-H), 5.67 (1 H, m, 5- or 4-H), 4.45 (1 H, dd, *J* 7.0 and 8.0 Hz, 7-H_α), 3.86 (1 H, dd, *J* 8.0 and 11.0 Hz, 7-H_β), 3.82 (3 H, s, CO_2Me), 3.56 (1 H, m, 3-H), 3.13 (1 H, m, 6-H), 2.94 (1 H, m, 3-H), and 2.83 (1 H, d, *J* 13.5 Hz, 1-H); δ_C 170.38, 169.01 (C-9 and CO_2Me), 128.60, 123.48 (C-4 and -5), 68.60 (C-7), 53.39 (OMe), 51.57 (C-2), 50.06 (C-1), 42.63 (C-3), and 40.12 (C-6); $\nu_{max.}(CHCl_3)$ 1 800, 1 740, 1 640, and 1 605 cm^{-1} [Found: *m/z*, 195.0627 (M^+ − Br, 6.5%), 163 (91.9), and 91 (100). $C_{10}H_{11}O_4$ requires *m/z*, 195.0657 (M^+ − Br)].

For compound (**32**) (Found: C, 43.6; H, 4.0%); δ_H 5.85 (1 H, m, 4- or 5-H), 5.74 (1 H, br d, *J* 10.0 Hz, 5- or 4-H), 4.43 (1 H, dd, *J* 9.0 and 5.5 Hz, 7-H_β), 4.19 (1 H, d, *J* 9.0 Hz, 7-H_α), 3.87 (3 H, s, CO_2Me), 3.79 (1 H, d, *J* 7.0 Hz, 1-H), 3.41 (1 H, m, 6-H), and 2.86 (2 H, complex, 3-H_2); δ_C 172.52, 169.66 (C-9 and CO_2Me), 126.34, 124.89 (C-4 and C-5), 71.68 (C-7), 54.30 (C-2), 53.31 (OMe), 48.14 (C-1), 37.47 (C-6), and 33.04 (C-3); $\nu_{max.}(CHCl_3)$ 1 780, 1 745, and 1 605 cm^{-1} [Found: *m/z*, 195.0657 (M^+ − Br, 12%) and 163 (100). $C_{10}H_{11}O_4$ requires *m/z*, 195.0657 (M^+ − Br)].

(1*RS*,2*SR*,6*RS*)-2-[Trimethylsilyl)ethyl 1,2-dichloro-9-oxo-8-oxabicyclo[4.3.0]non-4-ene-2-carboxylate (**25**), as an oil in 38% yield and (1*RS*,2*SR*,6*SR*)-2-(trimethylsilyl)ethyl 1,2-dichloro-9-oxo-8-oxabicyclo[4.3.0]non-4-ene-2-carboxylate (**30**), as an oil in 15% yield, from (*E*)-penta-2,4-dienyl 2-(trimethylsilyl)ethyl dichloromaleate (**12**), by heating for 36 h.

For compound (**25**) δ_H 5.75 (1 H, m, 4- or 5-H), 5.61 (1 H, m, 5- or 4-H), 4.45 (1 H, dd, *J* 7.0 and 8.0 Hz, 7-H_α), 4.30 (1 H, dd, *J* 8.0 and 10.5 Hz, 7-H_β), 4.29 (2 H, complex, $Me_3SiCH_2CH_2$), 3.47 (1 H, m, 6-H), 3.43 (1 H, m, 3-H), 2.91 (1 H, m, 3-H), 1.03 (2 H, complex, Me_3SiCH_2), and 0.00 (9 H, s, Me_3Si); δ_C 168.84 (C-9 and CO_2R), 130.37, 121.10 (C-4 and -5), 69.08, 67.88 (C-7 and $Me_3SiCH_2CH_2$), 45.87 (C-6), 41.36 (C-3), 18.67 (CH_2SiMe_3), 0.00 ($SiMe_3$), and 69.60 and 66.82 (C-1 and -2); $\nu_{max.}$($CHCl_3$) 1 810 and 1 740 cm^{-1}.

For compound (**30**) δ_H 5.70 (2 H, complex, 4- and 5-H), 4.72 (1 H, dd, *J* 6.0 and 9.0 Hz, 7-H_α), 4.30 (2 H, complex, $Me_3SiCH_2CH_2$), 4.09 (1 H, dd, *J* 9.0 and 1.0 Hz, 7-H_β), 3.40 (1 H, m, 6-H), 2.95 (1 H, m, 3-H), 2.86 (1 H, m, 3-H), 1.00 (2 H, complex, Me_3SiCH_2), and 0.00 (9 H, s, Me_3Si); $\nu_{max.}$($CHCl_3$) 1 790 and 1 735 cm^{-1}.

(1RS,2SR,6RS)-3,4-*Methylenedioxybenzyl* 1,2-*dichloro*-9-*oxo*-8-*oxabicyclo*[4.3.0]*non*-4-*ene*-2-*carboxylate* (**24**), as an oil in 33% yield from 3,4-methylenedioxybenzyl (*E*)-penta-2,4-dienyl dichloromaleate (**11**), by heating for 18 h [Found: *m/z*, 384.0120 (M^+, 7.6%) and 135 (100). $C_{17}H_{14}{}^{35}Cl_2O_6$ requires *M*, 384.0167]; δ_H 6.82 (3 H, complex, ArH), 6.01 (2 H, s, OCH_2O), 5.75 (1 H, m, 4- or 5-H), 5.55 (1 H, m, 5- or 4-H), 5.22 (1 H, d, *J* 12.0 Hz, ArC*H*H), 5.07 (1 H, d, *J* 12.0 Hz, ArCH*H*), 4.34 (1 H, dd, *J* 8.0 and 7.5 Hz, 7-H_α), 4.26 (1 H, dd, *J* 8.0 and 11.0 Hz, 7-H_β), 3.43 (1 H, m, 3-H), 3.23 (1 H, m, 6-H), and 2.91 (1 H, m, 3-H); δ_C 167.00, 166.83 (C-9 and CO_2CH_2Ar), 148.21, 148.01 (ArC), 128.55 (C-5 or -4), 127.87, 122.71 (ArC), 119.45 (C-4 or -5), 109.13, 108.38 (ArC), 101.34 (OCH_2O), 69.58 (C-1 or -2), 69.90 ($ArCH_2$), 67.44 (C-7), 66.89 (C-2 or -1), 44.19 (C-6), and 39.83 (C-3); $\nu_{max.}$($CHCl_3$) 1 805, 1 740, and 1 610 cm^{-1}.

(1RS,2RS,6RS)-*Methyl* 8-*oxabicyclo*[4.3.0]*non*-4-*ene*-2-*carboxylate* (**34**), as an oil, in 16% yield and (1RS,2RS,6SR)-*methyl* 8-*oxabicyclo*[4.3.0]*non*-4-*ene*-2-*carboxylate* (**33**), as a white crystalline solid in 32% yield, m.p. 125—126 °C (from chloroform–pentane), from methyl (*E*)-penta-2,4-dienyl fumarate (**20**), by heating for 18 h.

For compound (**34**) [Found: *m/z*, 196.0706 (M^+, 38.5%), 165 (M^+ − OMe, 23.8), and 91 (100). $C_{10}H_{12}O_4$ requires *M*, 196.0735]; δ_H 5.73 (1 H, m, 4- or 5-H), 5.63 (1 H, m, 5- or 4-H), 4.33 (1 H, dd, *J* 6.0 and 9.0 Hz, 7-H), 4.12 (1 H, d, *J* 9.0 Hz, 7-H_β), 3.73 (3 H, s, CO_2Me), 3.31 (1 H, dd, *J* 7.5 and 3.5 Hz, 1-H), 3.22 (2 H, complex, 2-and 6-H), 2.52 (1 H, ddd, *J* 18.0, 6.0, and 2.0 Hz, 3-H_α), and 2.28 (1 H, m, 3-H_β); δ_C 177.08 (C-9), 173.72 (CO_2Me), 127.99, 125.81 (C-4 and -5), 72.27 (C-7), 52.26 (OMe), 39.89 (C-6), 36.61, 34.03 (C-1 and -2), and 23.15 (C-3); $\nu_{max.}$($CHCl_3$) 1 775 and 1 735 cm^{-1}.

For compound (**33**) [Found: *m/z*, 196.0739 (M^+, 49.9%), 165 (16.7), and 91 (100). $C_{10}H_{12}O_4$ requires *M*, 196.0735]; δ_H 5.84 (1 H, m, 4- or 5-H), 5.79 (1 H, m, 5- or 4-H), 4.49 (1 H, dd, *J* 8.0 and 7.0 Hz, 7-H), 3.94 (1 H, dd, *J* 11.5 and 8.0 Hz, 7-H_β), 3.78 (3 H, s, CO_2Me), 2.88 (1 H, m, 6-H), 2.85 (1 H, ddd, *J* 12.0, 10.5, and 7.0 Hz, 2-H), 2.62 (1 H, dd, *J* 12.0 and 13.0 Hz, 1-H), 2.58 (1 H, ddd, *J* 18.0, 7.0, and 2.5 Hz, 3-H_β), and 2.37 (1 H, ddd, *J* 18.0, 10.5, and 3.5 Hz, 3-H_α); δ_C 174.04, 173.73 (C-9 and CO_2Me), 128.94, 123.68 (C-5 and -4), 70.73 (C-7), 52.07 (OMe), 44.47 (C-6), 40.27, 39.52 (C-1 and -2), and 30.50 (C-3); $\nu_{max.}$($CHCl_3$) 1 790 and 1 735 cm^{-1}.

(2aRS,3RS,8aSR,8bRS)-*Methyl* 2a,3,4,6,7,8,8a,8b-*octahydro*-2-*oxo*-1-*oxa*-*acenaphthene*-3-*carboxylate* (**57**), as a white crystalline solid, m.p. 75—76 °C (from ether–pentane), in 52% yield, from methyl 3-vinylcyclohex-2-enyl maleate (**19**), by heating for 18 h (Found: C, 66.1; H, 6.8. $C_{13}H_{16}O_4$ requires C, 66.1; H, 6.8%); δ_H 5.34 (1 H, m, 5-H), 4.65 (1 H, ddd, *J* 13.0, 8.5, and 4.5 Hz, 8a-H), 3.72 (3 H, s, CO_2Me), 3.28 (1 H, ddd, *J* 8.5, 4.5, and 2.5 Hz, 3-H), 3.10 (1 H, br dd, *J* 13.5 and 8.5 Hz, 8b-H), 2.64 (2 H, complex, 4-H_2), 2.50 (1 H, dd, *J* 13.5 and 4.5 Hz, 2a-H), 2.27 (2 H, complex, 6- or 7-H_2), 1.97 (1 H, m, 8-H), 1.86 (1 H, m, 7- or 6-H), 1.67 (1 H, m, 7- or 6-H), and 1.47 (1 H, m, 8-H); δ_C 173.77, 173.26 (C-2 and CO_2Me), 139.01 (C-5a), 119.86 (C-5), 77.46 (C-8a), 51.91 (OMe), 42.83, 37.41, 35.25 (C-8b, 2a, and -3), and 28.87, 25.79, 24.27, and 19.05 (C-4, -6, -7, and -8); $\nu_{max.}$($CHCl_3$) 1 780 and 1 735 cm^{-1} (Found: *m/z*, 236.1003 (M^+, 14.6%), 177 (M^+ − CO_2Me, 17.8), and 91 (100). $C_{13}H_{16}O_4$ requires *M*, 236.1049].

(2aRS,3SR,8aSR,8bRS)-*Methyl* 2a,3,4,6,7,8,8a,8b-*octahydro*-2-*oxo*-1-*oxa*-*acenaphthene*-3-*carboxylate* (**58**), as a white crystalline solid, m.p. 124—126 °C (from chloroform–pentane), in 66% yield from methyl 3-vinylcyclohex-2-enyl fumarate (**18**), by heating for 18 h (Found: C, 65.8; H, 6.8%); δ_H 5.39 (1 H, m, 5-H), 4.63 (1 H, ddd, *J* 12.5, 8.0, and 4.5 Hz, 8a-H), 3.77 (3 H, s, CO_2Me), 2.91 (1 H, dt, *J* 11.5 and 8.5 Hz, 3-H), 2.82 (1 H, m, 8b-H), 2.73 (1 H, dd, *J* 11.5 and 13.0 Hz, 2a-H), 2.61 (1 H, m, 4- or 6-H), 2.38 (1 H, m, 6- or 4-H), and 2.28—1.55 (6 H, complex, 4-, 6-H, and 7-, 8-H_2); δ_C 174.15, 173.73 (C-2 and CO_2Me), 138.70 (C-5a), 120.30 (C-5), 77.25 (C-8a), 52.05 (OMe), 42.76, 40.88, 39.04 (C-8b, -2a, and C-3), and 30.38, 25.60, 24.28, and 19.26 (C-4, -6, -7, and -8); $\nu_{max.}$($CHCl_3$) 1 785 and 1 740 cm^{-1} [Found: *m/z*, 236.1074 (M^+, 14.6%) and 91 (100). $C_{13}H_{16}O_4$ requires *M*, 236.1049].

(2aRS,3SR,8aRS,8bSR)-*Methyl* 3-*bromo*-2a,3,4,6,7,8,8a,8b-*octahydro*-2-*oxo*-1-*oxa*-*acenaphthene*-3-*carboxylate* (**61**), as a white crystalline solid, m.p. 158—160 °C (from chloroform–pentane), in 63% yield from (*E*)-methyl 2-bromo-3-(3-vinylcyclohex-2-enyloxycarbonyl)acrylate (**17**), by heating for 18 h (Found: C, 49.5; H, 4.8. $C_{13}H_{15}BrO_4$ requires C, 49.5; H, 4.8%); δ_H 5.28 (1 H, m, 5-H), 4.59 (1 H, ddd, *J* 13.0, 8.0, and 4.5 Hz, 8a-H), 3.83 (3 H, s, CO_2Me), 3.59 (1 H, br d, *J* 18.5 Hz, 4-H), 2.97 (3 H, complex, 2a-, 8b-, and 4-H), 2.24 (2 H, complex, 6-H_2), 1.99 (1 H, dddd, *J* 13.0, 6.0, 4.5, and 2.0 Hz, 8-H_β), 1.88 (1 H, m, 7-H), 1.71 (1 H, m, 7-H), and 1.46 (1 H, dddd, *J* 13.0, 13.0, 12.5, and 7.0 Hz, 8-H_α); δ_C 170.48, 169.48 (C-2 and CO_2Me), 137.66 (C-5a), 120.34 (C-5), 75.71 (C-8a), 53.66 (OMe), 52.41 (C-3), 48.44 (C-8b or -2a), 43.46 (C-4, -6, -7, or -8), 40.52 (C-2a or -8b), 25.48, 24.16, and 19.17 (3 carbons from C-4, -6, -7, and C-8); $\nu_{max.}$($CHCl_3$) 1 790 and 1 740 cm^{-1}.

Reactions of the Diels–Alder Adducts

Reductions.—(1RS,2SR,6RS)-*Methyl* 9-*oxo*-8-*oxabicyclo*[4.3.0]*non*-4-*ene*-2-*carboxylate* (**35**) *and* (1RS,2RS,6RS)-*methyl* 9-*oxo*-8-*oxabicyclo*[4.3.0]*non*-4-*ene*-2-*carboxylate* (**34**). (1*RS*,2*SR*,6*RS*)-Methyl 1,2-dichloro-9-oxo-8-oxabicyclo[4.3.0]non-4-ene-2-carboxylate (**22**) (400 mg, 1.5 mmol) and activated zinc dust (500 mg, 7.7 mmol) were stirred at 75 °C for 2.5 h. The mixture was poured into saturated aqueous sodium hydrogen carbonate (100 ml) and extracted with dichloromethane (2 × 50 ml). The extract was dried, and concentrated under reduced pressure to give a mixture of the two *cis*-fused lactones (**35**) and (**34**). Flash column chromatography (eluant ether–light petroleum, 4:1) afforded (1*RS*,2*RS*,6*RS*)-methyl 9-oxo-8-oxabicyclo[4.3.0]non-4-ene-2-carboxylate (**34**) as an oil (95 mg, 30%). Further elution afforded (1RS,2SR,6RS)-*methyl* 9-*oxo*-8-*oxabicyclo*[4.3.0]*non*-4-*ene*-2-*carboxylate* (**35**) (210 mg, 70%), as a white crystalline solid, m.p. 107–109 °C (from chloroform–pentane) (Found: C, 61.1; H, 6.2. $C_{10}H_{12}O_4$ requires C, 61.2; H, 6.1%); δ_H 5.92 (1 H, m, 4- or 5-H), 5.62 (1 H, br d, *J* 10.0 Hz, 5- or 4-H), 4.39 (1 H, dd, *J* 9.0 and 6.0 Hz, 7-H_α), 4.10 (1 H, d, *J* 9.0 Hz, 7-H_β), 3.77 (3 H, s, CO_2Me), 3.53 (1 H, dd, *J* 7.5 and 4.0 Hz, 1-H), 3.21 (1 H, m, 6-H), 2.80 (1 H, m, 2-H), and 2.34 (2 H, complex, 3-H_2); δ_C 175.90, 172.62 (C-9 and CO_2Me), 129.25, 125.77 (C-4 and -5), 71.96 (C-7), 52.02 (OMe), 40.25 (C-6), 36.99, 36.82 (C-2 and -1), and 22.86 (C-3); $\nu_{max.}$($CHCl_3$) 1 780 and 1 735 cm^{-1} [Found: *m/z*, 196.0744 (M^+, 0.9%), 165 (5.9), and 91 (100). $C_{10}H_{12}O_4$ requires *M*, 196.0735].

(1RS,2SR,6RS)-*Methyl* 1,2-*dichloro*-9-*oxo*-8-*oxabicyclo*[4.3.0]*nonane*-2-*carboxylate* (**46**). A solution of (1*RS*,2*SR*,6*RS*)-

methyl 1,2-dichloro-9-oxo-8-oxabicyclo[4.3.0]non-4-ene-2-carboxylate (**22**) (1.5 g, 5.7 mmol) in ethyl acetate (50 ml) was stirred with 10% palladium on charcoal (60 mg) under hydrogen until uptake was complete (40 min). The mixture was filtered and the filtrate was concentrated under reduced pressure to afford (1RS,2SR,6RS)-*methyl* 1,2-*dichloro*-9-*oxo*-8-*oxabicyclo*-[4.3.0]*nonane*-2-*carboxylate* (**46**) (1.4 g, 95%) as a white crystalline solid, m.p. 129—131 °C (from chloroform–pentane) (Found: C, 44.7; H, 4.4; Cl, 26.3. $C_{10}H_{12}Cl_2O_4$ requires C, 45.0; H, 4.5; Cl, 26.5%); δ_H 4.37 (1 H, dd, *J* 7.0 and 8.0 Hz, 7-H$_\alpha$, 4.13 (1 H, dd, *J* 8.0 and 10.0 Hz, 7-H$_\beta$), 3.89 (3 H, s, CO_2Me), 2.73 (1 H, m, 6-H), 2.58 (1 H, m, 3-, 4-, or 5-H), 2.37 (1 H, ddd, *J* 14.0, 14.0, and 4.5 Hz, 4-, 5-, or 3-H), 1.91 (1 H, m, 5-, 3-, or 4-H), 1.77 (2 H, complex, 2 Hs of 3-, 4-, or 5-H) and 1.35 (1 H, m, 5-, 4-, or 3-H); δ_C 168.71, 167.88 (C-9 and CO_2Me), 72.16 (C-1 or -2), 69.10 (C-7), 68.35 (C-2 or -1), 53.87 (OMe), 44.92 (C-6), and 35.37, 24.09, and 20.97 (C-3, -4, and -5); $\nu_{max.}$($CHCl_3$) 1 800 and 1 740 cm^{-1} [Found: *m*/*z* (chemical ionisation using NH_3) 267.0215 (M^+ + 1, 38.4%), 91 (29.5), and 69 (100). $C_{10}H_{13}{}^{35}Cl_2O_4$ requires *m*/*z*, 267.0191 (M^+ + 1)].

(2RS)-*Methyl* 9-*oxo*-8-*oxabicyclo*[4.3.0]*non*-1(6)-*ene*-2-*carboxylate* (**48**). A solution of (1*RS*,2*SR*,6*RS*)-methyl 1,2-dichloro-9-oxo-8-oxabicyclo[4.3.0]non-4-ene-2-carboxylate (**22**) (100 mg, 0.38 mmol) in methanol (20 ml) was stirred with platinum dioxide (70 mg) under hydrogen until uptake was complete (1 h). The mixture was filtered and the filtrate was concentrated under reduced pressure to afford (2RS)-*methyl* 9-*oxo*-8-*oxabicyclo*[4.3.0]*non*-1(6)-*ene*-2-*carboxylate* (**48**) (73 mg, 98%) as a white crystalline solid, m.p. 68—69 °C (from chloroform–pentane) (Found: C, 61.3; H, 6.2. $C_{10}H_{12}O_4$ requires C, 61.2; H, 6.1%); δ_H 4.79 (1 H, d, *J* 17.0 Hz, 7-H), 4.74 (1 H, dd, *J* 17.0 and 2.0 Hz, 7-H), 3.74 (3 H, s, CO_2Me), 3.37 (1 H, m, 2-H), 2.42 (2 H, complex, 5-H$_2$), and 1.95 (4 H complex, 3- and 4-H$_2$); δ_C 172.77 (CO_2Me), 163.16 (C-9), 124.25 (C-1 and -6), 72.03 (C-7), 52.20 (OMe), 37.05 (C-2), 26.01, 23.46, and 19.47 (C-3, -4, and -5); $\nu_{max.}$($CHCl_3$) 1 755, 1 735, and 1 680 cm^{-1} [Found: *m*/*z*, (chemical ionisation using NH_3) 197.0854 (M^+ + 1, 100%). $C_{10}H_{13}O_4$ requires *m*/*z*, 197.0814 (M^+ + 1)].

cis-5-*Chloro*-8-*oxabicyclo*[4.3.0]*non*-4-*en*-7-*one* (**54**). A solution of *cis*-5-chloro-8-oxabicyclo[4.3.0]nona-2,4-dien-7-one (**44**) (220 mg, 1.26 mmol) in ethyl acetate (20 ml) was stirred with 10% palladium on charcoal (40 mg) under hydrogen until uptake was complete (1 h). The mixture was filtered and the filtrate was concentrated to afford, after purification by flash column chromatography (eluant ether–light petroleum, 4:1), cis-5-*chloro*-8-*oxabicyclo*(4.3.0)*non*-4-*en*-7-*one* (**54**) (100 mg, 46%) as an oil (Found: *m*/*z*, 172.0258 (M^+, 16.6%) and 93 (100). $C_8H_9{}^{35}ClO_2$ requires *M*, 172.0291]; δ_H 6.07 (1 H, m, 4-H), 4.37 (1 H, dd, *J* 6.0 and 9.0 Hz, 9-H$_\beta$), 4.08 (1 H, dd, *J* 9.0 and 2.0 Hz, 9-H$_\alpha$), 3.28 (1 H, d, *J* 7.0 Hz, 6-H), 2.18 (1 H, m, 1-H), 2.22 (2 H, complex, 2- or 3-H$_2$), 1.87 (1 H, m, 3- or 2-H), and 1.55 (1 H, m, 3- or 2-H); δ_C 173.45 (C-7), 127.84 (C-4), 125.46 (C-5), 70.55 (C-9), 45.70 (C-6), 35.88 (C-1), and 24.20 and 22.58 (C-2 and -3); $\nu_{max.}$($CHCl_3$) 1 780, 1 645, and 1 600 cm^{-1}.

(1RS,2SR,6RS)-1,2-*Dichloro*-9-*oxo*-8-*oxabicyclo*-[4.3.0]-*nonane*-2-*carboxylic acid* (**40**). (1*RS*,2*SR*,6*RS*)-Benzyl 1,2-dichloro-9-oxo-8-oxabicyclo[4.3.0]non-4-ene-2-carboxylate (**23**) (160 mg, 0.47 mmol) in ethyl acetate (20 ml) was stirred with 10% palladium on charcoal (10 mg) under hydrogen until uptake was complete (2 h). The mixture was filtered and the filtrate was concentrated under reduced pressure to afford (1RS,2SR,6RS)-1,2-*dichloro*-9-*oxo*-8-*oxabicyclo*[4.3.0]*nonane*-2-*carboxylic acid* (**40**) as a white crystalline solid (110 mg, 87%), m.p. 170—172 °C (from methanol aqueous) [Found: *m*/*z* (chemical ionisation using CH_4) 253.0019 (M^+ + 1, 4.1%) and 142 (M^+ − HCl − CO_2, 100). $C_9H_{11}{}^{35}Cl_2O_4$ requires *m*/*z*, 253.0034 (M^+ + 1)]; δ_H[360 MHz, $(CD_3)_2CO$] 7.50 (1 H, br s, CO_2H), 4.44 (1 H, dd, *J* 7.0 and 8.5 Hz, 7-H$_\alpha$), 4.09 (1 H, dd, *J* 10.0 and 8.5 Hz, 7-H), 2.94 (1 H, m, 6-H), 2.55 (1 H, m, 3-, 4-, or 5-H), 2.36 (1 H, ddd, *J* 14.0, and 4.0 Hz, 3-, 4-, or 5-H), 2.07 (1 H, m, 4-, 5-, or 3-H), 1.92 (1 H, m, 4-, 5-, or 3-H), and 1.80 (2 H, complex, 2 Hs of 5-, 4-, or 3-H); δ_C 169.00, 168.80 (C-9 and CO_2H), 69.70 (C-7), 69.70 and (67.62 (C-1 and C-2), 45.68 (C-6), 36.46 (C-3), and 24.75 and 21.66 (C-4 and -5); $\nu_{max.}$($CHCl_3$) 3 300—2 500, 1 800, and 1 735 cm^{-1}.

(1RS,2SR,6RS)-*Methyl* 2-*bromo*-9-*oxo*-8-*oxabicyclo*[4.3.0]-*nonane*-2-*carboxylate* (**47**). A solution of (1*RS*,2*SR*)-methyl 2-bromo-9-oxo-8-oxabicyclo[4.3.0]non-4-ene-2-carboxylate (**32**) (300 mg, 1.1 mmol) in ethyl acetate (25 ml) was stirred with 10% palladium on charcoal (50 mg) under hydrogen until uptake was complete (4 h). The mixture was filtered and the filtrate was concentrated under reduced pressure to afford, after purification by flash column chromatography (eluant ether–light petroleum, 1:1), (1*RS*,2*SR*,6*RS*)-methyl 2-bromo-9-oxo-8-oxabicyclo-[4.3.0]nonane-2-carboxylate (**47**) (245 mg, 82%) as an oil, δ_H 4.37 (1 H, dd, *J* 7.0 and 8.0 Hz, 7-H), 3.83 (1 H, dd, *J* 8.0 and 11.0 Hz, 7-H$_\beta$), 3.82 (3 H, s, CO_2Me), 2.89 (1 H, m, 3-, 4-, or 5-H), 2.54 (1 H, d, *J* 13.5 Hz, 1-H), 2.54 (1 H, m, 6-H), 1.99 (2 H, complex, 3-, 4-, or 5-H), 1.87 (1 H, m, 4-, 5-, or 6-H), and 1.34 (2 H, complex, 2 Hs from 5-, 4-, or 3-H); δ_C 171.66, 168.75 (C-9 and CO_2Me), 69.85 (C-7), 54.39 (C-2), 53.24 (OMe), 52.99, 41.67 (C-1 and -6), and 41.39, 27.23, and 25.05 (C-3, (4, and -5); $\nu_{max.}$($CHCl_3$) 1 800 and 1 740 cm^{-1}.

Dehydrohalogenations.—*7-Methoxycarbonylphthalide* (**43**). (1*RS*,2*SR*,6*RS*)-Methyl 1,2-dichloro-9-oxo-8-oxabicyclo-[4.3.0]non-4-ene-2-carboxylate (**22**) (0.2 g, 0.8 mmol) and triethylamine (0.7 g, 7.2 mmol) were heated under reflux in THF (25 ml) for 7 h. The mixture was concentrated under reduced pressure and the residue was redissolved in dichloromethane (50 ml). This solution was washed successively with dil. hydrochloric acid (30 ml) and dil. aqueous sodium hydrogen carbonate (40 ml), dried, and concentrated to afford 7-methoxycarbonylphthalide (**43**) as a white solid (0.11 g, 76.5%), m.p. 105—107 °C (lit.,[23] 105—106 °C) [Found: *m*/*z*, 172.0258 (M^+, 16.6%) and 93 (100%). Calc. for $C_{10}H_8O_4$: *M*, 172.0291]; δ_H 7.80 (3 H, complex, ArH), 5.35 (2 H, s, CH_2O), and 4.00 (3 H, s, CO_2Me); $\nu_{max.}$($CHCl_3$) 1 775, 1 730, and 1 600 cm^{-1}.

Methyl-9-*oxo*-8-*oxabicyclo*[4.3.0]*nona*-1(16),2-*diene*-2-*carboxylate* (**49**) *and methyl*-9-*oxo*-8-*oxabicyclo*[4.3.0]*nona*-1(6),4-*diene*-2-*carboxylate* (**50**). (1*RS*,2*SR*,6*RS*)-Methyl 1,2-dichloro-9-oxo-8-oxabicyclo[4.3.0]nonane-2-carboxylate (**46**) (250 mg, 0.94 mmol) and triethylamine (700 mg, 7.20 mmol) were heated under reflux in THF (25 ml) for 18 h. The solvent was removed and the residue was redissolved in dichloromethane (50 ml). This solution was washed successively with dil. hydrochloric acid (30 ml) and water (40 ml), dried, and concentrated under reduced pressure to afford a mixture of the two bicyclic lactones (**49**) and (**50**). Purification by flash column chromatography (eluant ether) afforded *methyl* 9-*oxo*-8-*oxabicyclo*[4.3.0]*nona*-1(6),4-*diene*-2-*carboxylate* (**50**) as a white crystalline solid (53 mg, 28%), m.p. 101—102 °C (from chloroform–pentane) (Found: C, 61.4; H, 5.1. $C_{10}H_{10}O_4$ requires C, 61.8; H, 5.2%); δ_H 5.95 (2 H, complex, 4- and 5-H), 4.91 (1 H, d, *J* 17.0 Hz, 7-H), 4.83 (1 H, d, *J* 17.0 Hz, 7-H), 4.03 (1 H, m, 2-H), 3.75 (3 H, s, CO_2Me), and 3.10 (2 H, complex, 3-H$_2$); δ_C 170.29 (CO_2Me), 159.53 (C-9), 124.30, 122.89 (C-4 and -5), 122.71 (C-1 and -6), 71.87 (C-7), 52.54 (OMe), 39.53 (C-2), and 25.38 (C-3); $\nu_{max.}$($CHCl_3$) 1 765, 1 745, 1 700, and 1 635 cm^{-1} [Found: *m*/*z*, 194.0591 (M^+, 1.7%), 165 (5.6), and 91 (100). $C_{10}H_{10}O_4$ requires *M*, 194.0579].

Further elution afforded *methyl* 9-*oxo*-8-*oxabicyclo*-[4.3.0]*nona*-1(6),2-*diene*-2-*carboxylate* (**49**) as a white crystalline solid (63 mg, 35%), m.p. 103—104 °C (from chloroform–pentane) (Found: C, 61.8; H, 5.2%); δ_H 6.81 (1 H, t, *J* 4.0 Hz, 3-H), 4.85 (2 H, s, 7-H$_2$), 3.81 (3 H, s, CO_2Me), and 2.56 (4 H,

complex, 4- and 5-H_2); δ_C 165.09, 162.42 (C-9 and CO_2Me), 137.35 (C-3), 125.58, 122.85, 122.50 (C-1, -2, -6), 70.69 (C-7), 51.92 (OMe), 22.93 and 20.95 (C-4 and -5); $\nu_{max.}$($CHCl_3$) 1 765, 1 725, 1 650, and 1 605 cm^{-1} [Found: *m/z*, 194.0521 (M^+, 19.3%) and 165 ($M^+ - CO_2Me$, 100). $C_{10}H_{10}O_4$ requires *M*, 194.0579].

cis-*Methyl* 9-*oxo*-8-*oxabicyclo*[4.3.0]*nona*-2,4-*diene*-2-*carboxylate* (**45**). (1*RS*,2*SR*,6*SR*)-Methyl 2-bromo-9-oxo-8-oxabicyclo[4.3.0]non-4-ene-2-carboxylate (**32**) (175 mg, 0.64 mmol) and triethylamine (500 mg, 4.95 mmol) were heated under reflux in THF (25 ml) for 18 h. The solvent was removed and the residue was redissolved in dichloromethane (50 ml). This solution was washed successively with dil. hydrochloric acid (30 ml) and dil. aqueous sodium hydrogen carbonate (40 ml), dried, and concentrated under reduced pressure. The residue was purified by flash column chromatography (eluant ether–light petroleum, 1:1) to afford cis-*methyl* 9-*oxo*-8-*oxabicyclo*[4.3.0]-*nona*-2,4-*diene* (**45**) (105 mg, 85%) as a white crystalline solid, m.p. 75—77 °C (from chloroform–pentane) (Found: C, 61.6; H, 5.0%); δ_H 7.11 (1 H, d, *J* 6.0 Hz, 3-H), 6.24 (1 H, ddd, *J* 9.5, 6.0, and 2.5 Hz, 4-H), 5.98 (1 H, dd, *J* 9.5 and 2.5 Hz, 5-H), 4.60 (1 H, dd, *J* 6.0 and 9.0 Hz, 7-H_α), 4.47 (1 H, d, *J* 9.0 Hz, 7-H_β), 3.92 (1 H, d, *J* 10.5 H_γ, 1-H), 3.83 (3 H, s, CO_2Me), and 3.57 (1 H, m, 6-H); δ_C 176.12, 166.29 (C-9 and CO_2Me), 132.80, 132.38 (C-4 and -5), 125.22 (C-3), 122.94 (C-2), 72.58 (C-7), 52.14 (OMe), and 37.57 and 37.36 (C-1 and -6); $\nu_{max.}$($CHCl_3$) 1 785, 1 715, and 1 650 cm^{-1}.

7-[2-(*Trimethylsilyl*)*ethoxycarbonyl*]*phthalide* (**41**). (1*RS*,-2*SR*,6*RS*)-2-(Trimethylsilyl)ethyl 1,2-dichloro-9-oxo-8-oxabicyclo[4.3.0]non-4-ene-2-carboxylate (**25**) (90 mg, 0.25 mmol) and tetrabutylammonium fluoride (160 mg, 0.50 mmol) were dissolved in THF (5 ml) and the resulting mixture was stirred for 2 h at room temperature. Brine (10 ml) was added, and the mixture was extracted with ether (2 × 50 ml). The extract was dried, and concentrated under reduced pressure to afford 7-[2-(trimethylsilyl)ethoxycarbonyl]phthalide (**41**) (80 mg, 100%) as an oil, δ_H 7.72—7.50 (3 H, complex, ArH), 5.24 (2 H, s, 3-H_2), 4.42 (2 H, complex, ($Me_3SiCH_2CH_2O$), 1.12 (2 H, complex, Me_3SiCH_2), and 0.00 (9 H, s, Me_3Si); $\nu_{max.}$($CHCl_3$) 1 780, 1 725, and 1 600 cm^{-1}.

7-[2-(Trimethylsilyl)ethoxycarbonyl]phthalide (**41**) was converted into 7-carboxyphthalide (**42**), m.p. 165—166 °C (lit.,[24] 170—172 °C) by treatment with a further 2 mol equiv. of tetrabutylammonium fluoride, as above, in 74% yield.

Dechlorodecarboxylations.—5-*Chloro*-8-*oxabicyclo*[4.3.0]-*non*-5-*en*-7-*one* (**52**). (1*RS*,2*SR*,6*RS*)-1,2-Dichloro-9-oxo-8-oxabicyclo[4.3.0]nonane-2-carboxylic acid (**40**) (330 mg, 1.3 mmol) and triethylamine (700 mg, 7.2 mmol) were heated under reflux in THF (25 ml) for 2 h. The mixture was evaporated to dryness and the residue was redissolved in dichloromethane (50 ml). This solution was washed successively with dil. hydrochloric acid (40 ml) and dil. aqueous sodium hydrogen carbonate (30 ml), dried, and concentrated under reduced pressure to give 5-*chloro*-8-*oxabicyclo*[4.3.0]*non*-5-*en*-7-*one* (**52**) as a white crystalline solid (170 mg, 76%), m.p. 83—84 °C (from chloroform–pentane) [Found: *m/z*, 172.0295 (M^+ − Cl, 42), and 43 (100). $C_8H_9{}^{35}ClO_2$ requires *M*, 172.0291]; δ_H 4.52 (1 H, dd, *J* 8.5 and 8.5 Hz, 9-H_β), 3.78 (1 H, dd, *J* 8.5 and 10.0 Hz, 9-H_α), 3.12 (1 H, m, 1-H), 2.55 (2 H, complex, 4-H_2), 2.07 (2 H, complex, 2 Hs from 2- and 3-H), 1.75 (1 H, m, 2- or 3-H), and 1.27 (1 H, m, 3- or 2-H); δ_C 166.93 (C-7), 140.73 (C-5), 123.56 (C-6), 70.99 (C-9), 39.95 (C-1), 34.49 (C-4), 25.18 (C-2 or -3), and 22.89 (C-3 or -2); $\nu_{max.}$($CHCl_3$) 1 765 and 1 665 cm^{-1}.

cis-5-*Chloro*-8-*oxabicyclo*[4.3.0]*nona*-2,4-*dien*-7-*one* (**44**). (1*RS*,2*SR*,6*SR*)-1,2-Dichloro-9-oxo-8-oxabicyclo[4.3.0] non-4-ene-2-carboxylic acid (**26**) (100 mg, 0.4 mmol) and triethylamine (350 mg, 3.6 mmol) were heated under reflux in THF (25 ml) for 2 h. The solvent was removed and the residue was redissolved in dichloromethane (50 ml). This solution was washed successively with dil. hydrochloric acid (40 ml) and water (40 ml), dried, and concentrated under reduced pressure to afford, after flash column chromatography (eluant ether–light petroleum, 4:1), cis-5-*chloro*-8-*oxabicyclo*[4.3.0]*nona*-2,4-*dien*-7-*one* (**44**) as an oil (36 mg, 53%) [Found: *m/z*, 170.0035 (M^+, 10.9%) and 91 (100). $C_8H_7{}^{35}ClO_2$ requires *M*, 170.0135]; δ_H 6.19 (1 H, d, *J* 6.0 Hz, 4-H), 5.99 (1 H, ddd, *J* 9.5, 6.0, and 1.5 Hz, 3-H), 5.67 (1 H, dd, *J* 9.5 and 3.5 Hz, 2-H), 4.52 (1 H, dd, *J* 7.0 and 9.0 Hz, 9-H), 4.25 (1 H, dd, *J* 4.0 and 9.0 Hz, 9-H), 3.66 (1 H, m, 1-H), and 3.47 (1 H, d, *J* 11.0 Hz, 6-H); δ_C 174.50 (C-7), 125.80 (C-5), 124.70, 123.92, 122.65 (C-2, -3, and -4), 72.09 (C-9), 45.74 (C-6), and 38.60 (C-1); $\nu_{max.}$($CHCl_3$) 1 785, 1 645, and 1 605 cm^{-1}.

Acknowledgements

We thank the S.E.R.C. for financial support (M. J. B.) and Mrs. J. Street for recording spectra.

References

1 E. Ciganek, *Org. React.*, 1984, **32**, 1; A. G. Fallis, *Can. J. Chem.*, 1984, **62**, 183.
2 J. D. White, E. G. Nolen, and C. H. Miller, *J. Org. Chem.*, 1986, **51**, 1151.
3 J. D. White and B. G. Sheldon, *J. Org. Chem.*, 1981, **46**, 2273; J. D. White, B. G. Sheldon, J. Clardy, and B. A. Solheim, *Tetrahedron Lett.*, 1978, 5189.
4 J. Becher, H. Clausen, H. C. Nielson, and A. Ingendoh, *Tetrahedron Lett.*, 1985, **26**, 1249.
5 T. Schmidlin, W. Zurcher, and C. Tamm, *Helv. Chim. Acta*, 1981, **64**, 235; T. Schmidlin and C. Tamm, *ibid.*, 1978, **61**, 2096.
6 E. J. Corey, R. L. Danheiser, S. Chandrasekaran, G. E. Keck, B. Gopalan, S. D. Larsen, P. Siret, and J. L. Gras, *J. Am. Chem. Soc.*, 1978, **100**, 8034.
7 P. Yates and H. Auksi, *Can. J. Chem.*, 1979, **57**, 2853; *J. Chem. Soc., Chem. Commun.*, 1976, 1016.
8 J. M. Mellor and A. M. Wagland, following paper.
9 C. Soucy, D. Favreau, and M. M. Kayser, *J. Org. Chem.*, 1987, **52**, 129; M. M. Kayser, L. Breau, S. Eliev, P. Morand, and H. S. Ip, *Can. J. Chem.*, 1986, **64**, 104; M. M. Kayser and O. Eisenstein, *ibid.*, 1981, **59**, 2457.
10 S. F. Martin, S. A. Williamson, R. P. Gist, and K. M. Smith, *J. Org. Chem.*, 1983, **48**, 5170; H. Kotsuki, A. Kawamura, M. Ochi, and A. Tokoroyama, *Chem. Lett.*, 1981, 917; B. Fraser-Reid, Z. Benko, R. Guiliano, K. M. Sun, and N. Taylor, *J. Chem. Soc., Chem. Commun.*, 1984, 1029.
11 N. R. Eldred and D. M. Young, *J. Am. Chem. Soc.*, 1953, **75**, 4338; R. T. M. Fraser, *ibid., 1962*, **84**, 3436.
12 C. U. Kim and P. F. Misco, *Tetrahedron Lett.*, 1985, **26**, 2027.
13 M. Gerlach, *Helv. Chim. Acta*, 1977, **60**, 3039.
14 A. Pelter and B. Singaram, *J. Chem. Soc., Perkin Trans. 1*, 1983, 1383.
15 R. Baltzly and A. P. Phillips, *J. Am. Chem. Soc.*, 1946, **68**, 261.
16 G. E. Ham and W. P. Coker, *J. Org. Chem.*, 1964, **29**, 194.
17 K. C. Nicolaou and W. S. Li, *J. Chem. Soc., Chem. Commun.*, 1985, 421.
18 P. R. Jenkins, K. A. Menear, P. Barraclough, and M. S. Nobbs, *J. Chem. Soc., Chem. Commun.*, 1984, 1423; P. Magnus, C. Walker, P. R. Jenkins, and K. A. Menear, *Tetrahedron Lett.*, 1986, **27**, 651.
19 F. E. Ziegler, B. H. Jaynes, and M. T. Saindane, *Tetrahedron Lett.*, 1985, **26**, 3307.
20 E. R. Koft, A. S. Kotnis, and T. A. Broadbent, *Tetrahedron Lett.*, 1987, **28**, 2799.
21 S. D. Burke, S. M. Smith Strickland, and T. H. Powner, *J. Org. Chem.*, 1983, **48**, 454.
22 S. J. Hecker and C. H. Heathcock, *J. Org. Chem.*, 1985, **50**, 5159.
23 A. J. McAlees, R. McCrindle, and D. W. Sneddon, *J. Chem. Soc., Perkin Trans. 1*, 1977, 2030.
24 E. Wenkert, D. B. R. Johnston, and K. G. Dave, *J. Org. Chem.*, 1964, **29**, 2534.

Received 23*rd May* 1988; *Paper* 8/02055H