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Carbon–carbon bond formation by radical addition–fragmentation reactions of *O*-alkylated enols

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Received 12th May 2004, Accepted 8th July 2004
First published as an Advance Article on the web 10th August 2004

α-*tert*-Butoxystyrene [$H_2C{=}C(OBu^t)Ph$] reacts with α-bromocarbonyl or α-bromosulfonyl compounds [$R^1R^2C(Br)EWG$; EWG = –C(O)X or –S(O_2)X] to bring about replacement of the bromine atom by the phenacyl group and give $R^1R^2C(EWG)CH_2C(O)Ph$. These reactions take place in refluxing benzene or cyclohexane with dilauroyl peroxide or azobis(isobutyronitrile) as initiator and proceed by a radical-chain mechanism that involves addition of the relatively electrophilic radical $R^1R^2(EWG)C^{\bullet}$ to the styrene. This is followed by β-scission of the derived α-*tert*-butoxybenzylic adduct radical to give $Bu^{t\bullet}$, which then abstracts bromine from the organic halide to complete the chain. α-1-Adamantoxystyrene reacts similarly with $R^1R^2C(Br)EWG$, at higher temperature in refluxing octane using di-*tert*-amyl peroxide as initiator, and gives phenacylation products in generally higher yields than are obtained using α-*tert*-butoxystyrene. Simple iodoalkanes, which afford relatively nucleophilic alkyl radicals, can also be successfully phenacylated using α-1-adamantoxystyrene. *O*-Alkyl *O*-(*tert*-butyldimethylsilyl) ketene acetals $H_2C{=}C(OR)OTBS$, in which R is a secondary or tertiary alkyl group, react in an analogous fashion with organic halides of the type $R^1R^2C(Br)EWG$ to give the carboxymethylation products $R^1R^2C(EWG)CH_2CO_2Me$, after conversion of the first-formed silyl ester to the corresponding methyl ester. The silyl ketene acetals also undergo radical-chain reactions with electron-poor alkenes to bring about alkylation–carboxymethylation of the latter. For example, phenyl vinyl sulfone reacts with $H_2C{=}C(OBu^t)OTBS$ to afford $Bu^tCH_2CH(SO_2Ph)CH_2CO_2Me$ *via* an initial silyl ester. In a more complex chain reaction, involving rapid ring opening of the cyclopropyldimethylcarbinyl radical, the ketene acetal $H_2C{=}C(OCMe_2C_3H_5\text{-}cyclo)OTBS$ reacts with two molecules of *N*-methyl- or *N*-phenyl-maleimide to bring about [3 + 2] annulation of one molecule of the maleimide, and then to link the bicyclic moiety thus formed to the second molecule of the maleimide *via* an alkylation–carboxymethylation reaction.

Introduction

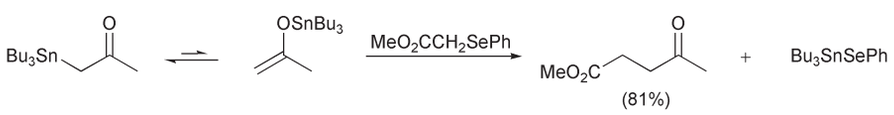
For a number of years now, a major objective of our research has been the development of synthetically useful radical-chain reactions that do not require the use of compounds of toxic heavy metals, notably tin and mercury, as key reagents.[1,2] For example, we have shown that simple trialkyl- or triaryl-silanes in conjunction with a thiol catalyst can often provide an effective and 'greener' replacement for the triorganotin hydrides that have played such an important role in the development of many useful radical-chain reactions.[1,2a,e,f] In this situation, the thiol serves as a *protic* polarity-reversal catalyst that mediates the abstraction by a nucleophilic carbon radical of the electron-rich hydrogen atom attached to silicon.[1] We have also demonstrated that amine–borane complexes can fulfil a complementary role as *hydridic* polarity-reversal catalysts and thereby promote the abstraction of electron-deficient hydrogen by electrophilic radicals.[1,2i]

Addition of a carbon-centred radical to an unsaturated carbon atom in an appropriate acceptor, followed by fragmentation of the adduct radical produced, is the key chain propagating event in several important reactions for the construction of carbon–carbon bonds. In particular, allylstannanes have been used widely as radical acceptors in this context.[3,4] Building on an earlier investigation by Russell and Herold[5] of the photo-induced reactions of *O*-tributylstannyl enolates with polyhalogenomethanes, Toru and co-workers[6] reported in 1990 that 1,4-dicarbonyl compounds could be prepared by similar radical-chain reactions of stannyl enolates with α-(phenylselenyl)carbonyl compounds, as illustrated in Scheme 1. The mechanism of this type of reaction is generalised in Scheme 2, although to ensure efficient chain propagation when R^2 is a simple alkyl group it is necessary for the addendum radical $R^{1\bullet}$ to be relatively electrophilic, a property that is conferred by the α-methoxycarbonyl group in $MeO_2CCH_2^{\bullet}$ (Scheme 1).

More recently, Hosomi and co-workers[7] have significantly expanded the use of stannyl enolates for the formation of carbon–carbon bonds by addition–fragmentation radical-chain reactions. These authors showed that stannyl enolates derived from aromatic ketones are sufficiently reactive towards addition even of relatively nucleophilic alkyl radicals to allow β-ketoalkylation of simple alkyl bromides and iodides to be carried out efficiently (Scheme 2, R^1 = alkyl, R^2 = aryl, Y = Br or I). Of particular note, it was shown that an effective three-component coupling reaction could be carried out in the presence of an electron-deficient alkene, as illustrated in Scheme 3 for methyl acrylate. Here the nucleophilic *tert*-butyl radical is trapped preferentially by the acrylate, while the resulting *more electrophilic* α-(methoxycarbonyl)alkyl radical subsequently adds to the stannyl enolate in preference to the acrylate.

While our own work in the area was in progress, Roepel[8] reported a means to avoid the use of organotin compounds in this type of reaction by replacing the stannyl enolate with an *O*-benzyl enol in conjunction with an α-phenylselenyl-malononitrile or -malonic ester as the source of an electrophilic carbon-radical addendum (see Scheme 4, EWG = electron-withdrawing group).

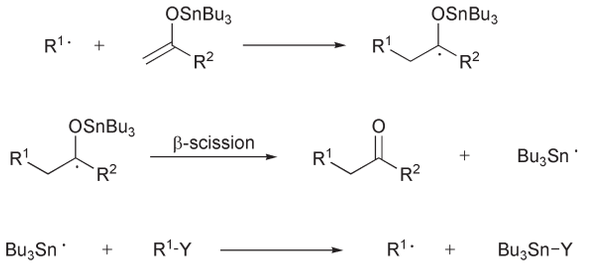
† Correspondence concerning the X-ray crystallography should be directed to this author.
‡ In part.



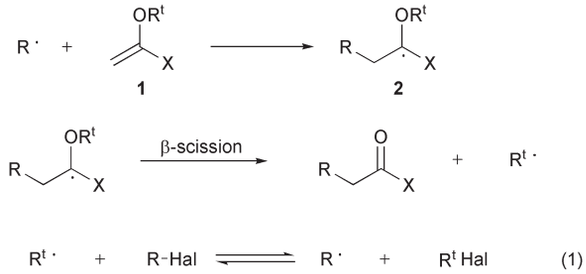
Conditions: *hν* (400 W Hg-lamp through pyrex), benzene, ambient temp., 1 h

Scheme 1

DOI: 10.1039/b407215b



Scheme 2



Scheme 5

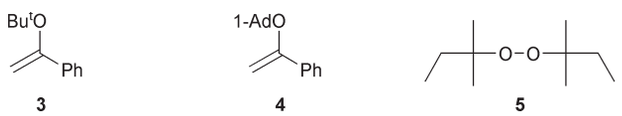
However, a major limitation to such use of *O*-benzyl enols is the requirement for effective chain propagation by the resonance stabilised and relatively unreactive benzyl radical. Our ongoing interest in the β-scission of α-alkoxyalkyl radicals, with regard to both mechanistic studies[9,10] and applications in synthesis,[2d,g] encouraged us to explore the use of *O-tert*-alkyl enols of the type **1** as radical acceptors for β-ketoalkylation of organic halides according to Scheme 5.[11] The initial reasoning behind our approach was based on the knowledge that *tert*-alkoxyalkyl radicals undergo β-scission relatively easily[9,10] and that, although it is well known that the C–H bond strength decreases appreciably along the series Me–H > Et–H > Pr^i–H > Bu^t–H, the corresponding bonds to more electronegative elements, including bromine and iodine, vary much less in strength.[10–12] For example, the C–I bond dissociation enthalpies for Me–I, Et–I, Pr^i–I and Bu^t–I are reported to be 239, 236, 234 and 231 kJ mol^{-1}, respectively, while D*H*(PhCH$_2$–I) is a lot smaller at 215 kJ mol^{-1}.[13] Thus, not only should an adduct radical of the type **2** undergo ready β-scission to give the tertiary alkyl radical R^t•, but the latter should (in contrast to a benzyl radical[8]) be relatively easily transformed into the desired addendum radical R• by transfer of an electronegative atom or group, as in the equilibrium process illustrated by eqn. (1) in Scheme 5.

We were delighted to discover that *O-tert*-alkyl enols could indeed be used successfully for carbon–carbon bond formation as illustrated in Scheme 5, and a preliminary report of our findings in this area has appeared already.[11] In the present paper we give a fuller account of this work and describe a number of extensions of the new methodology, including the reactions of *O*-alkyl *O*-silyl ketene acetals with electron-poor alkenes, some of which have also been described in a preliminary report.[14]

Results and discussion

Reactions of α-alkoxystyrenes with organic halides

Our work began with an investigation of the radical-chain reactions of α-*tert*-butoxystyrene[15] **3** with organic halides that yield relatively electrophilic carbon-centred radicals in the halogen-atom transfer step [eqn. (1)] of Scheme 5 (X = Ph). Because of the constraints imposed by its caged structure, the geometry at the radical centre in the tertiary 1-adamantyl radical (1-Ad•) is more strongly pyramidal than that in the *tert*-butyl radical and 1-Ad• often behaves differently from a simple acyclic tertiary alkyl radical. It is generally more reactive and probably more nucleophilic[16] than Bu^t• and 1-Ad–X bonds are stronger than the corresponding Bu^t–X bonds.[17] Therefore, we subsequently explored the use of α-1-adamantoxystyrene **4** for comparison with the *tert*-butyl analogue **3**. Although β-scission of an adduct radical of the type **2** to give 1-Ad• is expected to be slower than cleavage of the corresponding *O-tert*-butyl adduct to give Bu^t•,[18] this propagation step may not always be critical in determining the overall rate of the chain reaction, especially at higher temperatures. In the event, the 1-adamantyl derivative **4** turned out to be beneficially less reactive in a heterolytic sense than **3** (in particular, more stable towards hydrolysis), while its use for radical reactions of the type shown in Scheme 5 often proved advantageous compared with the corresponding reactions of **3**, presumably because of the increased efficiency of the halogen-atom transfer step.§ The choice of initiator depended on the temperature at which the reaction was carried out; azobis(isobutyronitrile) (AIBN) or dilauroyl peroxide (DLP) was used for reactions in refluxing benzene or cyclohexane and di-*tert*-amyl peroxide[19] (DTAP) **5** for reactions conducted in refluxing octane or chlorobenzene.



When α-*tert*-butoxystyrene **3** was heated alone in refluxing benzene under argon, no change was detected by NMR spectroscopy after 3 h. However, in the presence of 5 mol% AIBN or DLP, similar treatment resulted in the complete conversion of **3** to neopentyl phenyl ketone **6a**, which was isolated in *ca.* 95% yield. Under these conditions, **3** undergoes clean radical-chain rearrangement according to the mechanism shown in Scheme 6, resulting in the formal 1,3-shift of the *tert*-butyl group.[20]¶ However, when ethyl bromoacetate (3 equiv.) was present along with the AIBN, NMR analysis after removal of the solvent showed complete conversion of **3** to a mixture of ethyl 4-oxo-4-phenylbutanoate **7a** and **6a** in the ratio 70 : 30. The *tert*-butyl radical, resulting from the β-scission of the α-*tert*-butoxybenzylic radical of the type **2**, now abstracts bromine from BrCH$_2$CO$_2$Et in competition with its addition to the

§ An alternative approach, also designed to increase the efficiency of halogen-atom transfer, was described in our preliminary communication.[11] This involved using the *O*-cyclopropyldimethylcarbinyl analogue of **3**, when the *tertiary* cyclopropyldimethylcarbinyl radical produced in the β-scission step undergoes very rapid ring-opening rearrangement to give a *primary* but-3-enyl-type radical, which abstracts halogen more effectively than the *tert*-butyl radical.

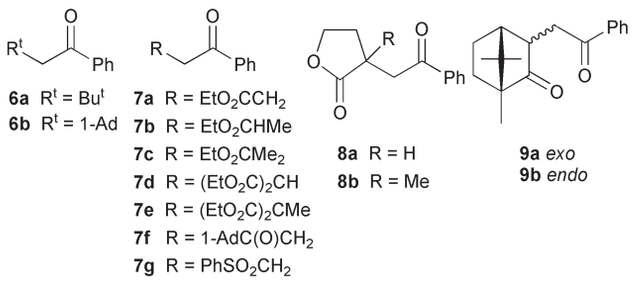
¶ Under the same conditions, α-benzyloxystyrene rearranged only partially (40%) to give PhCH$_2$CH$_2$C(O)Ph.

Conditions: AIBN initiator, benzene, 80 °C, 4 h

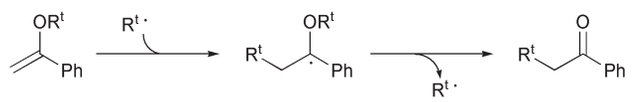
Scheme 3

Conditions: Sunlamp irradiation, chloroform, ambient temp., 12-17 h or AIBN initiator, refluxing benzene, 16 h

Scheme 4



styrene **3**. When the latter was added slowly by syringe pump to the bromoester and AIBN (10 mol%) in refluxing benzene, the product ratio **7a** : **6a** increased to 95 : 5. Slow addition of **3** was not necessary when the bromoacetate was replaced as halogen-atom donor by the much more reactive ethyl iodoacetate (2 equiv.) and **7a** was then produced in high yield without competitive formation of **6a**. For all radical reactions in the presence of halogen-atom donors, a small amount of 2,4,6-collidine or 2,2,6,6-tetramethylpiperidine was also added as a sterically hindered base to suppress acid-catalysed heterolytic reactions of the α-alkoxystyrenes, particularly their adventitious hydrolysis.

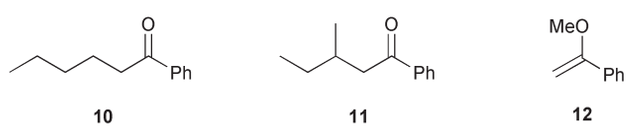


Scheme 6

α-1-Adamantoxystyrene **4** underwent a similar radical-chain 1,3-rearrangement to give the ketone **6b** when heated under reflux in octane containing DTAP initiator (20 mol%) and **6b** was isolated in 91% yield. When ethyl bromoacetate (2 equiv.) and 2,2,6,6-tetramethylpiperidine (TMP; 10 mol%) were included in the reaction mixture, the 1-adamantyl radical was efficiently diverted into abstracting halogen from the bromo ester and ethyl 4-oxo-4-phenylbutanoate **7a** was formed in high yield (Table 1, entry 12). Even with two equivalents of the bromo ester and without syringe pump addition of the alkoxystyrene, only *ca.* 5% of the ketone **6b** was present in the crude reaction product (*cf.* entry 1). Several similar reactions of the α-*tert*-alkoxystyrenes **3** and **4** with sources of relatively electrophilic carbon-radical addenda, to afford the phenyl ketones **7**–**9**, were also carried out and the results are collected in Table 1.

In general, although a higher reaction temperature was required, use of the alkoxystyrene **4** in place of **3** often resulted in improved yields of the desired phenacylation product, which contained only small amounts of the easily-separated 1,3-rearrangement product **6b** before purification. For example, the isolated yields of the lactone **8a** (entries 9 and 14) and of the camphor derivative **9** (entries 11 and 15) were significantly improved using the procedures based on **4**.

Phenyl ketones derived from reactions of the alkoxystyrenes **3** and **4** with sources of relatively *nucleophilic* radical addenda proved more difficult to obtain in preference to the styrene-rearrangement products **6a** and **6b**, although again α-1-adamantoxystyrene **4** was significantly more successful than **3** in this type of reaction. Thus, treatment of **3** with *n*-butyl iodide (5 equiv.) in refluxing benzene, containing AIBN (5 mol%) and collidine (10 mol%), resulted in its complete conversion to a 19 : 81 mixture of ketones **10** and **6a** after 3 h. Evidently, **3** is preferentially trapping the *tert*-butyl radical, rather than the *n*-butyl radical derived from the iodide. Slow addition of **3** using a syringe pump only raised the proportion of hexanophenone **10** to 34% and it appears that the equilibrium [eqn. (1)] in Scheme 5 lies too far to the left for the reaction to be useful in the case of a simple primary alkyl iodide. Replacing the *n*-butyl iodide with *s*-butyl iodide (3 equiv.), with all the reagents present initially, improved the situation such that the product ketone



ratio **11** : **6a** was 35 : 65. At higher temperature in refluxing octane solvent, in the presence of TMP (0.20 equiv.) with DTAP (0.30 equiv.) as initiator, the ratio **11** : **6a** could be raised to 52 : 48.

The selectivity for formation of **10** or **11** improved considerably when the *O*-1-adamantoxy analogue **4** was used in place of **3**. Thus, when an octane solution containing **4**, *n*-butyl iodide (5 equiv.), DTAP (0.30 equiv.) and TMP (0.20 equiv.) was heated under reflux for 4 h, the alkoxystyrene was converted to a 90 : 10 mixture of **10** and **6b** from which **10** was isolated in 83% yield by flash chromatography followed by Kugelrohr distillation. A similar reaction using *s*-butyl iodide (3 equiv.) afforded a crude product containing a 93 : 7 mixture of **11** and **6b** from which pure **11** was isolated in 86% yield.

In view of the reports by Giese and co-workers[21] that α-methoxystyrene **12** undergoes reductive carboxyalkylation when treated with an α-bromo ester and tributyltin hydride [*e.g.* to give $MeO_2CCH_2CH_2CH(OMe)Ph$ with methyl bromoacetate], we felt it was necessary to exclude the mechanism shown in Scheme 7 as a possible alternative pathway to the phenacylation products observed under our conditions.‖ However, when a benzene solution containing α-methoxystyrene, ethyl bromoacetate (3 equiv.), AIBN (0.05 equiv.) and collidine (0.10 equiv.) was heated under reflux for 3 h, conditions comparable to those which lead to complete consumption of α-*tert*-butoxystyrene to afford **7a**, there was no significant reaction of **12** as judged by NMR spectroscopy. There was also no reaction of α-methoxystyrene in a similar experiment when the α-bromo ester was replaced with *n*-butyl iodide (5 equiv.). Addition of R$^\bullet$ to α-methoxystyrene **12** should take place at least as rapidly as its addition to α-*tert*-butoxystyrene **3**, to form an adduct which should abstract halogen as readily as would the *O*-*tert*-butyl analogue **13** (Scheme 7). Hence, if **3** reacted with organic halides as shown in Scheme 7 under our conditions, we would expect extensive reaction of α-methoxystyrene to take place in the control experiments, to give either the *O*-methyl analogue of **14** or its heterolytic decomposition products. Therefore, we believe that the mechanism shown in Scheme 5 is followed under our conditions: in Giese's[21] reactions with α-methoxystyrene the intermediate *O*-methyl analogue of **13** must be trapped exclusively by the tin hydride, rather than by the organic halide, to give the reductive carboxyalkylation product and a stannyl radical that continues the chain by abstracting halogen from the halide.*

We have also examined briefly the addition–fragmentation radical-chain reactions of the α-1-adamantoxy-β-methylstyrene **16**, prepared as a 66 : 34 mixture of its *E* and *Z* isomers.[23] When an octane solution containing **16** and DTAP (0.20 equiv.) as initiator was heated under reflux for 4 h, only *ca.* 30% rearrangement to the ketone **17** took place, as judged by NMR spectroscopic analysis of the crude reaction product. The sluggish 1,3-rearrangement of **16**, compared with the corresponding rearrangement of its unmethylated parent **4** to give **6b**, is presumably a result of steric retardation of the addition of the relatively bulky 1-adamantyl radical to the β carbon in **16** and, in general, steric effects appear to exert a dominant influence on radical addition to this alkene. Thus, although benzoylalkylation of EtO_2CCH_2Br with **16** proceeded smoothly to give the phenyl ketone **18a** in near-quantitative yield, the corresponding reaction with EtO_2CCMe_2Br gave only *ca.* 10% of **18b**, as judged by NMR spectroscopy, and most of the bromo ester remained unchanged (Table 1, entries 16 and 17). Not only is the radical $EtO_2CCMe_2^\bullet$ more bulky than $EtO_2CCH_2^\bullet$, but it is also more nucleophilic and both factors act to slow the rate of its addition to the electron-rich double bond in **16** to a point where the benzoylalkylation reaction becomes non-viable.

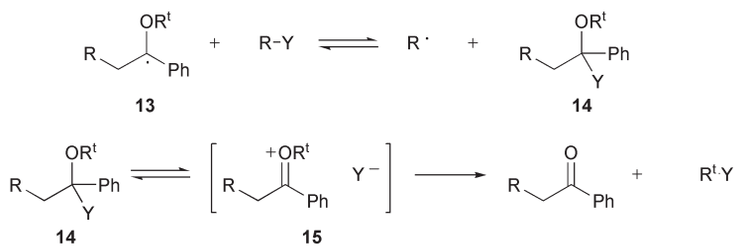
‖ In this mechanism the ion pair **15** might possibly be formed by dissociative electron transfer to R–Y from the α-alkoxybenzyl radical **13**, leading directly to R$^\bullet$ and Y$^-$.

* The reactions of some organic halides (RHal), including benzyl and *n*-butyl bromides, with α-methoxystyrene at very high temperatures (<200 °C) were described briefly in 1940.[22] Although $PhC(O)CH_2R$ was obtained in low yield from these reactions, the mechanism by which the ketones were formed is unclear.

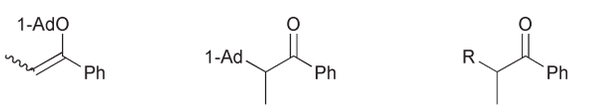
Table 1 Reactions of α-alkoxystyrenes **3**, **4** and **16** with organic halides that afford electrophilic radical addenda[a]

Entry	Styrene	Halogen donor (equiv.)	Initiator (equiv.)	Solvent	Product (isolated yield)
1	**3**[b]	EtO_2CCH_2Br (3.0)	AIBN (0.10)	Benzene[c]	**7a**[d] (85%)
2	**3**	EtO_2CCH_2I (2.0)	AIBN (0.05)	Benzene[c]	**7a** (82%)
3	**3**	$EtO_2CCHMeBr$ (3.0)	AIBN (0.05)	Benzene[c]	**7b** (86%)
4	**3**	EtO_2CCMe_2Br (3.0)	AIBN (0.05)	Benzene[c]	**7c** (85%)
5	**3**	$(EtO_2C)_2CHBr$ (2.0)	AIBN (0.05)	Benzene[c]	**7d** (84%)
6	**3**	$(EtO_2C)_2CMeBr$ (2.0)	AIBN (0.05)	Benzene[c]	**7e** (91%)
7	**3**	$AdC(O)CH_2Br$ (3.0)	AIBN (0.05)	Benzene[c]	**7f**[e] (78%)
8	**3**[b]	$PhSO_2CH_2Br$ (2.0)	AIBN (0.05)	Benzene[c]	**7g**[f] (75%)
9	**3**	α-Bromo-γ-butyrolactone (3.0)	AIBN (0.05)	Benzene[c]	**8a** (54%)
10	**3**	α-Bromo-α-methyl-γ-butyrolactone (3.0)	AIBN (0.05)	Benzene[c]	**8b** (55%)
11	**3**	(1*R*)-*endo*-(+)-3-Bromocamphor (3.0)	AIBN (0.05)	Benzene[c]	**9**[g] (25%)
12	**4**[h]	EtO_2CCH_2Br (2.0)	DTAP (0.20)	Octane[i]	**7a** (87%)
13	**4**[h]	$PhSO_2CH_2Br$ (2.0)	DTAP (0.20)	PhCl[i]	**7g** (84%)
14	**4**[h]	α-Bromo-γ-butyrolactone (2.0)	DTAP (0.20)	PhCl[i]	**8a** (90%)
15	**4**[h]	(1*R*)-*endo*-(+)-3-Bromocamphor (2.0)	DTAP (0.20)	PhCl[i]	**9**[g] (63%)
16	**16**[h]	EtO_2CCH_2Br (2.0)	DTAP (0.20)	Octane[j]	**18a** (95%)
17	**16**[h]	EtO_2CCMe_2Br (2.0)	DTAP (0.20)	Octane[j]	**18b**[j] (10%)

[a] Unless stated otherwise, 2,4,6-collidine (0.10 equiv.) was added to suppress acid-catalysed heterolytic reactions of the styrene and all reagents were present initially; the reaction time was usually 3 h. [b] The α-*tert*-butoxystyrene was added by syringe pump over the first 1.5 h. [c] Bath temp. 90 °C, internal temp. *ca.* 85 °C. [d] The crude product contained a 95 : 5 mixture of **7a** and **6a**. [e] The crude product contained an 84 : 16 mixture of **7f** and **6a**. [f] The crude product contained a 76 : 24 mixture of **7g** and **6a**. [g] The isolated product was a *ca.* 64 : 36 mixture of *exo* and *endo* isomers. [h] The collidine was replaced with TMP (0.10 equiv.). [i] Bath temp. 140 °C. [j] About 80% of the starting material remained unreacted.

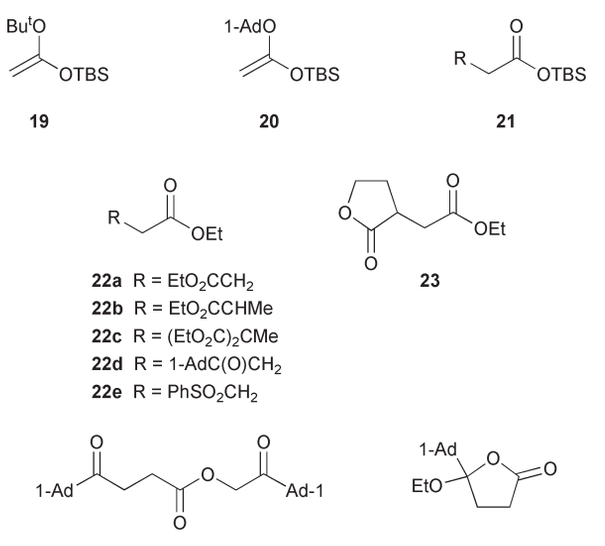


Scheme 7



Reactions of *O*-alkyl *O*-silyl ketene acetals

(a) Reactions with organic halides. Radical addition to the *O*-*tert*-alkyl *O*-(*tert*-butyldimethylsilyl) ketene acetals **19** and **20** (TBS = Bu^tMe_2Si) would be expected to be slower than addition to the α-alkoxystyrenes **3** and **4**, especially when the addendum radical is relatively nucleophilic, because the radical-stabilising phenyl group has been replaced by an electron-donating siloxy group.



However, both **19** and **20** reacted smoothly according to Scheme 5 (X = OTBS) with organic bromides that yield relatively *electrophilic* addenda. Because the *nucleophilic tert*-butyl and 1-adamantyl radicals add particularly slowly to the ketene acetals, there was no competing formation of their 1,3-rearrangement products, as in some reactions of the styrenes **3** and **4**. The initial products from **19** and **20** were silyl esters of the type **21** but, although these could be isolated by careful chromatography on Florisil®, because of their relatively high sensitivity to hydrolysis it was more convenient to convert them first into alkyl esters. This was usually done by treatment with tetrabutylammonium fluoride (TBAF) and the appropriate alkyl iodide[24] or, in some cases, by desilylation with oxalyl chloride in the presence of catalytic DMF, followed by *in situ* conversion of the resulting acid chloride to the ethyl ester by treatment with ethanol and pyridine.[25] The esters **22a–e** and **23** were obtained in this way and the results are summarised in Table 2.

Good isolated yields of the carboxymethylation products **22a–c** were obtained from reactions of representative α-bromo esters with the *O*-*tert*-butyl ketene acetal **19** (entries 1–3). Corresponding carboxymethylation of 1-adamantyl bromomethyl ketone to give **22d** was also successful when one equivalent of the bromo ketone was used in conjunction with TBAF–EtI for desilylation (entry 4). However, with two equivalents of the bromo ketone the latter reacted in preference to the ethyl iodide with the carboxylate derived from the initial silyl ester (see Scheme 8) to afford the compound **24** in excellent yield (entry 5). In an attempt to permit the use of excess bromo ketone in order to maximise the yield of **22d**, desilylation was carried out by reaction of the silyl ester with oxalyl chloride followed by treatment with ethanol and pyridine. However, rather than giving the normal ester **22d**, this procedure afforded the 'pseudo ester'[26] **25**, as shown in Scheme 8 (entry 6). The structure of **25** was confirmed by single-crystal X-ray diffraction. Carboxymethylation of bromomethyl phenyl sulfone to give **22e** was successful using 2 equivalents of the bromide, followed by desilylation with TBAF–EtI (entry 7), but with α-bromo-

Table 2 Reactions of the *O-tert*-alkyl *O*-silyl ketene acetals **19** and **20** with organic halides that afford electrophilic radical addenda[a]

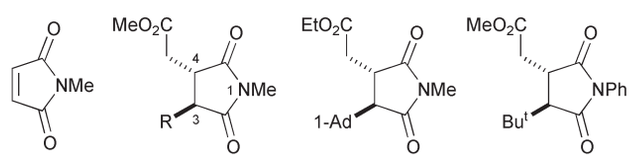
Entry	Silyl ketene acetal	Halogen donor (equiv.)	Solvent	Desilylation method[b]	Product[c] (isolated yield)
1	**19**	EtO_2CCH_2Br (2.0)	Cyclohexane	A	**22a** (83%)
2	**19**	$EtO_2CCHMeBr$ (2.0)	Cyclohexane	A	**22b** (67%)
3	**19**	$(EtO_2C)_2CMeBr$ (1.2)	Cyclohexane	A	**22c** (73%)
4	**19**	$AdC(O)CH_2Br$ (1.0)	Benzene	A	**22d** (83%)
5	**19**	$AdC(O)CH_2Br$ (2.0)	Benzene	A	**24** (91%)
6	**19**	$AdC(O)CH_2Br$ (2.0)	Benzene	B	**25** (59%)
7	**19**	$PhSO_2CH_2Br$ (2.0)	Benzene	A	**22e** (84%)
8	**19**	α-Bromo-γ-butyrolactone (2.0)	Benzene	B[d]	**23** (76%)
9	**20**	EtO_2CCH_2Br (2.0)	Cyclohexane	A	**22a** (95%)
10	**20**	$EtO_2CCHMeBr$ (2.0)	Cyclohexane	A	**22b** (77%)
11	**20**	$AdC(O)CH_2Br$ (1.0)	Cyclohexane	A	**22d** (85%)

[a] The initiator was DLP (0.05 equiv.) for all reactions and 2,4,6-collidine (0.10 equiv.) was added to suppress acid-catalysed heterolytic reactions of the ketene acetal. All reagents were present initially and the reaction mixture was heated under reflux, usually for 2.5 h. [b] A = Addition of methyl or ethyl iodide followed by treatment with TBAF in THF at 0 °C; B = treatment with oxalyl chloride followed by reaction of the acid chloride with ethanol and pyridine. [c] After conversion of the initially-formed silyl ester to the alkyl ester shown. [d] Method A afforded a mixture of **23** and the product formed by reaction of the excess α-bromo lactone with the carboxylate (*cf.* Scheme 8).

γ-butyrolactone the same procedure afforded a mixture of **23** and the product corresponding to **24**, formed by reaction of the carboxylate with the excess of the bromo lactone (*cf.* Scheme 8). However, the desired excess of the bromo lactone could be used provided the desilylation was accomplished with oxalyl chloride, when **23** could be obtained in good yield (entry 8).

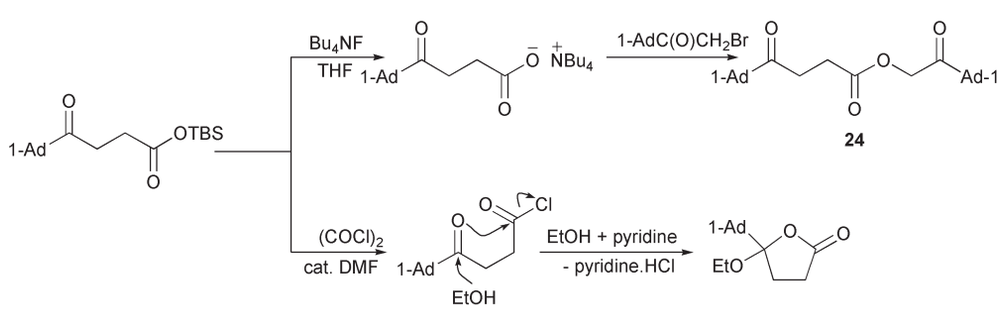
The *O*-1-adamantyl ketene acetal **20** gave equally good or rather better results when used in place of **19** for representative carboxymethylation reactions under the same conditions (entries 9–11). Further advantages of **20** over the *O-tert*-butyl analogue **19** were its greater thermal stability and lower heterolytic reactivity, especially its relatively slow hydrolysis.

(b) Reactions with electron-poor alkenes. Simple alkyl radicals are relatively nucleophilic and do not add readily to electron-rich alkenes such as **19** and **20**, while their addition to electron-poor alkenes is comparatively rapid.[27] Therefore, we reasoned that *O*-alkyl *O*-silyl ketene acetals **26** could react with electron-poor alkenes to give compounds of the type **28** according to the radical-chain mechanism generalised in Scheme 9, provided that β-scission of the adduct radical **27** is sufficiently rapid. The *O-tert*-butyl ketene acetal **19** reacted as predicted with *N*-methylmaleimide **29** (NMM, 1.2 equiv.) when heated for 3 h in refluxing benzene containing DLP (0.05 equiv.) and the *O*-1-adamantyl analogue **20** reacted in a similar way with NMM in refluxing chlorobenzene using DTAP (0.20 equiv.) as initiator.†† The silyl esters of type **28** produced initially were converted to the methyl esters **30a** and **30b**, by treatment with TBAF and methyl iodide, and the *trans* stereochemistry of the products (expected on steric grounds) was confirmed by NMR spectroscopy and by single-crystal X-ray diffraction for the ethyl ester **31**.‡‡ *N*-Phenylmaleimide (NPM) reacted with **19** in a similar manner in refluxing benzene to afford the 1-phenylpyrrolidine-2,5-dione **32** in 71% yield. The results are summarised in Table 3.

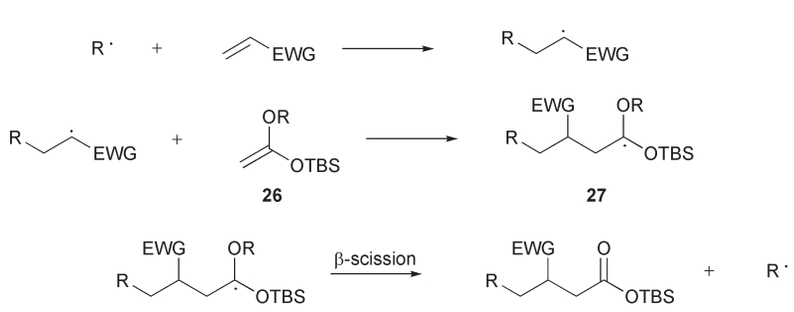


29 **30a** R = Bu^t **31** **32**
30b R = 1-Ad
30c R = Cyclohexyl

†† Di-*tert*-butyl peroxide could also be used as initiator, but the yields were generally lower than with DTAP.
‡‡ The ethyl ester **31** formed crystals more suitable for X-ray diffraction than did the methyl ester **30b**.



Scheme 8



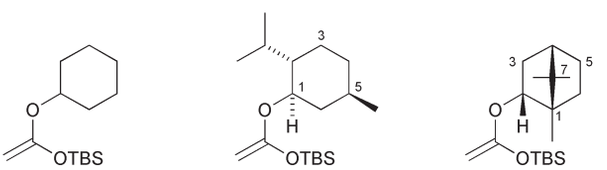
Scheme 9

Table 3 Reactions of acyclic *O*-alkyl *O*-silyl ketene acetals with electron-poor alkenes

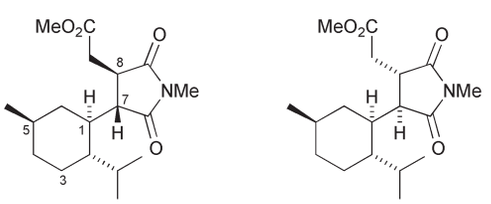
Entry	Silyl ketene acetal	Electron-poor alkene (equiv.)	Conditions[a,b]	Product[e] (isolated yield)
1	**19**	NMM (1.2)	A	**30a** (68%)
2	**20**	NMM (1.2)	B	**30b** (66%)
3	**20**	NMM (1.2)	B	**31** (67%)
4	**19**	NPM (1.1)	A	**32** (71%)
5	**33**	NMM (1.2)	B[c]	**30c** (70%)
6	**34**	NMM (1.5)	B[c]	**36a** + **36b** (65%)
7	**35**	NMM (1.5)	B[c]	**37a–d** (67%)
8	**20**	Dimethyl maleate (1.2)	B	**38a** (70%)
9	**20**	Dimethyl fumarate (1.2)	B	**38a** (71%)
10	**33**	Dimethyl fumarate (1.2)	B	**38b** (62%)
11	**20**	5*H*-Furan-2-one (1.2)	B	**41a** (61%)
12	**33**	5*H*-Furan-2-one (1.5)	B	**41b** (60%)
13	**19**	Phenyl vinyl sulfone (1.2)	A	**42a** (43%)
14	**19**	Phenyl vinyl sulfone (0.5)	A[d]	**42a** (89%)
15	**20**	Phenyl vinyl sulfone (1.2)	B	**42b** (45%)
16	**20**	Phenyl vinyl sulfone (0.5)	B[d]	**42b** (87%)
17	**33**	Phenyl vinyl sulfone (0.5)	B[d]	**42c** (80%)

[a] The reaction mixture was heated under reflux for 3 h. [b] A = DLP initiator (0.05 equiv.), benzene solvent, bath temp. 90 °C; B = DTAP initiator (0.20 equiv.), chlorobenzene solvent, bath temp. 140 °C. [c] Slow addition of NMM in chlorobenzene during the first 1 h using a syringe pump. [d] Amount of initiator based on phenyl vinyl sulfone. [e] After conversion of the initially-formed silyl ester to the alkyl ester shown by treatment with TBAF and methyl or ethyl iodide in THF at 0 °C.

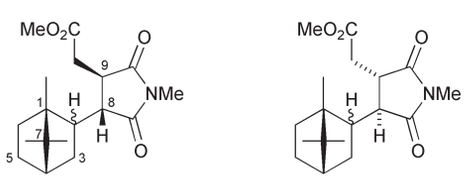
Despite the fact that an α-alkoxyalkyl radical of the type **27** (Scheme 9) will undergo β-scission less readily when R is a secondary alkyl group than when it is tertiary, we were pleased to find that *O*-*sec*-alkyl *O*-silyl ketene acetals participated successfully in analogous reactions with NMM in refluxing octane or chlorobenzene using DTAP as initiator. Initial experiments were carried out with the *O*-cyclohexyl ketene acetal **33**, but the ketene acetals **34** and **35** behaved similarly and the reaction should be fairly general for secondary *O*-alkyl groups; the results are included in Table 3.



33 **34** **35**



36a **36b**



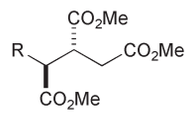
37a *endo*(8*R*) **37c** *endo*(8*S*)
37b *exo*(8*R*) **37d** *exo*(8*S*)

The *O*-cyclohexyl ketene acetal **33** afforded the pyrrolidine-2,5-dione **30c** in 70% isolated yield. The enantiomerically-pure *O*-(1*R*)-menthyl analogue **34** gave a 1 : 1 mixture of the two diastereoisomeric adducts **36a** and **36b** in 65% total yield. The isomer **36a** could be isolated by crystallisation and its structure was confirmed by X-ray diffraction. The adduct **36b** failed to crystallise and could not be freed from traces of **36a**, but examination of its ^{1}H NMR spectrum leaves not doubt as to the structure. The formation of **36a** and **36b**, in preference to the other two possible diastereoisomers in which the pyrrolidinedione ring is *cis* to the isopropyl group, would be expected on the basis of steric effects which direct the approach of NMM to the less hindered face of the intermediate menthyl radical and place the new substituent in an equatorial site *trans* to the isopropyl group. A similar reaction of the *O*-bornyl ketene acetal **35** with NMM afforded a 41 : 25 : 20 : 14 mixture of all four possible diastereoisomers **37a**–**d** in a total yield of 67%. The major product was shown by X-ray analysis to be the pyrrolidinedione **37a**. The isomer present originally as 20% of the crude product crystallised particularly well and was shown by X-ray diffraction to have the structure **37b**. The remaining two diastereoisomers **37c** and **37d** could not be obtained free from the other isomers and their structures could not be determined unambiguously. The major product **37a** arises as a result of preferential attack by the intermediate 2-bornyl radical from its less hindered *endo* face at an *Re* facial terminus of the C=C bond in NMM and the diastereoselectivity of this radical addition is significantly greater than for the corresponding addition of the menthyl radical to NMM. Preferential addition of NMM to the *endo* face of the 2-bornyl radical is in accord with the preferred formation of the *endo*-peroxyl radical when dioxygen reacts with the bornyl radical during autoxidation of the mixture of *exo* and *endo* Grignard reagents derived from bornyl chloride.[28] Addition at an *Si* facial terminus of NMM leads to **37c** and **37d** and, assuming preferential attack of the bornyl radical from its *endo* face, the crude reaction product would contain 25% of **37c** and 14% of **37d**; the spectroscopic assignments reported in the Experimental section are made on this basis. Future work on this type of carbon–carbon bond-forming reaction of *O*-alkylated enols should address the general problem of controlling the diastereoselectivity of radical addition to the electrophilic alkene.

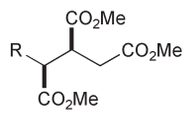
The ketene acetal **20** reacted in a similar fashion with dimethyl maleate (1.2 equiv.) in refluxing chlorobenzene containing DTAP initiator and the first-formed monosilyl ester was converted to the trimethyl ester, which was isolated in 70% yield as a single diastereoisomer and shown by X-ray crystallography to be the *anti* compound **38a**. A small amount (*ca.* 5%) of the *syn* trimethyl ester **39a** was detected in the crude reaction product and dimethyl fumarate afforded the same mixture of diastereoisomers in similar yield.§§ This result implies that addition of the 1-adamantyl radical to the maleate or to the fumarate gives an adduct radical **40** which is conformationally equilibrated before it adds to **20**. On both steric and electrostatic grounds, the conformation **40a** should be preferred

§§ The *syn* isomers **39a** and **39b** eluted after the *anti* compounds and were difficult to obtain free from the latter by column chromatography; they were also contaminated with the corresponding adduct resulting from trapping of the ethyl radical (arising from the DTAP initiator). Identification of the *syn* isomers was based on comparison of their NMR spectra with those of the *anti* forms **38a** and **38b**.

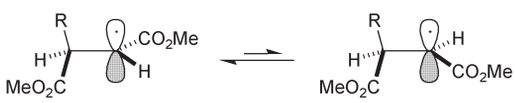
and this would be expected to add to **20** from its less shielded face *anti* to the bulky adamantyl group,[7,29] leading ultimately to the *anti* diastereoisomer **38a** as the major product.¶¶ A similar reaction of the *O*-cyclohexyl ketene acetal **33** with dimethyl fumarate afforded the *anti* trimethyl ester **38b** as the major product in 62% isolated yield. About 10% of the *syn* isomer **39b** was detected in the crude reaction mixture, indicating that the preference for formation of the *anti* isomer increases with the bulk of the group R in the radical **40**.



38a R = 1-Ad
38b R = Cyclohexyl

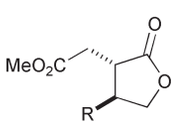


39a R = 1-Ad
39b R = Cyclohexyl

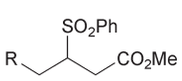


40a **40b**

Selected reactions of the silyl ketene acetals with other electrophilic alkenes, as represented by 5*H*-furan-2-one and phenyl vinyl sulfone, were also examined and the results are given in Table 3. The *O*-1-adamantyl and *O*-cyclohexyl silyl ketene acetals reacted with 5*H*-furan-2-one in refluxing chlorobenzene in the presence of DTAP as initiator to give the lactones **41a** and **41b**, respectively, in about 60% isolated yield after conversion to the methyl esters (entries 11 and 12). Phenyl vinyl sulfone afforded very good yields of the sulfones **42a–c** with two equivalents of the ketene acetals **19**, **20** and **33**, respectively (entries 14, 16 and 17), although the yields were appreciably lower when the phenyl vinyl sulfone was present in slight excess (entries 13 and 15).



41a R = 1-Ad
41b R = Cyclohexyl

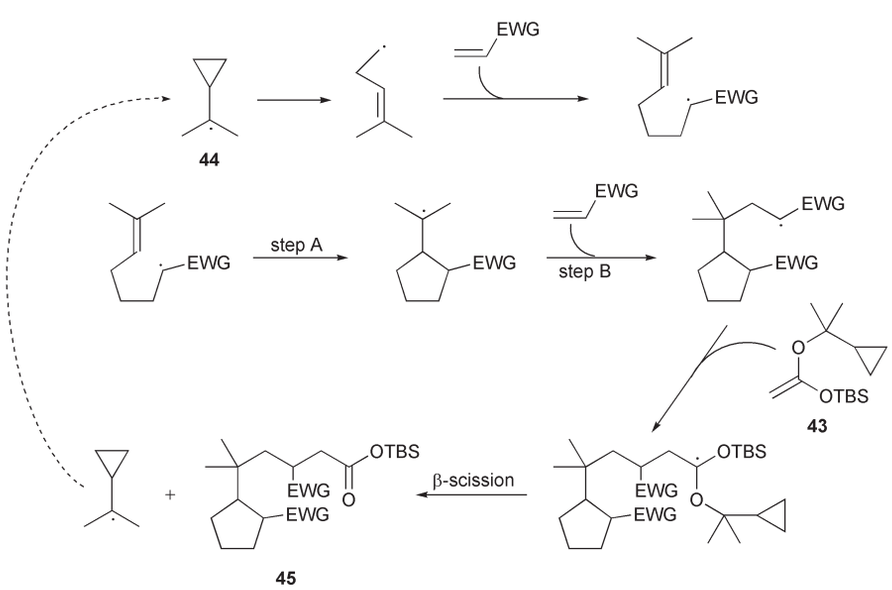


42a R = Bu^t
42b R = 1-Ad
42c R = Cyclohexyl

¶¶ See ref. 7 for a report of related radical-chain reactions between α-(tributylstannyloxy)styrene, an alkyl iodide and dimethyl maleate (*cf.* Scheme 3), in which the stereochemistry of the major product was presumed on similar grounds, but not proven.

On the basis of these results, we reasoned that the *O*-cyclopropyldimethylcarbinyl *O*-silyl ketene acetal **43** might react with electron-poor alkenes to bring about [3 + 2] annulation of the latter, according to the general mechanism shown in Scheme 10 and involving ring opening[30] of the cyclopropyldimethylcarbinyl radical **44** as a key step. Polar effects on the rates of radical addition reactions[27] are of crucial importance in directing the course of this complex chain process, which results in the formation of four new C–C bonds. As envisaged, when the ketene acetal **43** was heated for 3 h in refluxing benzene with NMM (2.2 equiv.) and DLP (0.05 equiv.), an annulated product of the type **45** was formed and this was isolated as the diastereoisomerically-pure methyl ester **46**. However, under these conditions significant amounts of by-products analogous to **30** were formed as a result of trapping by NMM of the undecyl radical (from DLP) and of the cyclopropyldimethylcarbinyl radical **44**; some oligomerisation of the NMM also appeared to take place. These complications could be minimised by slow addition over 2 h of the NMM (2.2 equiv.) in benzene to a refluxing solution of **43** and DLP (0.10 equiv.) in the same solvent. Now, the crystalline compound **46** could be isolated in 30% yield and its structure was determined by X-ray diffraction (see Fig. 1). In the reaction of **43** with NMM, the 5-*exo* cyclisation (step A, Scheme 10) preferentially places the exocyclic dimethylcarbinyl radical centre in the *endo* position on the new bicyclic skeleton, in agreement with previous observations.[31] In the next stage of the propagation cycle (step B, Scheme 10), the addition of this tertiary alkyl radical to NMM takes place preferentially to generate a new chiral centre at C-10 with a configuration opposite (according to the Cahn–Ingold–Prelog rules) from that at C-6 which is separated from it by the dimethylcarbinyl group. Addition to form a new radical (centred at C-14) in which C-6 and C-10 have the same configuration is predicted by molecular mechanics calculations to be less favourable thermodynamically, although by only 4.5 kJ mol^{-1}.[32]

A corresponding reaction of the ketene acetal **43** with *N*-phenylmaleimide provided the annulation product **47** in a similarly modest isolated yield of 37%. Although the compound **47** did not form crystals suitable for X-ray diffraction, the close similarity of its ^{1}H NMR spectrum to that of **46** leaves little doubt as to the structure. While the yields of **46** and **47** are not high, this type of metal- and halogen-free reaction is of significant interest in that it involves the formation, in a single pot from two readily obtained starting materials, of a cyclopentane ring and four new C–C bonds in a stereocontrolled manner. In general, the highly functionalised molecules that result from the alkylation–carboxymethylation and annulation reactions of electrophilic alkenes described in this paper should be readily amenable to further elaboration, making the chemistry of potential use in the construction of complex molecules.



44 **43** **45**

Scheme 10

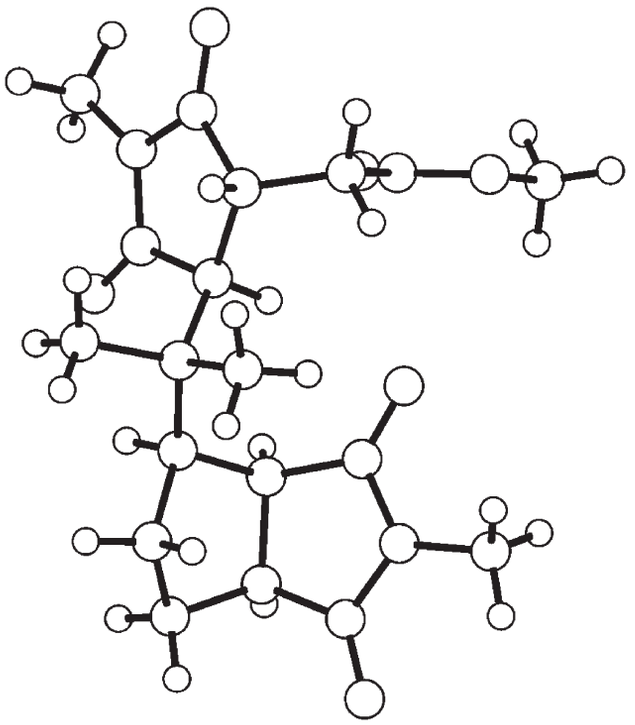
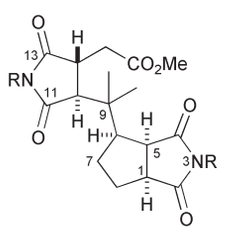


Fig. 1 Structure of compound **46** as determined by single-crystal X-ray diffraction.



46 R = Me
47 R = Ph

Experimental

NMR spectra were recorded using a Bruker AVANCE 500 instrument (500 MHz for ^{1}H, 125.7 MHz for ^{13}C). Unless stated otherwise, the solvent was $CDCl_3$ and chemical shifts are reported relative to residual $CHCl_3$ (δ_H = 7.26) or to $CDCl_3$ (δ_C = 77.0 ppm); *J* values are quoted in Hz and the use of [multiplet] indicates an apparent multiplet associated with an observed line spacing. When these were not obvious, assignments of the ^{1}H NMR spectra were made with the aid of COSY and NOE techniques; in complex situations where there are spin systems showing strong coupling the reported *J* values will be approximate. Column chromatography and TLC were carried out using Merck Kieselgel 60 (230–400 mesh) and Kieselgel 60 F_{254} aluminium-backed pre-coated plates, respectively. Optical rotations were measured using an AA Series Polaar 2000 polarimeter (Optical Activity Ltd.) in a 1 dm cell and are given in units of 10^{-1} deg cm^2 g^{-1}. Infrared (IR) spectra were obtained from liquid films or KBr pellets using a Shimadzu FTIR-8700 spectrophotometer; wavenumbers (cm^{-1}) are reported only for strong characteristic bands.

All manipulations and reactions of air-sensitive materials were carried out under an atmosphere of dry argon and all extracts were dried over anhydrous $MgSO_4$ unless stated otherwise. Petroleum refers to the fraction of bp 40–60 °C.

Materials

Anhydrous octane and chlorobenzene were obtained commercially (Aldrich); benzene was dried by distillation from sodium wire and stored under argon. 2,4,6-Trimethylpyridine (collidine), 2,2,6,6-tetramethylpiperidine, *N*-methylmaleimide, *N*-phenylmaleimide, dimethyl maleate, dimethyl fumarate, 5*H*-furan-2-one, phenyl vinyl sulfone, dilauroyl peroxide and di-*tert*-butyl peroxide were all obtained from Aldrich and were used as received. Azobis(isobutyronitrile) was also obtained commercially (Merck/BDH) and recrystallised from diethyl ether: di-*tert*-amyl peroxide was prepared as described by Milas and Surgenor.[19] Tetrabutylammonium fluoride (1 M in tetrahydrofuran) was purchased from Aldrich and used as received.

α-Alkoxystyrenes

α-*tert*-Butoxystyrene **3** was prepared by a modification of the methods reported by Kostikov *et al.*[15] and Wiberg *et al.*;[20] the final elimination of HI to produce **3** was accomplished using a method described by Middleton and Simpkins for a related compound.[33] To a mixture of 2-methyl-2-propanol (5.56 g, 0.075 mol), iodine (12.7 g, 0.05 mol) and mercuric oxide (6.5 g, 0.03 mol) in diethyl ether (20 mL) was added slowly with stirring a solution of styrene (5.75 mL, 0.05 mol) in diethyl ether (10 mL). After stirring at room temperature for 3 h, the mixture was filtered through Celite and the filter cake was washed with ether. The filtrate was washed with a solution of potassium iodide with small portions of sodium bisulfite until the dark colour of iodine was discharged. The ether layer was separated, washed with water, dried and concentrated under reduced pressure. The residue was added to a stirred solution of potassium *tert*-butoxide (11.2 g, 0.10 mol) in dry THF (50 mL) at room temperature. After stirring at room temperature overnight, the mixture was diluted with petroleum (100 mL) and filtered through Celite. The filtrate was concentrated under reduced pressure. The residue was diluted with ether, washed with water, dried over K_2CO_3 and concentrated under reduced pressure. The residue was purified by distillation under reduced pressure to give α-*tert*-butoxystyrene **3** (6.69 g, 76%) as a colourless oil, bp 48–54 °C/0.05 mm Hg; δ_H 1.42 (9 H, s, Bu^t), 4.57 (1 H, d, *J* 1.4, =C*H*^{A}H^B), 4.96 (1 H, d, *J* 1.4, =CH^A*H*^{B}), 7.26–7.60 (5 H, m, Ph); δ_C 28.6, 78.2, 93.7, 125.7, 128.0 (2 C), 139.1, 156.8. Found: C, 81.8; H, 9.1. $C_{12}H_{16}O$ requires C, 81.8; H, 9.2%.

α-1-Adamantoxystyrene **4** was prepared in 60% yield by the method described above, although the crude product contained *ca.* 20% α-iodostyrene which was removed by Kugelrohr distillation at 0.05 mm Hg (oven temp. 150 °C) to afford **4** as a colourless oil; δ_H 1.61 (6 H, brs, Ad), 1.92 (6 H, br d, *J* 3.0, Ad), 2.14 (3 H, br s, Ad), 4.70 (1 H, d, *J* 1.1, =C*H*^{A}H^B), 5.09 (1 H, d, *J* 1.1, =CH^A*H*^{B}), 7.27–7.61 (5 H, m, Ph); δ_C 30.9, 36.2, 42.5, 78.0, 98.3, 125.8, 127.9(2), 127.9(4), 139.6, 156.0. Found: C, 84.9; H, 8.9. $C_{18}H_{22}O$ requires C, 85.0; H, 8.7%.

α-Methoxystyrene[34] **12** was prepared in 79% yield using the method described above, and α-adamantoxy-β-methylstyrene[23] **16** were prepared as described in the literature.

O-Alkyl *O*-(*tert*-butyldimethylsilyl) ketene acetals

The silyl ketene acetals were prepared from the acetate esters by treatment with lithium diisopropylamide in THF at −78 °C, followed by quenching of the lithium enolate with *tert*-butyldimethylchlorosilane in the presence of hexamethylphosphoramide at −78 °C and subsequent warming to room temperature, as described by Danishefsky *et al.*;[35] the yields ranged from 73 to 90% and the characteristic properties are given below.

O-*tert*-Butyl *O*-(*tert*-butyldimethylsilyl) ketene acetal 19[35]

Oil, bp 80–84 °C/15 mm Hg; δ_H 0.19 (6 H, s, $SiMe_2$), 0.93 (9 H, s, SiBu^t), 1.35 (9 H, s, OBu^t), 3.45 (1 H, d, *J* 1.3, =C*H*^{A}H^B), 3.47 (1 H, d, *J* 1.3, =CH^A*H*^{B}); δ_C −4.8, 18.0, 25.7, 28.5, 72.7, 78.0, 157.7. Found: C, 62.5; H, 11.4. $C_{12}H_{26}O_2Si$ requires C, 62.6; H, 11.4%.

O-1-Adamantyl *O*-(*tert*-butyldimethylsilyl) ketene acetal 20

Oil, bp 98–100 °C/0.05 mm Hg; δ_H 0.19 (6 H, s, $SiMe_2$), 0.94 (9 H, s, Bu^t), 1.62 (6 H, m, Ad), 1.92 (6 H, m, Ad), 2.16 (3 H, br s, Ad), 3.51(8) (1 H, d, *J* 1.1, =C*H*^{A}H^B), 3.52(4) (1 H, d, *J* 1.1, =CH^A*H*^{B}); δ_C −4.8, 18.1, 25.7, 30.9, 36.2, 42.3, 74.6, 77.5, 156.9. Found: C, 69.9; H, 10.6. $C_{18}H_{32}O_2Si$ requires C, 70.1; H, 10.5%.

_O_-Cyclohexyl _O_-(_tert_-butyldimethylsilyl) ketene acetal 33[36]

Oil, bp 60–64 °C/0.06 mm Hg; δ_H 0.18 (6 H, s, $SiMe_2$), 0.93 (9 H, s, Bu^t), 1.28–1.92 (10 H, m, _c_-Hex), 3.10 (1 H, d, _J_ 2.2, $=CH^AH^B$), 3.26 (1 H, d, _J_ 2.2, $=CH^AH^B$), 3.92 (1 H, tt, _J_ 8.9 and 3.7, OCH); δ_C −4.5, 18.1, 23.7, 25.6, 25.7, 31.3, 61.3, 75.3, 159.7. Found: C, 65.6; H, 11.2. $C_{14}H_{28}O_2Si$ requires C, 65.6; H, 11.0%. Contrary to suggestions in the literature,[36] this compound was obtained in an analytically pure state after simple distillation.

_O_-(1_R_)-Menthyl _O_-(_tert_-butyldimethylsilyl) ketene acetal 34

This compound was prepared starting from (1_R_)-(−)-menthyl acetate (Aldrich, 98% ee by GLC). Oil, bp 88–89 °C/0.05 mm Hg, $[\alpha]_D^{21}$ −80.7 (_c_ = 2.2, $CHCl_3$); δ_H 0.17 (3 H, s, SiMe), 0.18 (3 H, s, SiMe), 0.77 (3 H, d, _J_ 7.0, Me), 0.89 (3 H, d, _J_ 7.0, Me), 0.91 (3 H, d, _J_ 7.0, Me), 0.81–0.96 (2 H, masked, ring-H), 0.93 (9 H, s, Bu^t), 1.01 (1 H, m, ring-H), 1.35 (2 H, m, ring-H), 1.66 (2 H, m, ring-H), 2.13 (1 H, septet of doublets, _J_ 7.0 and 2.7, Me_2CH), 2.22 (1 H, m, ring-H), 3.13 (1 H, d, _J_ 2.2, $=CH^AH^B$), 3.23 (1 H, d, _J_ 2.2, $=CH^AH^B$), 3.72 (1 H, [t]d, _J_ 10.6 and 4.1, H-1); δ_C −4.6, −4.5, 16.3, 18.1, 20.8, 22.1, 23.3, 25.6, 25.8, 31.4, 34.5, 39.6, 47.7, 61.1, 76.9, 159.7. Found: C, 69.0; H, 11.5. $C_{18}H_{36}O_2Si$ requires C, 69.2; H, 11.6%.

_O_-Bornyl _O_-(_tert_-butyldimethylsilyl) ketene acetal 35[37]

This compound was prepared starting from (1_S_)-(−)-bornyl acetate (Aldrich, _ca._ 90% ee by optical rotation). Oil, bp 85–88 °C/0.05 mm Hg; δ_H 0.19 (3 H, s, SiMe), 0.20 (3 H, s, SiMe), 0.87(6) (3 H, s, Me), 0.87(9) (3 H, s, Me), 0.89 (3 H, s, Me), 0.94 (9 H, s, Bu^t), 1.10 (1 H, dd, _J_ 13.5 and 3.4, ring-H), 1.22 (1 H, m, ring-H), 1.28 (1 H, m, ring-H), 1.68 (1 H, [t], _J_ 4.6, ring-H), 1.73 (1 H, m, ring-H), 2.02 (1 H, m, ring-H), 2.23 (1 H, m, ring-H), 2.95 (1 H, d, _J_ 2.1, $=CH^AH^B$), 3.24 (1 H, d, _J_ 2.1, $=CH^AH^B$), 4.07 (1 H, m, OCH); δ_C −4.5, −4.4, 13.8, 18.0, 18.9, 19.7, 25.6, 27.0, 27.8, 36.3, 44.9, 47.5, 49.1, 61.6, 82.8, 161.2. Found: C, 69.8; H, 11.1. $C_{18}H_{34}O_2Si$ requires C, 69.6; H, 11.0%.

_O_-Cyclopropyldimethylcarbinyl _O_-(_tert_-butyldimethylsilyl) ketene acetal 43

Oil, bp 90–92 °C/1.0 mm Hg; δ_H 0.19 (6 H, s, $SiMe_2$), 0.38 (4 H, m, 2 ring-CH_2), 0.93 (9 H, s, Bu^t), 1.11 (1 H, m, ring-CH), 1.25 (6 H, s, CMe_2), 3.47 (1 H, d, _J_ 1.1, $=CH^AH^B$), 3.52 (1 H, d, _J_ 1.1, $=CH^AH^B$); δ_C −4.9, 1.8, 18.0, 21.0, 25.1, 25.7, 73.3, 79.7, 157.6. Found: C, 65.6; H, 10.9. $C_{14}H_{28}O_2Si$ requires C, 65.6; H, 11.0%.

Representative procedures

Reactions with organic halides

Example 1. α-1-Admantoxystyrene **4** (0.508 g, 2.0 mmol), α-bromo-γ-butyrolactone (0.660 g, 4.0 mmol), di-_tert_-amyl peroxide (69.6 mg, 0.40 mmol), 2,2,6,6-tetramethylpiperidine (33.8 µl, 0.20 mmol) and dry chlorobenzene (4 mL) were added to a dry, argon-filled flask, containing a magnetic stirrer bar and equipped with a condenser. The flask was then immersed in an oil bath, pre-heated to 140 °C, and the reaction mixture was stirred at reflux under argon for 3 h. The solvent was removed by rotary evaporation and the residue was purified by flash chromatography on silica gel, using petroleum–diethyl ether–CH_2Cl_2 (3 : 1 : 1) as eluent, to give the lactone **8a** (0.368 g, 90%) as a colourless oil, which was recrystallised from hexane–CH_2Cl_2, mp 73–75 °C.

Example 2. _O-tert_-Butyl _O_-(_tert_-butyldimethylsilyl) ketene acetal **19** (0.461 g, 2.0 mmol), diethyl 2-bromo-2-methyl malonate (0.607 g, 2.4 mmol), dilauroyl peroxide (39.9 mg, 0.10 mmol), 2,4,6-collidine (26.4 µl, 0.20 mmol) and cyclohexane (4 mL) were added to a dry, argon-filled flask, containing a magnetic stirrer bar and equipped with a condenser. The flask was then immersed in an oil bath, pre-heated to 90 °C, and the reaction mixture was stirred at reflux under argon for 3 h. The solvent was removed by rotary evaporation and ethyl iodide (1.25 g, 8.0 mmol) and dry THF (2 mL) were added to the residue. The resulting solution was cooled in an ice-water bath before the addition of tetrabutylammonium fluoride (1 M in THF, 2.2 mL) and the mixture was stirred at 0 °C for 2 h, followed by the addition of saturated aqueous NH_4Cl solution (10 mL). The mixture was extracted with CH_2Cl_2 (3 × 10 mL), the combined extracts were dried and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel, using petroleum–diethyl ether (4 : 1) as eluent, to give the ester **22c** (0.379 g, 73%) as a colourless oil.

Reactions with electron-poor alkenes

O-tert-Butyl _O_-(_tert_-butyldimethylsilyl) ketene acetal **19** (0.920 g, 4.0 mmol), phenyl vinyl sulfone (0.336 g, 2.0 mol), dilauroyl peroxide (39.9 mg, 0.10 mmol) and benzene (4 mL) were added to a dry, argon-filled flask, containing a magnetic stirrer bar and equipped with a condenser. The flask was then immersed in an oil bath, pre-heated to 90 °C, and the reaction mixture was stirred at reflux under argon for 3 h. The solvent was removed by rotary evaporation and methyl iodide (2.27 g, 16.0 mmol) and dry THF (2 mL) were added to the residue. The resulting solution was cooled in an ice-water bath before the addition of tetrabutylammonium fluoride (1 M in THF, 4.4 mL) and the mixture was stirred at 0 °C for 2 h, followed by the addition of saturated aqueous NH_4Cl solution (15 mL). The mixture was extracted with CH_2Cl_2 (3 × 15 mL), the combined extracts were dried and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel, using petroleum–diethyl ether–CH_2Cl_2 (17 : 3 : 5) as eluent, to give the sulfone **42a** (0.532 g, 89%) as a colourless oil.

Characteristic data for reaction products

The ketones **6a**[38] and **6b**[39] and the esters **7a**[40] and **7b**[41] showed physical properties and NMR spectroscopic data in agreement with those reported in the literature. Characteristic data for products that have not been reported previously, or are inadequately described in the literature, are given below.

Ethyl 2-methyl-2-phenacylpropanoate 7c. Oil, 85% yield from **3**; δ_H 1.21 (3 H, t, _J_ 7.1, CH_2Me), 1.32 (6 H, s, 2 Me), 3.29 (2 H, s, CH_2COPh), 4.13 (2 H, q, _J_ 7.1, OCH_2), 7.44–7.95 (5 H, m, Ph); δ_C 14.1, 25.8, 40.1, 48.4, 60.5, 127.9, 128.5, 133.0, 137.1, 177.3, 197.6. Found: C, 71.8; H, 7.6. $C_{14}H_{18}O_3$ requires C, 71.8; H, 7.7%.

Diethyl phenacylmalonate 7d[42]. Oil, 84% yield from **3**; δ_H 1.29 (6 H, t, _J_ 7.1, 2 CH_2Me), 3.62 (2 H, d, _J_ 7.1, CH_2COPh), 4.06 (1 H, t, _J_ 7.1, CH), 4.23 (4 H, m, 2 CH_2Me), 7.46–8.00 (5 H, m, Ph); δ_C 14.0, 37.8, 47.2, 61.7, 128.1, 128.6, 133.5, 136.0, 169.0, 196.5. Found: C, 64.9; H, 6.4. $C_{15}H_{18}O_5$ requires C, 64.7; H, 6.5%.

Diethyl methyl(phenacyl)malonate 7e. Oil, 91% yield from **3**; δ_H 1.24 (6 H, t, _J_ 7.1, 2 CH_2Me), 1.60 (3 H, s, Me), 3.67 (2 H, s, CH_2COPh), 4.21 (4 H, q, _J_ 7.1, 2 CH_2Me), 7.44–7.98 (5 H, m, Ph); δ_C 13.9, 20.5, 44.2, 51.5, 61.6, 128.0, 128.6, 133.3, 136.6, 171.6, 196.5. Found: C, 65.7; H, 7.1. $C_{16}H_{20}O_5$ requires C, 65.7; H, 6.9%.

1-Adamantyl-1-phenylbutan-1,4-dione 7f. Mp 85–87 °C, 78% yield from **3**; δ_H 1.71 and 1.76 (6 H, ABq, _J_ 12.2, Ad), 1.89 (6 H, m, Ad), 2.06 (3 H, br s, Ad), 2.92 (2 H, t, _J_ 6.5, CH_2COAd), 3.24 (2 H, t, _J_ 6.5, CH_2COPh), 7.43–7.99 (5 H, m, Ph); δ_C 28.0, 30.3, 32.2, 36.6, 38.4, 46.2, 128.0, 128.5, 133.0, 136.8, 199.0, 214.3. Found: C, 81.1; H, 8.2. $C_{20}H_{24}O_2$ requires C, 81.0; H, 8.2%.

3-Benzenesulfonyl-1-phenylpropan-1-one 7g. Mp 92–94 °C, 84% yield from **4**; δ_H 3.50 (2 H, m, CH_2), 3.57 (2 H, m, CH_2), 7.46–7.97 (10 H, m, Ph); δ_C 31.3, 51.0, 128.0, 128.1, 128.8, 129.4, 133.8, 133.9, 135.8, 139.0, 195.4. Found: C, 65.7; H, 5.2. $C_{15}H_{14}O_3S$ requires C, 65.7; H, 5.1%.

Lactone 8a. Mp 73–75 °C, 90% yield from **4**; δ_H 1.98 (1 H, m, $OCH_2CH^AH^B$), 2.67 (1 H, m, $OCH_2CH^AH^B$), 3.17 (2 H, m,

CH_2COPh), 3.69 (1 H, m, COCH), 4.29 (1 H, ddd, *J* 10.4, 9.1 and 6.6, OCH^AH^B), 4.45 (1 H, [t]d, *J* 8.9 and 2.0, OCH^AH^B), 7.47–7.99 (5 H, m, Ph); δ_C 29.2, 35.2, 39.4, 66.8, 128.0, 128.7, 133.6, 136.1, 179.1, 197.0. Found: C, 70.5; H, 6.0. $C_{12}H_{12}O_3$ requires C, 70.6; H, 5.9%.

Lactone 8b. Oil, 55% yield from **3**; δ_H 1.39 (3 H, s, Me), 2.15 (1 H, ddd, *J* 12.7, 7.7 and 3.0, $OCH_2CH^AH^B$), 2.49 (1 H, d[t], 12.7 and 9.2, $OCH_2CH^AH^B$), 3.34 and 3.45 (2 H, ABq, *J* 18.2, CH_2COPh), 4.34 (1 H, [q], *J* 9.0, OCH^AH^B), 4.49 (1 H, [t]d, *J* 9.2 and 3.1, OCH^AH^B), 7.45–7.96 (5 H, m, Ph); δ_C 23.6, 33.8, 40.0, 45.6, 65.3, 128.0, 128.7, 133.5, 136.5, 181.7, 197.0. Found: C, 71.6; H, 6.3. $C_{13}H_{14}O_3$ requires C, 71.5; H, 6.5%.

Diones 9a and 9b. These were isolated chromatographically in 63% total yield from **4** as a 64 : 36 mixture of *exo* and *endo* isomers; δ_C (*exo* + *endo*) 9.4(5), 9.4(9), 19.3, 19.6, 20.3, 20.4, 21.5, 29.0, 29.2, 31.2, 35.9, 40.7, 45.9, 46.1, 46.6, 46.8, 48.1, 49.0, 57.3, 58.5; (*exo*) 128.1, 128.6, 133.2, 136.5, 198.1, 221.2; (*endo*) 128.0, 128.6, 133.2, 136.7, 198.3, 221.1. Found: C, 79.9; H, 8.2. $C_{18}H_{22}O_2$ requires C, 80.0; H, 8.2%.

***exo*-Dione 9a.** δ_H 0.88 (3 H, s, Me), 0.94 (6 H, s, 2 Me), 1.60 (2 H, m, ring-H), 1.69 (2 H, m, ring-H), 1.96 (1 H, d, *J* 3.9, bridgehead-H), 2.68 (1 H, dd, *J* 9.8 and 2.7, $CHCH_2COPh$), 2.95 (1 H, dd, *J* 17.9 and 9.8, CH^AH^BCOPh), 3.60 (1 H, dd, *J* 17.9 and 2.7, CH^AH^BCOPh), 7.45–7.98 (5 H, m, Ph).

***endo*-Dione 9b.** δ_H 0.95 (3 H, s, Me), 0.97 (3 H, s, Me), 1.01 (3 H, s, Me), 1.28 (1 H, m, ring-H), 1.44 (1 H, m, ring-H), 1.78 (1 H, m, ring-H), 2.06 (1 H, m, ring-H), 2.30 (1 H, [t], *J* 4.2, bridgehead-H), 2.95 (1 H, dd, *J* 17.9 and 10.0, CH^AH^BCOPh), 3.12 (1 H, d[t], *J* 10.0 and 4.0, $CHCH_2COPh$), 3.46 (1 H, dd, *J* 17.9 and 3.5, CH^AH^BCOPh), 7.45–7.98 (5 H, m, Ph).

Hexanophenone **10** (Aldrich), 3-methyl-1-phenylpentan-1-one[43] **11** and ethyl 3-methyl-4-oxo-4-phenylbutanoate[44] **18a** showed spectroscopic data in accord with those of the authentic compounds.

Reactions of *O*-alkyl *O*-silyl ketene acetals with organic halides

The products **22a** (Aldrich) and **22e**[45] showed spectroscopic data in agreement with those of the authentic compounds.

Diethyl 2-methylbutan-1,4-dioate 22b[46]. Oil, 67% yield from **19**; δ_H 1.21 (3 H, d, *J* 7.2, $CHMe$), 1.24(8) (3 H, t, *J* 7.2, CH_2Me), 1.25(4) (3 H, t, *J* 7.2, CH_2Me), 2.39 (1 H, dd, *J* 16.4 and 6.1, $CH^AH^BCO_2Et$), 2.72 (1 H, dd, *J* 16.4 and 8.2, $CH^AH^BCO_2Et$), 2.89 (1 H, m, $CHMe$), 4.13 (2 H, q, *J* 7.2, CH_2Me), 4.15 (2 H, q, *J* 7.2, CH_2CH_3); δ_C 14.1, 14.2, 17.0, 35.8, 37.7, 60.5, 60.6, 171.9, 175.3. Found: C, 57.4; H, 8.7. $C_9H_{16}O_4$ requires C, 57.4; H, 8.6%.

Ester 22c. Oil, 73% yield from **19**; δ_H 1.23 (3 H, t, *J* 7.1, CH_2Me), 1.25 (6 H, t, *J* 7.1, 2 CH_2Me), 1.53 (3 H, s, Me), 2.92 (2 H, s, CH_2CO_2Et), 4.11 (2 H, q, *J* 7.1, CH_2Me), 4.19(2) (2 H, q, *J* 7.1, CH_2Me), 4.19(4) (2 H, q, *J* 7.1, CH_2Me); δ_C 13.9, 14.1, 20.3, 40.3, 51.6, 60.7, 61.6, 170.3, 171.1. Found: C, 55.4; H, 7.8. $C_{12}H_{20}O_6$ requires C, 55.4; H, 7.7%.

Ester 22d. Oil, 83% yield from **19**; δ_H 1.24 (3 H, t, *J* 7.1, CH_2Me), 1.68 and 1.75 (6 H, ABq, *J* 12.1, Ad), 1.83 (6 H, d, *J* 2.5, Ad), 2.04 (3 H, br s, Ad), 2.54 (2 H, t, *J* 6.5, CH_2COAd), 2.76 (2 H, t, *J* 6.5, CH_2CO_2Et), 4.11 (2 H, q, *J* 7.1, CH_2Me); δ_C 14.2, 27.9, 28.0, 31.0, 36.5, 38.3, 46.1, 60.5, 173.1, 213.8; IR (liq. film) 1738 (ester), 1703 (ketone). Found: C, 72.7; H, 9.3. $C_{16}H_{24}O_3$ requires C, 72.7; H, 9.2%.

Lactone 23. Oil, 76% yield from **19**; δ_H 1.27 (3 H, t, *J* 7.1, CH_2Me), 2.05 (1 H, m, ring-H), 2.53 (1 H, dd, *J* 17.0 and 8.7, $CH^AH^BCO_2Et$), 2.54 (1 H, m, ring-H), 2.90 (1 H, dd, *J* 17.0 and 4.0, $CH^AH^BCO_2Et$), 2.95 (1 H, m, ring-H), 4.17 (2 H, q, *J* 7.1, CH_2Me), 4.23 (1 H, m, ring-H), 4.40 (1 H, [t]d, *J* 8.9 and 2.0, ring-H); δ_C 14.1, 28.6, 34.7, 35.9, 61.0, 66.5, 171.2, 178.1; IR (liq. film) 1771 (lactone), 1732 (ester). Found: C, 55.8; H, 7.1. $C_8H_{12}O_4$ requires C, 55.8; H, 7.0%.

Compound 24. Mp 114–116 °C, 91% yield from **19**; δ_H 1.68 (12 H, m, Ad), 1.82 (6 H, d, *J* 2.7, Ad), 1.86 (6 H, d, *J* 2.7, Ad), 2.04 (6 H, br s, Ad), 2.68 (2 H, t, *J* 6.6, CH_2COAd), 2.82 (2 H, t, *J* 6.6, CH_2CO_2R), 4.86 (2 H, s, OCH_2); δ_C 27.6(5), 27.6(9), 27.9, 31.1, 36.4, 36.5, 37.9, 38.3, 45.2, 46.1, 64.6, 172.6, 207.5, 213.7; IR (KBr disc) 1751 (ester), 1717 (ketone), 1701 (ketone). Found: C, 75.8; H, 8.6. $C_{26}H_{36}O_4$ requires C, 75.7; H, 8.8%.

Psuedo ester 25. Mp 98–100 °C (from hexane–CH_2Cl_2), 59% yield from **19**; δ_H 1.96 (3 H, t, *J* 6.9, CH_2Me), 1.66 (12 H, m, Ad), 1.99 (3 H, br s, Ad), 2.00 (1 H, ddd, *J* 14.2, 11.3 and 5.4, ring-H), 2.41 (1 H, ddd, *J* 14.2, 11.4 and 6.6, ring-H), 2.51 (1 H, ddd, *J* 18.3, 11.4 and 5.4, ring-H), 2.65 (1 H, ddd, *J* 18.3, 11.3 and 6.6, ring-H), 3.45 (2 H, m, CH_2Me); δ_C 15.2, 23.4, 28.0, 29.6, 35.4, 36.9, 40.7, 57.5, 114.8, 176.1; IR (KBr disc) 1760 (lactone). Found: C, 72.7; H, 9.2. $C_{16}H_{24}O_3$ requires C, 72.7; H, 9.2%. The structure of this compound was confirmed by X-ray diffraction.

Reactions of *O*-alkyl *O*-silyl ketene acetals with electron-poor alkenes

Pyrrolidinedione 30a. Mp 73–75 °C (from hexane–CH_2Cl_2), 68% yield from **19**; δ_H 1.04 (9 H, s, Bu^t), 2.36 (1 H, d, *J* 4.7, H-3), 2.63 (1 H, dd, *J* 17.1 and 4.8, $CH^AH^BCO_2Me$), 2.77 (1 H, [q], *J* 4.7, H-4), 2.99 (3 H, s, NMe), 3.03 (1 H, dd, *J* 17.1 and 4.7, $CH^AH^BCO_2Me$), 3.67 (3 H, s, OMe); δ_C 24.8, 27.3, 33.7, 35.0, 39.2, 52.0, 54.9, 171.2, 177.6, 178.3; IR (KBr disc) 1763 (imide), 1728 (ester), 1693 (imide). Found: C, 62.9; H, 7.9; N, 5.2. $C_{12}H_{19}NO_4$ requires C, 62.8; H, 8.1; N, 5.2%.

Pyrrolidinedione 30b. Mp 115–117 °C (from hexane–CH_2Cl_2), 66% yield from **20**; δ_H 1.49 (3 H, dd, *J* 12.0 and 1.8, Ad), 1.64 and 1.71 (6 H, ABq, *J* 12.3, Ad), 1.83 (3 H, dd, *J* 12.0 and 1.8, Ad), 2.00 (3 H, br s, Ad), 2.21 (1 H, d, *J* 4.6, H-3), 2.60 (1 H, dd, *J* 17.0 and 4.9, $CH^AH^BCO_2Me$), 2.86 (1 H, [q], *J* 4.8, H-4), 2.97 (3 H, s, NMe), 2.99 (1 H, dd, *J* 17.0 and 4.9, $CH^AH^BCO_2Me$), 3.66 (3 H, s, OMe); δ_C 24.7, 28.2, 35.2, 35.8, 36.6, 37.4, 39.5, 52.0, 55.7, 171.2, 177.2, 178.4; IR (KBr disc) 1773 (imide), 1732 (ester), 1697 (imide). Found: C, 67.6; H, 7.9; N, 4.4. $C_{18}H_{25}NO_4$ requires C, 67.7; H, 7.9; N, 4.4%. The structure of this compound was confirmed by X-ray diffraction.

Pyrrolidinedione 30c. Mp 76–78 °C (from hexane–CH_2Cl_2), 70% yield from **33**; δ_H 1.00–1.98 (11 H, m, *c*-Hex), 2.53 (1 H, [t], *J* 4.6, H-3), 2.66 (1 H, dd, *J* 17.0 and 4.6, $CH^AH^BCO_2Me$), 2.82 (1 H, [q], *J* 5.1, H-4), 2.93 (1 H, dd, *J* 17.0 and 5.6, $CH^AH^BCO_2Me$), 2.99 (3 H, s, NMe), 3.67 (3 H, s, OMe); δ_C 24.8, 25.8(9), 25.9(3), 26.2, 28.4, 30.1, 34.6, 38.6(6), 38.7(0), 50.9, 52.0, 171.2, 178.2, 178.5; IR (KBr disc) 1773 (imide), 1749 (ester), 1699 (imide). Found: C, 62.8; H, 8.0; N, 5.2. $C_{14}H_{21}NO_4$ requires C, 62.9; H, 7.9; N, 5.2%.

Pyrrolidinedione 31. Mp 141–143 °C (from hexane–CH_2Cl_2), 67% yield from **20**; δ_H 1.23 (3 H, t, *J* 7.2, CH_2Me), 1.49 (3 H, dd, *J* 12.0 and 1.8, Ad), 1.64 and 1.71 (6 H, ABq, *J* 12.3, Ad), 1.84 (3 H, dd, *J* 12.0 and 1.8, Ad), 2.01 (3 H, br s, Ad), 2.21 (1 H, d, *J* 4.6, H-3), 2.58 (1 H, dd, *J* 17.1 and 4.8, $CH^AH^BCO_2Et$), 2.86 (1 H, [q], *J* 4.7, H-4), 2.98 (3 H, s, NMe), 3.02 (1H, dd, *J* 17.1 and 4.8, $CH^AH^BCO_2Et$), 4.11 (2 H, m, CH_2Me); δ_C 14.1, 24.7, 28.2, 35.4, 35.8, 36.6, 37.4, 39.4, 55.7, 61.1, 170.7, 177.3, 178.6. Found: C, 68.5; H, 8.3; N, 4.4. $C_{19}H_{27}NO_4$ requires C, 68.4; H, 8.2; N, 4.4%.

Pyrrolidinedione 32. Mp 95–97 °C (from hexane–CH_2Cl_2), 71% yield from **19**; δ_H 1.13 (9 H, s, Bu^t), 2.50 (1 H, d, *J* 4.6, H-3), 2.72 (1 H, dd, *J* 17.4 and 4.6, $CH^AH^BCO_2Me$), 2.92 (1 H, [q], *J* 4.6, H-4), 3.20 (1 H, dd, *J* 17.4 and 4.6, $CH^AH^BCO_2Me$), 3.71 (3 H, s, OMe), 7.27–7.48 (5 H, m, Ph); δ_C 27.3, 34.1, 35.3, 39.3, 52.2, 54.9, 126.7, 128.6, 129.1, 132.3, 171.2, 176.7, 177.5. Found: C, 67.3; H, 7.0; N, 4.6. $C_{17}H_{21}NO_4$ requires C, 67.4; H, 7.0; N, 4.7%.

Pyrrolidinedione 36a. Mp 128–130 °C (from hexane–CH_2Cl_2), $[\alpha]_D^{20}$ +12.9 (c = 2.0, $CHCl_3$); δ_H 0.65 (1 H, [q], J 11.9, H-6ax), 0.80 (3 H, d, J 6.9, Me), 0.83 (3 H, d, J 6.5, Me), 0.84 (1 H, m, H-4ax), 0.92 (3 H, d, J 6.9, Me), 1.04 (1 H, m, H-2ax), 1.06 (1 H, m, H-3ax), 1.30 (1 H, m, H-6eq), 1.40 (1 H, m, C*H*Me_2), 1.67–1.74 (3 H, complex, H-3eq, H-4eq and H-5ax), 2.15 (1 H, m, H-1ax), 2.58 (1 H, dd, J 17.3 and 4.8, C*H*^{A}H^BCO_2Me), 2.86 (1 H, [q], J 4.9, H-8), 2.96 (1 H, [t], J 4.3, H-7), 3.00 (1 H, dd, J 17.3 and 4.7, CH^A*H*^{B}CO_2Me), 3.02 (3 H, s, NMe), 3.69 (3 H, s, OMe); δ_C 15.1, 21.3, 22.5, 23.9, 25.0, 27.2, 32.2, 34.1, 34.8, 35.7, 37.0, 39.2, 43.6, 46.1, 52.1, 171.2, 178.9, 179.7; IR (KBr disc) 1780 (imide), 1725 (ester), 1709 (imide). Found: C, 66.7; H, 9.2; N, 4.4. $C_{18}H_{29}NO_4$ requires C, 66.8; H, 9.0; N, 4.3%. The structure of this compound was confirmed by X-ray diffraction.

Pyrrolidinedione 36b. Oil; δ_H (part spectrum only) 0.68 (3 H, d, J 6.9, Me), 0.84 (3 H, d, J 6.5, Me), 0.92 (3 H, d, J 6.9, Me), 1.98 (1 H, m, H-1ax), 2.96 (3 H, s, NMe), 3.68 (3 H, s, OMe); δ_C 15.0, 21.4, 22.5, 24.2, 24.7, 26.6, 32.8, 34.6, 34.8, 36.6, 41.2, 41.7, 43.5, 46.0, 52.1, 171.3, 177.6, 178.5.

Pyrrolidinedione 37a. Mp 93–95 °C (from hexane–CH_2Cl_2), $[\alpha]_D^{19}$ +2.8 (c = 2.1, $CHCl_3$); δ_H 0.74 (1 H, dd, J 12.7 and 5.6, H-3A), 0.86(4) (3 H, s, Me), 0.86(8) (3 H, s, Me), 0.87(2) (3 H, s, Me), 1.08 (1 H, m, H-6A), 1.42–1.46 (2 H, complex, H-5A and H-6B), 1.64 (1 H, [t], J 4.5, H-4), 1.78 (1 H, m, H-5B), 1.92 (1 H, m, H-3B), 2.26 (1 H, m, H-2), 2.61 (1 H, dd, J 5.6 and 3.7, H-8), 2.73 (1 H, dd, J 17.0 and 5.1, C*H*^{A}H^BCO_2Me), 2.82 (1 H, [q], J 4.4, H-9), 2.99 (3 H, s, NMe), 3.03 (1 H, dd, J 17.0 and 4.8, CH^A*H*^{B}CO_2Me), 3.67 (3 H, s, OMe); δ_C 14.4, 18.5, 19.3, 25.1, 28.5, 29.4, 32.2, 35.3, 41.1, 44.2, 46.1, 46.4, 48.5, 49.6, 52.1, 171.1, 178.8, 179.6; IR (KBr disc) 1767 (imide), 1730 (ester), 1701 (imide). Found: C, 67.3; H, 8.6; N, 4.4. $C_{18}H_{27}NO_4$ requires C, 67.3; H, 8.5; N, 4.4%. The structure of this compound was confirmed by X-ray diffraction.

Pyrrolidinedione 37b. Mp 160–162 °C (from hexane–CH_2Cl_2), $[\alpha]_D^{22}$ +72.7 (c = 2.0, $CHCl_3$); δ_H (C_6D_6 solvent) 0.57 (3 H, s, Me-1), 0.65 (3 H, s, Me-7*anti*), 0.84 (3 H, s, Me-7*syn*), 0.83 (1 H, m, H-6A), 0.99 (1 H, m, H-5A), 1.30 (1 H, m, H-6B), 1.54–1.59 (2 H, complex, H-4 and H-5B), 2.18–2.22 (2 H, complex, H–3A and H–3B), 2.42–2.47 (2 H, complex, H-9 and C*H*^{A}H^BCO_2Me), 2.50 (1 H, m, H-8), 2.68 (1 H, m, H-2), 2.77 (1 H, [dd], J 18.4 and 5.6, CH^A*H*^{B}CO_2Me), 2.84 (3 H, s, NMe), 3.16 (3 H, s, OMe); δ_C ($CDCl_3$ solvent) 14.2, 20.0, 20.5, 24.9, 27.1, 33.7, 35.0, 39.9, 44.8, 45.6, 48.0, 48.1, 48.3, 51.8, 52.1, 170.9, 178.5, 178.7; IR (KBr disc) 1771 (imide), 1744 (ester), 1699 (imide). Peak separation in the ^{1}H NMR spectrum was better in C_6D_6 solvent than in $CDCl_3$. Found: C, 67.3; H, 8.6; N, 4.4. $C_{18}H_{27}NO_4$ requires C, 67.3; H, 8.5; N, 4.4%. The structure of this compound was confirmed by X-ray diffraction.

Pyrrolidinedione 37c. δ_H (part spectrum only) 0.77 (3 H, s, Me), 0.84 (3 H, s, Me), 1.11 (3 H, s, Me), 2.70 (1 H, dd, J 17.5 and 5.0, C*H*^{A}H^BCO_2Me), 2.98 (3 H, s, NMe), 3.16 (1 H, dd, J 17.5 and 4.0, CH^A*H*^{B}CO_2Me), 3.66 (3 H, s, OMe).

Pyrrolidinedione 37d. δ_H (part spectrum only) 0.85 (3 H, s, Me), 0.86 (3 H, s, Me), 0.87 (3 H, s, Me), 2.61 (1 H, dd, J 10.3 and 4.5, H-8), 3.00 (3 H, s, NMe), 3.06 (1 H, dd, J 17.1 and 4.3, CH^A*H*^{B}CO_2Me), 3.68 (3 H, s, OMe).

Trimethyl ester 38a. Mp 87–89 °C (from hexane–CH_2Cl_2 or from ethanol), 70% yield from **20** and dimethyl maleate; δ_H 1.53 (3 H, d, J 12.0, Ad), 1.62 and 1.69 (6 H, Abq, J 12.0, Ad), 1.75 (3 H, d, J 12.0, Ad), 1.98 (3 H, br s, Ad), 2.55 (1 H, dd, J 16.8 and 3.3, C*H*^{A}H^BCO_2Me), 2.56 (1 H, d, J 5.9, C*H*Ad), 2.71 (1 H, dd, J 16.8 and 11.0, CH^A*H*^{B}CO_2Me), 3.25 (1 H, m, C*H*CH_2CO_2Me), 3.64 (3 H, s, Me), 3.66 (3 H, s, Me), 3.71 (3 H, s, Me); δ_C 28.5, 35.0, 35.5, 36.7, 38.3, 39.8, 51.1, 51.8, 52.2, 57.1, 172.3, 172.6, 174.9. Found: C, 64.8; H, 8.0. $C_{19}H_{28}O_6$ requires C, 64.8; H, 8.0%. The structure of this compound was confirmed by X-ray diffraction using crystals obtained from ethanol.

Trimethyl ester 38b. Oil, 62% yield from **33** and dimethyl maleate; δ_H 0.95–1.78 (11 H, m, c-Hex), 2.43 (1 H, dd, J 17.1 and 3.1, C*H*^{A}H^BCO_2Me), 2.63 (1 H, dd, J 8.3 and 6.6, C*H*Hex-c), 2.79 (1 H, dd, J 17.1 and 11.5, CH^A*H*^{B}CO_2Me), 3.27 (1 H, m, C*H*CH_2CO_2Me), 3.64 (3 H, s, Me), 3.67 (3 H, s, Me), 3.71 (3 H, s, Me); δ_C 26.1, 30.4, 30.6, 32.2, 37.2, 40.5, 51.5, 51.9, 52.1, 52.4, 172.5, 173.1, 174.1. Found: C, 60.0; H, 8.0. $C_{15}H_{24}O_6$ requires C, 60.0; H, 8.1%.

Trimethyl ester 39a. Oil; δ_H 1.57–1.75 (12 H, m, Ad), 1.98 (3 H, br s, Ad), 2.28 (1 H, d, J 3.5, C*H*Ad), 2.60 (1 H, dd, J 16.7 and 4.7, C*H*^{A}H^BCO_2Me), 2.92 (1 H, dd, J 16.7 and 10.3, CH^A*H*^{B}CO_2Me), 3.27 (1 H, m, C*H*CH_2CO_2Me), 3.64 (3 H, s, Me), 3.67 (3 H, s, Me), 3.68 (3 H, s, Me).

Trimethyl ester 39b. Oil; δ_H 0.95–1.87 (11 H, m, c-Hex), 2.56 (1 H, dd, J 8.0 and 6.0, C*H*Hex-c), 2.61 (1 H, dd, J 16.8 and 4.7, C*H*^{A}H^BCO_2Me), 2.73 (1 H, dd, J 16.8 and 9.1, CH^A*H*^{B}CO_2Me), 3.29 (1 H, m, C*H*CH_2CO_2Me), 3.67 (3 H, s, Me), 3.69(0) (3 H, s, Me), 3.69(4) (3 H, s, Me).

Lactone 41a. Oil, 61% yield from **20**; δ_H 1.46 and 1.52 (6 H, Abq, J 12.0, Ad), 1.63 and 1.73 (6 H, Abq, J 12.0, Ad), 2.01 (3 H, br s, Ad), 2.06 (1 H, [q], J 7.9, C*H*Ad), 2.69 (1 H, dd, J 16.7 and 4.8, C*H*^{A}H^BCO_2Me), 2.80 (1 H, m, C*H*CH_2CO_2Me), 2.87 (1 H, dd, J 16.7 and 5.3, CH^A*H*^{B}CO_2Me), 3.71 (3 H, s, Me), 4.20 (1 H, dd, J 9.3 and 7.0, OC*H*^{A}H^B), 4.31 (1 H, [t], J 9.0, OCH^A*H*^{B}); δ_C 28.1, 33.9, 35.7, 36.1, 36.8, 39.4, 50.2, 52.0, 66.9, 171.5, 178.9; IR (liq. film) 1774 (lactone), 1740 (ester). Found: C, 69.8; H, 8.4. $C_{17}H_{24}O_4$ requires C, 69.8; H, 8.3%.

Lactone 41b. Oil, 60% yield from **33**; δ_H 0.82–1.77 (11 H, m, c-Hex), 2.24 (1 H, [quintet], J 8.4, C*H*Hex-c), 2.69–2.81 (3 H, C*H*$_2CO_2$Me and C*H*CH_2CO_2Me), 3.70 (3 H, s, Me), 3.97 (1 H, [t], J 8.9, OC*H*^{A}H^B), 4.39 (1 H, [t], J 8.9, OCH^A*H*^{B}); δ_C 25.9, 26.0, 26.1, 29.6, 31.0, 34.4, 39.5, 40.6, 45.6, 52.0, 69.9, 171.5, 178.5; IR (liq. film) 1771 (lactone), 1738 (ester). Found: C, 64.9; H, 8.4. $C_{13}H_{20}O_4$ requires C, 65.0; H, 8.4%.

Sulfone 42a. Oil, 89% yield from **19**; δ_H 0.83 (9 H, s, Bu^t), 1.33 (1 H, dd, J 14.7 and 8.3, C*H*^{A}H^{B}Bu^t), 1.98 (1 H, dd, J 14.7 and 1.4, CH^A*H*^{B}Bu^t), 2.54 (1 H, dd, J 17.5 and 2.7, C*H*^{A}H^BCO_2Me), 2.97 (1 H, dd, J 17.5 and 9.1, CH^A*H*^{B}CO_2Me), 3.57 (3 H, s, Me), 3.69 (1 H, [br t], J 8.5, C*H*SO_2Ph), 7.55–7.92 (5 H, m, Ph); δ_C 29.1, 31.0, 35.8, 41.1, 52.1, 57.9, 129.1, 129.3, 133.8, 137.3, 170.7; IR (liq. film) 1740 (ester), 1306 (sulfone), 1148 (sulfone). Found: C, 60.2; H, 7.5. $C_{15}H_{22}O_4S$ requires C, 60.4; H, 7.4%.

Sulfone 42b. Oil, 87% yield from **20**; δ_H 1.20 (1 H, dd, J 14.8 and 8.3, C*H*^{A}H^{B}Ad), 1.30 and 1.43 (6 H, Abq, J 12.0, Ad), 1.56 and 1.65 (6 H, Abq, J 12.2, Ad), 1.81 (1 H, dd, J 14.8 and 1.0, CH^A*H*^{B}Ad), 1.91 (3 H, br s, Ad), 2.51 (1 H, dd, J 17.4 and 2.7, C*H*^{A}H^BCO_2Me), 2.93 (1 H, dd, J 17.4 and 9.3, CH^A*H*^{B}CO_2Me), 3.57 (3 H, s, Me), 3.75 (1 H, [br t], J 8.4, C*H*SO_2Ph), 7.54–7.91 (5 H, m, Ph); δ_C 28.3, 32.7, 36.1, 36.6, 41.9(0), 41.9(4), 52.1, 56.1, 129.0, 129.3, 133.8, 137.3, 170.7; IR (liq. film) 1739 (ester), 1306 (sulfone), 1148 (sulfone). Found: C, 67.0; H, 7.6. $C_{21}H_{28}O_4S$ requires C, 67.0; H, 7.5%.

Sulfone 42c. Oil, 80% yield from **33**; δ_H 0.83–1.64 (11 H, m, c-Hex), 1.38 (1 H, ddd, J 14.3, 9.1 and 5.4, C*H*^{A}H^{B}Hex-c), 1.78 (1 H, ddd, J 14.3, 8.8 and 4.5, CH^A*H*^{B}Hex-c), 2.46 (1 H, dd, J 16.8 and 5.9, C*H*^{A}H^BCO_2Me), 2.87 (1 H, dd, J 16.8 and 6.7, CH^A*H*^{B}CO_2Me), 3.61 (3 H, s, Me), 3.70 (1 H, m, C*H*SO_2Ph), 7.55–7.90 (5 H, m, Ph); δ_C 25.8, 26.0, 26.2, 32.1, 33.6, 33.7, 34.7, 35.8, 52.2, 58.6, 129.0(6), 129.1(4), 133.8, 137.3, 170.8; IR (liq. film) 1742 (ester),

1308 (sulfone), 1148 (sulfone). Found: C, 62.8; H, 7.5. $C_{17}H_{24}O_4S$ requires C, 62.9; H, 7.5%.

Annulation product 46. Mp 182–184 °C (from hexane–CH_2Cl_2), 30% yield from **43**; δ_H 0.85 (3 H, s, CMe), 0.89 (3 H, s, CMe), 1.21 (1 H, m, H–7A), 1.72 (1 H, m, H–7B), 1.85 (1 H, m, H–8A), 2.23 (1 H, dd, *J* 13.0 and 6.1, H–8B), 2.78 (1 H, dd, *J* 17.0 and 5.2, C*H*^{A}H^{B}CO$_2$Me), 2.82 (1 H, [q], *J* 4.6, H-14), 2.87 (1 H, m, H-6), 2.96 (3 H, s, NMe), 3.01 (3 H, s, NMe), 3.13 (1 H, dd, *J* 17.0 and 3.6, CH^A*H*^{B}CO$_2$Me), 3.23 (1 H, [t], *J* 8.7, H-1), 3.56 (1 H, [t], *J* 8.4, H-5), 3.72 (3 H, s, OMe), 4.09 (1 H, d, *J* 4.9, H-10); δ_C 20.1, 24.4, 24.8, 25.1, 25.3, 28.4, 34.4, 36.8, 38.9, 45.3, 45.7, 50.3, 52.0, 53.2, 171.6, 178.6, 178.7, 180.1, 180.2; IR (KBr disc) 1767 (imide), 1736 (ester), 1695 (br, imide). Found: C, 60.3; H, 6.9; N, 7.3. $C_{19}H_{26}N_2O_6$ requires C, 60.3; H, 6.9; N, 7.4%. The structure of this compound was confirmed by X-ray diffraction and is shown in Fig. 1.

Annulation product 47. Mp 168–170 °C (from methanol), 37% yield from **43**; δ_H 1.01 (3 H, s, CMe), 1.07 (3 H, s, CMe), 1.43 (1 H, m, H–7A), 1.82 (1 H, m, H–7B), 1.93 (1 H, m, H–8A), 2.35 (1 H, dd, *J* 13.1 and 6.1, H–8B), 2.83 (1 H, dd, *J* 17.5 and 4.6, C*H*^{A}H^{B}CO$_2$Me), 2.94–3.00 (2 H, complex, H-6 and H-14), 3.19 (1 H, dd, *J* 17.5 and 4.2, CH^A*H*^{B}CO$_2$Me), 3.37 (1 H, [t], *J* 8.7, H-1), 3.67 (3 H, s, OMe), 3.80 (1 H, [t], *J* 8.4, H-5), 4.24 (1 H, d, *J* 4.8, H-10), 7.21–7.49 (10 H, m, 2 Ph); δ_C 20.2, 24.5, 25.5, 28.9, 34.8, 37.3, 39.0, 45.4, 45.7, 50.5, 52.0, 53.6, 126.6, 126.7, 128.6, 128.7, 129.1, 129.2, 132.1, 132.2, 171.6, 177.7, 177.8, 179.1, 179.2; IR (KBr disc) 1773 (imide), 1729 (ester), 1700 (br, imide). Found: C, 69.1; H, 6.0; N, 5.6. $C_{29}H_{30}N_2O_6$ requires C, 69.3; H, 6.0; N, 5.6%.

X-Ray crystallography|| ||

Single crystals were mounted on glass fibres and all geometric and intensity data were collected from these samples using a Bruker SMART APEX CCD diffractometer, in conjunction with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Data reduction and integration were carried out with Bruker SAINT+ software[47] and absorption corrections were applied using the program SADABS.[48] Structures were solved by direct methods and developed using alternating cycles of least-squares refinement and difference-Fourier synthesis. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and their thermal parameters linked to those of the atoms to which they were attached (riding model). Structure solution and refinement used the SHELXTL PLUS V6.12 program package.[49]

Crystal data for the pseudo ester 25. Data collected at 150 K. $C_{16}H_{24}O_3$, M = 264.35, monoclinic, space group $P2_1/c$, a = 12.9963(15), b = 15.2812(17), c = 15.4858(17) Å, β = 113.494(2)°, U = 2820.5(5) Å^3, Z = 8, F(000) = 1152, D_c = 1.245 g cm^{-3}, μ(Mo-Kα) = 0.084 mm^{-1}, colourless crystal 0.48 × 0.46 × 0.38 mm^3. Full matrix least-squares refinement on 353 parameters gave R = 0.0572 (R_w = 0.1588) for 5697 independent reflections [$I > 2\sigma(I)$] and R = 0.0634 (R_w = 0.1661) for all 6578 independent reflections for θ in the range 1.71 to 28.32°. The terminal carbon atom of the ethyl group is disordered over two sites with 50% occupancy; the hydrogen atoms are omitted from the disordered model. The final electron density map was featureless with the largest peak 0.475 e Å^{-3}.

Crystal data for the pyrrolidinedione 30b. Data collected at 150 K. $C_{19}H_{27}NO_4$, M = 333.42, monoclinic, space group $P2_1/c$, a = 6.7197(6), b = 20.8230(17), c = 12.2379(10) Å, β = 98.890(2), U = 1691.8(2) Å^3, Z = 4, F(000) = 720, D_c = 1.309 g cm^{-3}, μ(Mo-Kα) = 0.091 mm^{-1}, colourless crystal 0.36 × 0.12 × 0.08 mm^3. Full matrix least-squares refinement on 217 parameters gave R = 0.0521 (R_w = 0.1255) for 4058 independent reflections [$I > 2\sigma(I)$] and R = 0.0694 (R_w = 0.1363) for all 3215 independent reflections for θ in the range 1.95 to 28.30°. The final electron density map was featureless with the largest peak 0.366 e Å^{-3}.

Crystal data for the pyrrolidinedione 36a. Data collected at 293 K. $C_{18}H_{29}NO_4$, M = 323.42, orthorhombic, space group $P2_12_12_1$, a = 8.1750(15), b = 10.6612(19), c = 20.842(4) Å, U = 1816.5(6) Å^3, Z = 4, F(000) = 704, D_c = 1.183 g cm^{-3}, μ(Mo-Kα) = 0.083 mm^{-1}, colourless crystal 0.48 × 0.45 × 0.37 mm^3. Full matrix least-squares refinement on 209 parameters gave R = 0.0474 (R_w = 0.1281) for 4055 independent reflections [$I > 2\sigma(I)$] and R = 0.0494 (R_w = 0.1301) for all 4242 independent reflections for θ in the range 1.95 to 28.34°. The final electron density map was featureless with the largest peak 0.202 e Å^{-3}.

Crystal data for the pyrrolidinedione 37a. Data collected at 150 K. $C_{18}H_{27}NO_4$, M = 321.41, orthorhombic, space group $C222_1$, a = 8.2843(8), b = 10.1695(9), c = 41.757(4) Å, U = 3517.9(6) Å^3, Z = 8, F(000) = 1392, D_c = 1.214 g cm^{-3}, μ(Mo-Kα) = 0.085 mm^{-1}, colourless crystal 0.50 × 0.42 × 0.03 mm^3. Full matrix least-squares refinement on 208 parameters gave R = 0.0879 (R_w = 0.2223) for 3685 independent reflections [$I > 2\sigma(I)$] and R = 0.0976 (R_w = 0.2304) for all 4212 independent reflections for θ in the range 1.95 to 28.26°. The final electron density map was featureless with the largest peak 0.742 e Å^{-3}.

Crystal data for the pyrrolidinedione 37b. Data collected at 293 K. $C_{18}H_{27}NO_4$, M = 321.41, orthorhombic, space group $P2_12_12_1$, a = 6.9054(5), b = 9.2827(7), c = 27.029(2) Å, U = 1732.6(2) Å^3, Z = 4, F(000) = 696, D_c = 1.232 g cm^{-3}, μ(Mo-Kα) = 0.086 mm^{-1}, colourless crystal 0.48 × 0.16 × 0.08 mm^3. Full matrix least-squares refinement on 208 parameters gave R = 0.0588 (R_w = 0.1452) for 3589 independent reflections [$I > 2\sigma(I)$] and R = 0.0672 (R_w = 0.1513) for all 4169 independent reflections for θ in the range 1.51 to 28.30°. The final electron density map was featureless with the largest peak 0.245 e Å^{-3}.

Crystal data for the trimethyl ester 38a. Data collected at 150 K. $C_{19}H_{28}O_6$, M = 352.41, orthorhombic, space group $Pbca$, a = 16.5381(12), b = 11.3348(8), c = 19.0816(14) Å, U = 3577.0(4) Å^3, Z = 8, F(000) = 1520, D_c = 1.309 g cm^{-3}, μ(Mo-Kα) = 0.096 mm^{-1}, colourless crystal 0.38 × 0.08 × 0.06 mm^3. Full matrix least-squares refinement on 226 parameters gave R = 0.0802 (R_w = 0.1464) for 3387 independent reflections [$I > 2\sigma(I)$] and R = 0.1112 (R_w = 0.1589) for all 4396 independent reflections for θ in the range 2.13 to 28.31°. The final electron density map was featureless with the largest peak 0.342 e Å^{-3}.

Crystal data for the annulation product 46. Data collected at 150 K. $C_{19}H_{26}N_2O_6$, M = 378.42, orthorhombic, space group $Pbca$, a = 18.717(3), b = 10.0246(14), c = 19.808(3) Å, U = 3716.6(10) Å^3, Z = 8, F(000) = 1616, D_c = 1.353 g cm^{-3}, μ(Mo-Kα) = 0.101 mm^{-1}, colourless crystal 0.60 × 0.45 × 0.09 mm^3. Full matrix least-squares refinement on 249 parameters gave R = 0.0629 (R_w = 0.1335) for 4548 independent reflections [$I > 2\sigma(I)$] and R = 0.0748 (R_w = 0.1391) for all 3899 independent reflections for θ in the range 2.06 to 28.30°. The final electron density map was featureless with the largest peak 0.44 e Å^{-3}. The structure is shown in Fig. 1.

Acknowledgements

We are grateful to Dr A. E. Aliev for his help in assigning a number of ^{1}H NMR spectra. Support for this work from the EPSRC is acknowledged.

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