# Radical-chain reductive alkylation of electron-rich alkenes mediated by silanes in the presence of thiols as polarity-reversal catalysts

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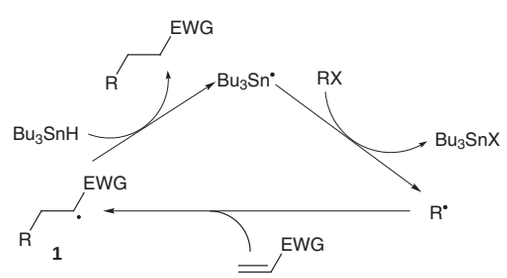
In the presence of a thiol catalyst, triphenylsilane mediates the reductive alkylation of electron-rich terminal alkenes $R^1R^2C{=}CH_2$ by organic halides $R^3Hal$ *via* electrophilic carbon-centred radicals $R^{3\bullet}$. Reactions were carried out in benzene or dioxane solvent using di-*tert*-butyl hyponitrite (at 60 °C) or dilauroyl peroxide (at 80 °C) as initiators and good yields of the adducts $R^1R^2CHCH_2R^3$ were obtained with either methyl thioglycolate or triphenylsilanethiol as catalysts (5–10 mol% based on alkene). In the presence of the thiol, the slow direct abstraction of hydrogen from the silane by the nucleophilic adduct radical $R^1R^2\dot{C}CH_2R^3$ is replaced by a cycle of more rapid polarity-matched reactions in which hydrogen-atom transfer to the adduct radical from the thiol is followed by abstraction of hydrogen from the silane by the derived thiyl radical, to regenerate the catalyst. In the absence of thiol, negligible yields of reductive alkylation products were obtained. The homochiral thiols, 1-thio-β-D-mannopyranose tetraacetate and 1-thio-β-D-glucopyranose tetraacetate, and the tetrapivalate and tetrabenzoate analogues of the latter were effective catalysts and reductive carboxyalkylation products with enantiomeric excesses up to 72% were obtained from prochiral alkenes. Homochiral samples of two of these adducts were obtained by recrystallisation and their absolute configurations were determined by X-ray diffraction.

In recent years, free-radical chemistry has provided a number of useful methods for the selective formation of carbon–carbon bonds.[1] The key step in these reactions generally involves the inter- or intra-molecular addition of a carbon-centred radical to a multiply-bonded carbon acceptor, often followed by atom- or group-transfer to the resulting adduct radical to give the final product and a new radical which goes on to propagate a chain process. The reductive alkylation of electron-poor alkenes, using alkyl halides or pseudohalides (RX) in the presence of tributyltin hydride, constitutes an important example of such a C–C bond-forming reaction.[2] The propagation stage of this radical-chain process is shown in Scheme 1




**Scheme 1**

(EWG = electron-withdrawing group) and both addition of a nucleophilic alkyl radical to the alkene and abstraction of hydrogen from the tin hydride by the electrophilic adduct radical **1** are facilitated by the favourable polar effects which operate in the respective transition states.[3]

In common with other reactions that are mediated by trialkyltin hydrides, this reductive alkylation suffers from drawbacks arising from the toxicity of organotin compounds and the difficulty of completely removing tin residues from the final product.[4] Furthermore, because of the high rate at which alkyl radicals abstract hydrogen from the tin hydride, it is also usually necessary to keep the concentration of the latter low relative to the concentration of the alkene, in order to suppress premature trapping of $R^\bullet$ by the tin hydride to give RH in competition with addition of $R^\bullet$ to the alkene to produce **1**.

We have shown that, in conjunction with a thiol catalyst, simple trialkyl- or triaryl-silanes can serve as effective replacements for trialkyltin hydrides for the reduction of alkyl halides, sulfides and xanthates to hydrocarbons.[5] In the absence of thiol catalyst, the direct abstraction of electron-rich hydrogen from silicon by a nucleophilic alkyl radical [reaction (1)] is rel-

$$R^\bullet + R'_3SiH \longrightarrow RH + R'_3Si^\bullet \quad (1)$$

$$R^\bullet + XSH \longrightarrow RH + XS^\bullet \quad (2)$$

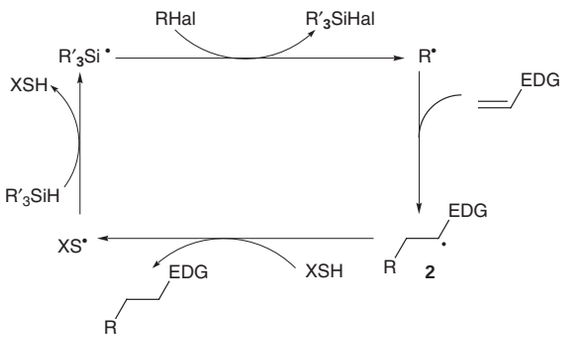
$$XS^\bullet + R'_3SiH \longrightarrow XSH + R'_3Si^\bullet \quad (3)$$

atively sluggish, because of adverse polar effects, and is usually too slow to maintain the chain. In the presence of thiol, the direct hydrogen transfer is replaced by the catalytic cycle as shown in reactions (2) and (3), both of which benefit from favourable polar effects and are relatively rapid, because the thiyl radical is electrophilic and the sulfhydryl hydrogen atom is electron-poor.‡§ The thiol acts as a *protic polarity-reversal catalyst* for reaction (1).[6] Similarly, because of catalysis of reactions of type (1), radical-chain hydrosilylation of alkenes by simple silanes is also catalysed by thiols.[8,9]

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

‡ It should be noted that factors other than polar effects must be considered in order to understand the relative rates of hydrogen-atom transfer to alkyl radicals from silanes and from thiols.[6,7]
§ For discussion of the reversibility of reaction (3), see refs. 6 and 7.

We reasoned that favourable polar effects should also make the silane–thiol couple an effective mediator of the reductive alkylation of an electron-rich alkene by an organic halide RHal which gives rise to a relatively electrophilic radical R$^{\bullet}$. The proposed propagation cycle is shown in Scheme 2 (EDG = electron-donating group). Addition of the electrophilic carbon radical to the electron-rich alkene will be rapid and will necessarily yield a nucleophilic adduct radical **2**, which in turn rapidly abstracts the electron-deficient hydrogen from sulfur in the thiol catalyst. Such a chain process is complementary to the tin hydride-mediated reaction shown in Scheme 1, which is particularly suited to the reductive alkylation of electron-deficient alkenes. A preliminary report of the realisation of reactions based on Scheme 2 has appeared [10] and, in the present paper, we give a full account of this work and its extension to enantioselective reductive alkylation catalysed by homochiral thiols.

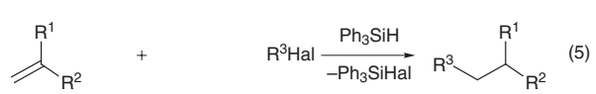



**Scheme 2**

## Results and discussion

Initial reactions were carried out at 60 °C and were initiated by thermal decomposition of di-*tert*-butyl hyponitrite (TBHN, $t_{1/2}$ = *ca.* 55 min),[11,12] which produces *tert*-butoxyl radicals [eqn. (4)] that go on to abstract hydrogen from the silane and/or the thiol to afford chain-carrying silyl or thiyl radicals. When a dioxane solution containing isopropenyl acetate **3a** (2.50 mmol), triphenylsilane (3.25 mmol), dimethyl chloromalonate **4a** (3.75 mmol) and TBHN (0.125 mmol) was heated under argon for 2 h, examination of the reaction mixture by $^1$H NMR spectroscopy showed that <1% of the adduct **5aa**¶ had been formed. However, when the experiment was repeated in the presence of methyl thioglycolate ($MeO_2CCH_2SH$, MTG, 0.125 mmol, 5 mol% based on alkene) under otherwise identical conditions, the adduct **5aa** was isolated in 78% yield. A somewhat higher yield was obtained in the presence of triphenylsilanethiol (TPST, 5 mol%) as catalyst (Table 1, entries 1 and 2) and this thiol was used as the achiral catalyst in most subsequent experiments. Thus, the reductive alkylation of **3a** [eqn. (5)] evidently proceeds by the radical-chain mechanism shown in Scheme 2.

$$Bu^tON{=}NOBu^t \longrightarrow 2\ Bu^tO^{\bullet} + N_2 \qquad (4)$$




(5)

**3a** $R^1$ = OAc, $R^2$ = Me
**b** $R^1$ = OAc, $R^2$ = $Bu^t$
**c** $R^1$ = $OSiMe_2Bu^t$, $R^2$ = Me
**d** $R^1$ = OBu, $R^2$ = H
**e** $R^1$ = Pentyl, $R^2$ = Me
**f** $R^1$ = $CH_2OAc$, $R^2$ = Me

**4a** $(MeO_2C)_2CHCl$
**b** $MeO_2CCH_2Br$
**c** $(EtO_2C)_2CMeBr$
**d** 1-AdO$_2$CCH$_2$Br
**e** 1-AdC(O)CH$_2$Br
**f** $PhSO_2CH_2Br$

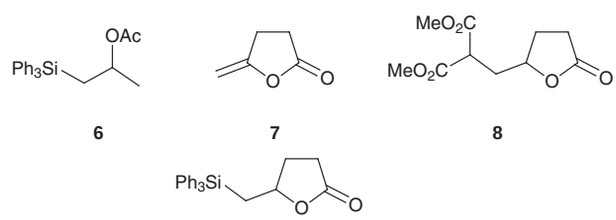
**5**

**Table 1** Reductive alkylation of alkenes using organic halides in the presence of triphenylsilane, catalysed by thiol and initiated by TBHN[a] in dioxane at 60 °C

| Entry | Alkene | $R^3$Hal | Thiol[a] | Adduct | Adduct yield (%)[b] |
|---|---|---|---|---|---|
| 1 | **3a** | **4a** | MTG | **5aa** | 78 |
| 2 | **3a** | **4a** | TPST | **5aa** | 88[c] |
| 3 | **3a** | **4b** | MTG | **5ab** | 75 |
| 4 | **3a** | **4b** | TPST | **5ab** | 72 |
| 5 | **3a** | **4c** | TPST | **5ac** | 78 |
| 6 | **3a** | **4d** | TPST | **5ad** | 83 |
| 7 | **3a** | **4e** | MTG | **5ae** | 76 |
| 8 | **3b** | **4a** | TPST | **5ba** | 86 |
| 9 | **3b** | **4b** | TPST | **5bb** | 75 |
| 10 | **3c** | **4a** | TPST | **5ca** | 85 |
| 11 | **3d** | **4a** | TPST | **5da** | 78 |
| 12 | **3e** | **4a** | TPST | **5ea** | 60 |
| 13 | **3f** | **4a** | TPST | **5fa** | 63 |
| 14[d] | **3a** | **4a** | MTG | **5aa** | 89 |
| 15[d] | **3a** | **4a** | TPST | **5aa** | 92 |
| 16[d] | **3a** | **4g** | MTG | **5af** | 48 |

[a] Each 5 mol% based on alkene. [b] Isolated yields based on alkene. [c] The yield was similar in benzene solvent. Only a trace of adduct was formed in the absence of thiol. [d] The reaction was carried out in benzene solvent under gentle reflux, using dilauroyl peroxide (5 mol%) as initiator.

A good yield of the adduct **5ab** was obtained when the chloromalonate was replaced by methyl bromoacetate, using either MTG or TPST as catalyst (entries 3 and 4), but with methyl chloroacetate under the same conditions the yield of **5ab** was reduced to 40% and a large amount of the silane adduct **6** was also isolated. Evidently, the triphenylsilyl radical adds to isopropenyl acetate and abstracts the halogen from the chloroacetate at comparable rates, whilst with the more reactive bromoacetate, halogen abstraction becomes the major pathway. Reductive carboxyalkylation of isopropenyl acetate using diethyl 2-bromo-2-methylmalonate afforded the adduct **5ac** in good yield (entry 5), showing that the more sterically-hindered and less electrophilic radical $MeC^{\bullet}(CO_2Et)_2$ adds effectively to the alkene under the reaction conditions.[13]




**6** **7** **8**

**9**

Triphenylbromosilane is formed as a by-product in all reactions that involve organic bromides as the source of radical addenda. This bromosilane is a moderately strong Lewis acid, and is also readily hydrolysed to give HBr, and thus care must be exercised when working with compounds that are sensitive to such acids. Similar, though less severe problems could arise from the presence of triphenylchlorosilane. Precautions should be taken to exclude moisture during the reactions and the standard work-up procedure involves neutralisation of the reaction mixture with aqueous sodium bicarbonate at an early stage.

Similar reductive alkylation reactions were carried out with the acyclic terminal alkenes **3b**–**f** and the results are summarised in Table 1 (entries 8–13); in no case was a significant amount of product formed in the absence of thiol catalyst. In order to make the procedure more convenient, reactions were also carried out at *ca.* 80 °C in gently-refluxing benzene solvent,

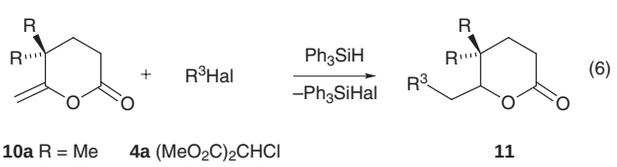
¶ The adduct **5aa** arises from **3a** and **4a**, the adduct **5ab** arises from **3a** and **4b** and so on.

using commercially available dilauroyl peroxide (DLP, 5 mol% based on alkene) as initiator. The yield of **5aa** obtained from isopropenyl acetate and dimethyl chloromalonate was similar to that obtained at 60 °C using TBHN as initiator (entries 14 and 15). Reductive sulfonylmethylation using $PhSO_2CH_2Br$ proved somewhat problematic and major amounts of the simple reduction product, methyl phenyl sulfone, were obtained under the usual reaction conditions. However, a moderate yield of the adduct **5af** was obtained when the thiol concentration was kept low by slowly adding a solution containing MTG and DLP (5 mol% of each) to the reaction mixture (entry 16).

Tris(trimethylsilyl)silane (TTMSS) is a much more reactive hydrogen atom donor than simple trialkyl- or triaryl-silanes and has been used successfully as an effective replacement for tributyltin hydride in reductive alkylation reactions and in several other types of radical-chain processes.[4,14] It was thus important to compare the efficiency of TTMSS with that of the triphenylsilane–thiol couple used in the present work. When the reaction between isopropenyl acetate and dimethyl chloromalonate was carried out under the conditions of the first entry in Table 1, except that the triphenylsilane was replaced by TTMSS, the reductive alkylation product **5aa** was formed in 31% yield, as judged by $^1$H NMR spectroscopy. Under these conditions, dimethyl malonate was also formed in 55% yield, as a result of relatively rapid trapping by the silane of the *electrophilic* radical $(MeO_2C)_2\dot{C}H$ prior to its addition to the alkene.

Reductive alkylation of the methylenelactones **7** and **10a** and **b** proceeded smoothly at 60 °C (TBHN initiator) or at 80 °C (DLP initiator), using either MTG or TPST (5–10 mol%) as catalyst, although the latter usually gave somewhat higher yields. Again, essentially no products were obtained in the absence of thiol. The silane adduct **9** was obtained as a by-product (15% yield) in the reaction of **7** with dimethyl chloromalonate, as a result of trapping of the triphenylsilyl radical by the alkene in competition with the abstraction of chlorine. Similarly, minor and variable amounts of **12a** and **b** were obtained from reactions of the methylenelactones **10**. The isolated yields of racemic adducts **8** and **11** are given in the Experimental section.

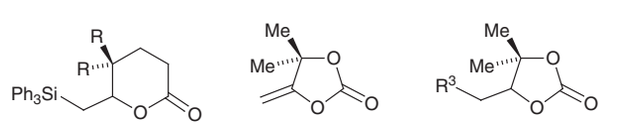
Reductive alkylation of the unsaturated cyclic carbonate **13** to give **14a** and **b** proceeded smoothly at 80 °C (DLP initiator)




**10a** R = Me
**b** R = Ph

**4a** $(MeO_2C)_2CHCl$
**b** $MeO_2CCH_2Br$
**d** $1\text{-}AdO_2CCH_2Br$
**e** $1\text{-}AdC(O)CH_2Br$
**f** $PhSO_2CH_2Br$
**g** $Bu^tC(O)CH_2Br$
**h** $(Bu^tO_2C)_2CHCl$
**i** $(EtO_2C)_3CCl$
**j** $Bu^tO_2CCH_2Br$

**11**




**12a** R = Me
**b** R = Ph

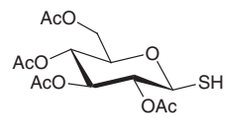
**13**

**14a** $R^3 = (MeO_2C)_2CH$
**b** $R^3 = PhSO_2CH_2$

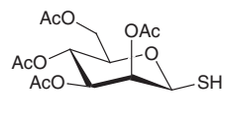
using TPST as catalyst, showing that this sensitive functionality can tolerate the presence of $Ph_3SiBr$ under the reaction conditions.

The final product-forming step in the thiol-catalysed reductive alkylation process (Scheme 2) is hydrogen-atom transfer from the thiol to the adduct radical **2** and, if the latter is prochiral at the radical centre and the thiol is homochiral, then this step should be enantioselective. We have shown previously[9e] that thiol-catalysed hydrosilylation can similarly be rendered enantioselective by the use of homochiral thiols as catalysts and, for example, the silane adducts **12a** and **b** have been obtained in moderate to high enantiomeric purity by this route.

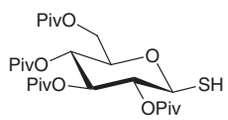
For the present work, the carbohydrate-derived thiols **15**–**18**



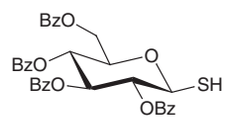

**15**




**16**



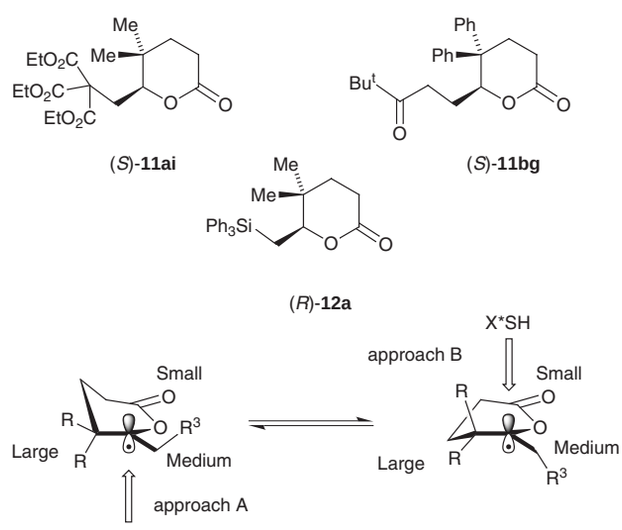

**17**




**18**

were chosen as homochiral catalysts, but it seems likely that improved asymmetric induction could be obtained using more specifically designed thiol catalysts. A selection of reductive alkylation reactions of **10** and **13** was carried out using DLP as initiator in refluxing benzene and the results are summarised in Table 2; 10 mol% of thiol and initiator were used in these experiments. Chemical yields were generally good, in some cases better than those of the racemic products obtained using MTG or TPST as catalysts under the same conditions, and the enantiomeric excess (ee) was determined either by chiral-stationary-phase HPLC or by $^1$H NMR spectroscopy using (+)-tris[3-(heptafluoropropylhydroxymethylene)camphorato]-europium(III) [$Eu(hfc)_3$] as a homochiral shift reagent. The enantiomeric purities of the adducts **11ai** and **11bg** could be upgraded by recrystallisation and the absolute configurations of the homochiral compounds were determined by X-ray diffraction; the structures are shown in Figs. 1 and 2.

Both reductive alkylation products have the *S*-configuration at C-6 (Scheme 3). The adduct **12a**, obtained by thiol-promoted




**Scheme 3**

addition of triphenylsilane to the methylenelactone **10a**, has been shown to have the *R*-configuration at C-6, when either **15** or **16** was used as catalyst.[9e] Thus, in all three cases the products are formed by selective transfer of hydrogen from the β-D-pyranose thiols to topologically-similar faces of the adduct radical intermediate, as shown in Scheme 3. The adduct radical should exist as a rapidly-equilibrating pair of enantiomers and,

**Table 2** Enantioselective reductive alkylation of alkenes mediated by triphenylsilane in the presence of homochiral thiol catalysts initiated by DLP[a] in benzene at *ca*. 80 °C

| Entry | Alkene | $R^3Hal$ | Thiol[a] | Product and isolated yield (%)[b] | Product ee (%) | $[\alpha]_D^{21 \pm 1}$[c] |
|---|---|---|---|---|---|---|
| 1 | **10a** | **4a** | **15** | **11aa** (62) | 28 | −14.6 (2.24) |
| 2 | **10a** | **4b** | **15** | **11ab** (85) | 19 | −18.5 (1.74) |
| 3 | **10a** | **4f** | **15** | **11af** (72) | 7 | −3.5 (2.54) |
| 4 | **10a** | **4i** | **15** | **11ai** (67) | 46 | — |
| 5 | **10a** | **4i** | **16** | **11ai** (65) | 72 | −26.9 (1.71) |
| 6 | **10b** | **4a** | **15** | **11ba** (90) | 54 | −117.0 (2.15) |
| 7 | **10b** | **4a** | **16** | **11ba** (92) | 52 | −112.5 (2.23) |
| 8 | **10b** | **4b** | **15** | **11bb** (75) | 41 | −95.4 (1.70) |
| 9 | **10b** | **4b** | **16** | **11bb** (80) | 45 | — |
| 10 | **10b** | **4d** | **15** | **11bd** (57) | 52 | −130.5 (1.65) |
| 11 | **10b** | **4e** | **15** | **11be** (52) | 41 | −98.4 (2.24) |
| 12 | **10b** | **4f** | **15** | **11bf** (58) | 53 | −115.2 (1.78) |
| 13 | **10b** | **4g** | **15** | **11bg** (70) | 54 | −143.6 (1.62) |
| 14 | **10b** | **4g** | **16** | **11bg** (74) | 53 | −141.0 (1.42) |
| 15 | **10b** | **4g** | **17** | **11bg** (71) | 52 | −138.1 (1.75) |
| 16 | **10b** | **4g** | **18** | **11bg** (75) | 60 | −159.6 (1.56) |
| 17 | **10b** | **4h** | **15** | **11bh** (70) | 33 | −83.2 (1.45) |
| 18 | **10b** | **4j** | **15** | **11bj** (70) | 50 | −117.5 (1.74) |
| 19 | **13** | **4a** | **15** | **14a** (74) | 8 | −18.5 (2.84) |

[a] Each 10 mol% based on alkene. [b] Isolated yields based on alkene. [c] $CHCl_3$ solvent, *c* (g/100 $cm^3$) shown in parentheses

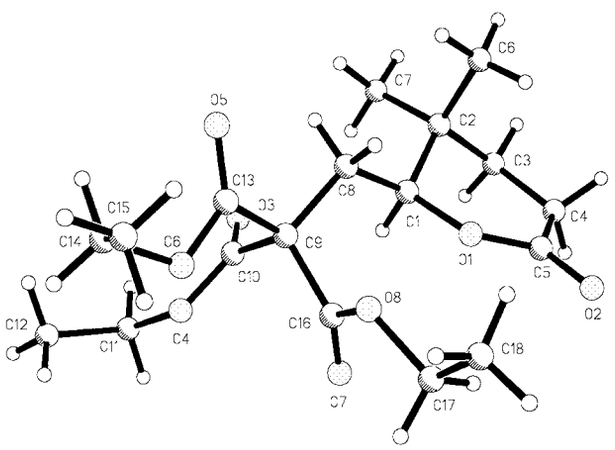



**Fig. 1** Structure of (*S*)-(−)-6-[2,2,2-tris(ethoxycarbonyl)ethyl]-5,5-dimethyltetrahydropyran-2-one, (*S*)-**11ai**, determined by X-ray crystallography. Selected geometrical parameters (bond lengths in Å, bond angles in degrees): C2–C3 1.533(4), C3–C4 1.481(4), C4–C5 1.496(4), C5–O1 1.350(3), C1–O1 1.465(3), C1–C2 1.528(3), C5–O2 1.200(3), C1–C8 1.526(3), C2–C7 1.526(3), C2–C6 1.528(4), C2–C1–O1 111.72(16), C2–C1–C8 114.79(18), C8–C1–O1 104.30(17), C1–O1–C5 121.15(18), C4-C5–O1 119.2(2).

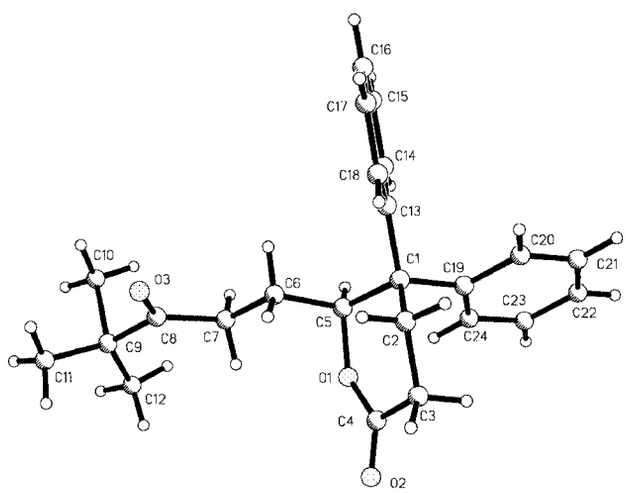



**Fig. 2** Structure of (*S*)-(−)-6-(4,4-dimethyl-3-oxopentyl)-5,5-diphenyltetrahydropyran-2-one, (*S*)-**11bg**, determined by X-ray crystallography. Selected geometrical parameters (bond lengths in Å, bond angles in degrees): C1–C2 1.530(2), C2–C3 1.521(3), C3–C4 1.496(3), C4–O1 1.347(3), C5–O1 1.460(2), C1–C5 1.548(2), C4–O2 1.192(3), C5–C6 1.527(3), C1–C13 1.530(2), C1–C19 1.542(3), C1–C5–O1 112.38(13), C1–C5–C6 115.45(15), C6–C5–O1 106.97(14), C5–O1–C4 123.63(15), O1–C4–C3 119.52(17).

assuming that approach of the thiol takes place preferentially in a direction *anti* to the substituent $R^3$, the diastereoisomeric transition state resulting from approach A is evidently of lower energy than that resulting from approach B for hydrogen-atom transfer from the homochiral catalysts **15** and **16**. Approach A involves attack of the thiol at the face where the substituents at the radical centre are arranged in the clockwise order large, medium and small.

Comparison of the pairs of entries 1 and 6, 2 and 8, and 3 and 12 shows that the ees of adducts obtained from **10b** are appreciably greater than those obtained from **10a**, presumably as a result of the increased bulk of the large substituent in the intermediate radicals derived from the former alkene. For reductive carboxyalkylation of **10a** using triethyl chloromethanetricarboxylate **4i**, the ee obtained using the mannopyranose thiol **16** as catalyst was appreciably higher than that obtained using the glucopyranose thiol **15** (entries 4 and 5). Unfortunately, the 5,5-diphenyl analogue **10b** failed to undergo reductive carboxyalkylation with **4i**. In other reductive alkylation reactions of **10b**, no significant differences in the ees of the products were found between the four thiol catalysts **15**–**18** (entries 6 and 7, 8 and 9, and 13 and 16). Reductive carboxyalkylation of **10b** using dimethyl chloromalonate gave a product of higher ee than that obtained from di-*tert*-butyl chloromalonate (entries 6 and 17), perhaps because the larger bulk of the medium-sized substituent in the intermediate adduct radical derived from the latter makes this group more similar in size to the large substituent, thus reducing the steric chirality at the radical centre. In contrast, the product derived from *tert*-butyl bromoacetate showed a somewhat higher ee than that obtained from methyl bromoacetate (entries 8 and 18).

Enantioselective reductive carboxylation of **10a** could also be mediated by tributyltin hydride. Thus, when a dioxane solution containing the tin hydride (1.3 equiv.) and TBHN (5 mol% based on alkene) was added slowly during 2 h to a dioxane solution containing the methylenelactone **10a** (1 equiv.), dimethyl chloromalonate (1.3 equiv.), the thiol **15** (1 mol%) and TBHN (1 mol%) at 60 °C, followed by further heating at 60 °C

for 1 h, the adduct **11aa** was isolated in 74% yield and showed an ee of 26%. The adduct with the same ee was obtained in 68% yield when the experiment was repeated using triphenylsilane in a one-pot reaction in which all the silane was present initially. In the $Bu_3SnH$-mediated reaction, the chemical yield and adduct ee both drop if the tin hydride is added rapidly, because the latter then becomes a competitive achiral donor of hydrogen to the adduct radical **2**, as well as prematurely trapping the electrophilic malonyl radical. When the reaction was repeated with slow addition of TTMSS in place of the tin hydride, the adduct **11aa** was isolated in 67% yield and showed an ee of 26%. When all the TTMSS was added at the start of the reaction, the yield of adduct was very low and dimethyl malonate was the major product. These results demonstrate that thiols can act as polarity-reversal catalysts for the abstraction of hydrogen by nucleophilic radicals from both tributyltin hydride and from TTMSS. Similarly, the thiols **15** and **16** have been shown to catalyse the enantioselective hydrosilylation of **10a** by TTMSS, confirming that these thiols are acting here as hydrogen donors to the silyl-radical adduct of the alkene, under the conditions used.[9e]

We conclude that the triphenylsilane–thiol couple is an effective mediator of the reductive alkylation of electron-rich alkenes by halides that yield electrophilic carbon radicals; slow addition techniques are not necessary because this silane is a poorer hydrogen-atom donor, towards the electrophilic radical addenda involved, than tributyltin hydride or tris(trimethylsilyl)silane. Enantioselective reductive alkylation of the prochiral alkenes, mediated by triphenylsilane in the presence of homochiral thiol catalysts, gave products of moderate enantiomeric purity. However, the SH groups in the four carbohydrate-derived thiols **15**–**18** are not in particularly chiral environments and there would appear to be considerable scope for the rational design of homochiral thiols that would be more discriminating donors of hydrogen to the different enantiotopic faces of the intermediate prochiral adduct radical. Further work is clearly needed to identify structural factors in both the thiol catalyst and the prochiral adduct radical that lead to high enantioselectivity in the hydrogen-atom transfer reaction.

## Experimental

NMR spectra were recorded using a Varian VXR-400 instrument (400 MHz for $^1H$). The solvent was $CDCl_3$ and chemical shifts are reported relative to $Me_4Si$; *J* values are quoted in Hz. Infrared spectra were recorded for liquid films or Nujol mulls using a Perkin-Elmer 1600 series FTIR spectrometer; the units are $cm^{-1}$. 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. Determination of enantiomeric excess by HPLC was carried out using a Chiralcel-OD column (4.6 mm × 250 mm; Daicel Chemical Industries Ltd.) in conjunction with hexane–isopropyl alcohol eluent (flow rate 1 $cm^3$ $min^{-1}$). The proportion of alcohol in the mobile phase and retention times of the two enantiomers are given in the text; UV detection was at 254 nm (unless stated otherwise) and in all cases the major enantiomer was eluted first. Determination of enantiomeric excess by $^1H$ NMR analysis was carried out using (+)-tris[3-(heptafluoropropylhydroxymethylene)camphorato]europium(III) [$Eu(hfc)_3$] as shift reagent. Optical rotations were measured on an AA Series Polaar 2000 polarimeter (Optical Activity Ltd.) using a 1 dm cell and are given in units of $10^{-1}$ deg $cm^2$ $g^{-1}$.

All manipulations of air-sensitive substances were carried out under an atmosphere of dry argon or nitrogen. Light petroleum refers to the fraction of distillation range 40–60 °C. Dioxane and benzene were dried by heating under reflux over calcium hydride and were distilled and stored under argon. TBHN was prepared by the reaction of sodium hyponitrite with *tert*-butyl bromide in diethyl ether, in the presence of zinc chloride, using the method described by Mendenhall.[12] Triphenylsilanethiol, methyl thioglycolate and 2,3,4,6-tetra-*O*-acetyl-1-sulfanyl-β-D-glucopyranose were obtained commercially (Aldrich) and were used as received. 2,3,4,6-Tetra-*O*-acetyl-1-sulfanyl-β-D-mannopyranose **16** and 2,3,4,6-tetra-*O*-pivaloyl-1-sulfanyl-β-D-glucopyranose **17** were prepared as described previously.[9e] The thiol **18** was prepared by the same general procedure starting from 2,3,4,6-tetra-*O*-benzoyl-*α*-D-glucopyranosyl bromide.[15] The enol acetate **3b**,[16] the silyl enol ether **3c**,[17] the methylenelactones **7**,[18] **10a**[9e] and **10b**[9e,19] and the cyclic carbonate **13**[20] were prepared according to published methods, as was triethyl chloromethanetricarboxylate **4i**.[21]

**Admantyl bromoacetate 4d.** Bromoacetyl bromide (6.7 g, 33 mmol) was added dropwise to a stirred solution of admantan-1-ol (5.0 g, 33 mmol) and *N*,*N*-dimethylaniline (4.4 g, 36 mmol) in dry diethyl ether (25 $cm^3$), with cooling in an ice–water bath. After the addition was complete, the mixture was stirred at room temperature for 4 h and the precipitated hydrobromide salt was removed by filtration. The filtrate was diluted with diethyl ether (50 $cm^3$), washed with 5% aqueous HCl (3 × 5 $cm^3$), then with saturated brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel, using light petroleum–diethyl ether (10:1) as eluent, to give the product (8.5 g, 94%) as an oil. Recrystallisation from light petroleum gave **4d** as a solid, mp 35 °C; $\delta_H$ 1.66 (6 H, br s, 3 $CH_2$ of Ad), 2.11 (6 H, br s, 3 $CH_2$ of Ad), 2.18 (3 H, br s, 3 CH of Ad), 3.74 (2 H, s, $CH_2Br$); $\delta_C$ 27.7, 30.8, 36.0, 41.0, 82.9, 165.8; $\nu_{max}$ (mull) 1736, 1273, 1105, 1054, 968 (Found: C, 52.5; H, 6.1. $C_{12}H_{17}BrO_2$ requires C, 52.76; H, 6.27%).

**Di-*tert*-butyl chloromalonate 4h.** A solution of butyllithium in hexane (1.6 mol $dm^{-3}$, 27.0 $cm^3$, 43 mmol) was added dropwise to a stirred solution of di-*tert*-butyl malonate (8.7 g, 40 mmol) in dry tetrahydrofuran (80 $cm^3$) cooled in a solid $CO_2$–ethanol bath. The resulting mixture was stirred at −78 °C for 30 min and then liquid chlorine (*ca.* 1.5 $cm^3$, *ca.* 60 mmol) was allowed to evaporate and the gas was carried, in a slow stream of nitrogen, into the stirred solution. The mixture was allowed to warm to room temperature during 1 h and then stirred for a further 1 h. The solvents were removed by evaporation under reduced pressure and the residue was diluted with diethyl ether (100 $cm^3$), washed with 5% aqueous $NaHCO_3$ (15 $cm^3$) and dried over $MgSO_4$. The ether was removed under reduced pressure and the residue was distilled to give **4h** (4.5 g, 55%) as a clear oil, bp 59–60 °C/0.1 mm Hg; $\delta_H$ 1.49 (18 H, 6 Me), 4.65 (1 H, CHCl); $\delta_C$ 27.7, 44.3, 83.9, 163.5; $\nu_{max}$ (film) 2982, 1754, 1368, 1140, 844 (Found: C, 52.8; H, 7.5. $C_{11}H_{19}ClO_4$ requires C, 52.70; H, 7.64%).

Other materials were commercially available and were used as received, except bromomethyl phenyl sulfone **4f** (Aldrich) which was purified by column chromatography (diethyl ether–light petroleum 2:1 eluent), followed by recrystallisation from light petroleum–diethyl ether.

### Representative procedure for thiol-catalysed reductive alkylation mediated by triphenylsilane

A solution in dry dioxane (4 $cm^3$) containing isopropenyl acetate (**3a**, 0.250 g, 2.50 mmol), triphenylsilane (0.846 g, 3.25 mmol), dimethyl chloromalonate (**4a**, 0.625 g, 3.75 mmol), TBHN (22 mg) and triphenylsilanethiol (37 mg) was stirred and heated at 60 °C for 2 h under an atmosphere of dry argon. The solvent was removed by evaporation under reduced pressure, the residue was dissolved in diethyl ether (10 $cm^3$), and the solution was washed with 5 % aqueous $NaHCO_3$ (2 × 10 $cm^3$), then with saturated brine (10 $cm^3$) and dried ($MgSO_4$). After evaporation of the ether, light petroleum (5 $cm^3$) was added and the slurry was filtered to remove most of the triphenylsilanol, which

was washed on the sinter with a little light petroleum. After removal of the solvent from the filtrate, the residue was purified by column chromatography (light petroleum–diethyl ether 95 : 5 to 5 : 1 gradient elution) to give the adduct **5aa** (0.51 g, 88%) as a clear oil.

Benzene functioned equally well as the solvent and, when DLP was used as initiator, all reductive alkylation reactions were carried out at *ca.* 80 °C under gentle reflux in this solvent. The characteristics of the racemic adducts **5**, **6**, **8**, and **9** are given below.

**Dimethyl (2-acetoxypropyl)malonate 5aa.** Oil; $\delta_H$ 1.24 (3 H, d, *J* 6.2, Me), 2.00 (3 H, s, Ac), 2.35 (2 H, m, $CH_2$), 3.46 (1 H, dd, *J* 8.6 and 6.1, CH), 3.72(7) (3 H, s, $OMe^A$), 3.73(2) (3 H, s, $OMe^B$), 4.89 (1 H, m, OCH); $\delta_C$ 20.1, 21.1, 34.7, 48.4, 52.7(5), 52.7(7), 68.7, 169.3, 169.5, 170.4; $\nu_{max}$ (film) 2956, 2361, 1738, 1438, 1375, 1244, 1158, 1066, 953 (Found: C, 51.8; H, 6.8. $C_{10}H_{16}O_6$ requires C, 51.72; H, 6.94%).

**Methyl 4-acetoxypentanoate 5ab.** Oil; $\delta_H$ 1.21 (3 H, d, *J* 6.3, Me), 1.87 [2 H, m, $CH_2C(O)$], 2.00 (3 H, s, Ac), 2.34 (2 H, m, $CH_2CO$), 3.65 (3 H, s, OMe), 4.89 (1 H, m, OCH); $\delta_C$ 19.8, 21.2, 30.1, 30.8, 51.6, 69.9, 170.6, 173.4; $\nu_{max}$ (film) 2980, 2953, 1738, 1439, 1375, 1245, 1077, 964, 707 (Found: C, 55.4; H, 8.0. $C_8H_{14}O_4$ requires C, 55.16; H, 8.10%).

**Diethyl (2-acetoxypropyl)methylmalonate 5ac.** Oil; $\delta_H$ 1.21–1.28 (9 H, m, 3 Me), 1.40 (3 H, s, Me), 1.95 (3 H, s, Ac), 2.10 (1 H, dd, *J* 15.0 and 3.0, $CH_2^A$), 2.33 (1 H, dd, *J* 15.0 and 10.5, $CH_2^B$), 4.15 (4 H, m, $OCH_2$), 5.03 (1 H, m, OCH); $\delta_C$ 14.0, 19.4, 21.0, 40.7, 52.0, 61.1, 61.4, 67.4, 170.3, 171.8, 172.1); $\nu_{max}$ (film) 2984, 2940, 1736, 1454, 1376, 1296, 1242, 1116, 1020, 951, 862 (Found: C, 57.2; H, 8.2. $C_{13}H_{22}O_6$ requires C, 56.92; H, 8.08%).

**Admantyl 4-acetoxypentanoate 5ad.** Oil; $\delta_H$ 1.21 (3 H, d, *J* 6.3, Me), 1.65 ( 6 H, br s, 3 $CH_2$ of Ad), 1.82 (2 H, m, $CH_2CH_2CH$), 2.01 (3 H, s, Ac), 2.08 (6 H, br s, 3 $CH_2$ of Ad), 2.13 (3 H, br s, 3 CH of Ad), 2.24 (2 H, m, $OCCH_2$), 4.90 (1 H, m, CHOAc); $\delta_C$ 19.9, 21.3, 30.8, 31.0, 31.7, 36.2, 41.3, 70.1, 80.5, 170.6, 172.0; $\nu_{max}$ (film) 2914, 2856, 1735, 1452, 1373, 1243, 1181, 1056, 966, 869 (Found: C, 69.6; H, 9.0. $C_{17}H_{26}O_4$ requires C, 69.36; H, 8.90%).

**1-(4-Acetoxy-1-oxopentyl)admantane 5ae.** Oil; $\delta_H$ 1.21 (3 H, d, *J* 6.3, Me), 1.69–1.90 (17 H, complex Ad and $CH_2$), 2.02 (3 H, s, Ac), 2.47 (2 H, m, $OCCH_2$), 4.87 (1 H, m, CHOAc); $\delta_C$ 20.1, 21.4, 27.9, 29.7, 31.9, 36.5, 38.3, 46.3, 70.5, 170.7, 214.6; $\nu_{max}$ (film) 2908, 2852, 1736, 1698, 1451, 1373, 1244, 1013, 952, 707 (Found: C, 73.5; H, 9.3. $C_{17}H_{26}O_3$ requires C, 73.35; H, 9.41%).

**3-Acetoxybutyl phenyl sulfone 5af.** Oil; $\delta_H$ 1.21 (3 H, d, *J* 6.0, Me), 1.98 (2 H, m, $CH_2$), 2.00 (3 H, s, Ac), 3.13 (2 H, m, $CH_2SO_2$), 4.92 (1 H, m, C*H*OAc), 7.59 (2 H, m, Ph), 7.91 (1 H, m, Ph), 7.93 (2 H, m, Ph); $\delta_C$ 19.9, 21.2, 28.8, 52.8, 68.8, 128.1, 129.4, 133.9, 138.9, 170.2; $\nu_{max}$ (film) 1736, 1447, 1374, 1307, 1243, 1148, 1088 (Found: C, 56.2; H, 6.5; S, 12.3. $C_{12}H_{16}O_4S$ requires C, 56.23; H, 6.29; S, 12.51%).

**Dimethyl 2-acetoxy-3,3-dimethylbutylmalonate 5ba.** Oil; $\delta_H$ 0.90 ( 9 H, s, $Bu^t$), 1.98 (1 H, ddd, *J* 14.4, 11.1 and 4.8, $CH^AH^B$), 2.05 (3 H, s, Ac), 2.28 (1 H, ddd, *J* 14.4, 9.9 and 2.0, $CH^AH^B$), 3.33 [1 H, dd, *J* 9.9 and 4.8, CHC(O)], 3.72 (3 H, s, $OMe^A$), 3.74 (3 H, s, $OMe^B$), 4.73 (1 H, dd, *J* 11.1 and 2.0, AcOC*H*); $\delta_C$ 20.8, 25.7, 29.2, 34.7, 48.7, 52.7, 78.2, 169.8, 171.0; $\nu_{max}$ (film) 2961, 1738, 1437, 1372, 1243, 1155, 1022, 958, 892 (Found: C, 56.9; H, 8.0. $C_{13}H_{22}O_6$ requires C, 56.92; H, 8.08%).

**Methyl 4-acetoxy-5,5-dimethylhexanoate 5bb.** Oil; $\delta_H$ 0.91 (9 H, s, $Bu^t$), 1.75 (1 H, m, $CH^AH^B$), 1.95 (1 H, m, $CH^AH^B$), 2.06 (3 H, s, Ac), 2.28 (2 H, t, *J* 7.9, $CH_2CO$), 3.68 (3 H, s, OMe), 4.72 (1 H, dd, *J* 11.0 and 2.2, OCH); $\delta_C$ 20.9, 24.9, 25.9, 31.0, 34.6, 51.6, 79.9, 171.1, 173.7; $\nu_{max}$ (film) 2966, 1739, 1435, 1371, 1242, 1167, 1021, 960, 878, 707 (Found: C, 61.1; H, 9.2. $C_{11}H_{20}O_4$ requires C, 61.09; H, 9.32%).

**Dimethyl (2-*tert*-butyldimethylsiloxypropyl)malonate 5ca.** Oil; $\delta_H$ 0.01 (3 H, s, SiMe), 0.04 (3 H, s, SiMe), 0.87 (9 H, s, $Bu^t$), 1.15 (3 H, d, *J* 6.1, *Me*CH), 1.93 (1 H, ddd, *J* 13.8, 8.9 and 4.8, $CH^AH^B$), 2.07 (1 H, ddd, *J* 13.8, 9.6 and 3.7, $CH^AH^B$), 3.62 (1 H, dd, *J* 9.6 and 4.8, CH), 3.73 (3 H, s, $OMe^A$), 3.74 (3 H, s, $OMe^B$), 3.83 (1 H, m, OCH); $\delta_C$ −5.1, −4.3, 19.0, 23.9, 25.8, 38.3, 48.2, 52.4, 52.6, 66.0, 170.0, 170.3; $\nu_{max}$ (film) 2956, 2858, 1739, 1438, 1342, 1253, 1152, 1001, 837, 777 (Found: C, 56.6; H, 7.4. $C_{13}H_{22}O_6Si$ requires C, 56.35; H, 7.43%).

**Dimethyl 3-oxaheptylmalonate 5da.** Oil; $\delta_H$ 0.89 (3 H, t, *J* 7.3, Me), 1.43 (2 H, m, $CH_2$), 1.50 (2 H, m, $CH_2$), 2.16 (2 H, m, $CH_2$), 3.36 (2 H, t, *J* 6.5, $CH_2O$), 3.43 (2 H, t, *J* 6.0, $CH_2O$), 3.56 (1 H, t, *J* 7.3, CH), 3.72 (6 H, s, 2 OMe); $\delta_C$ 13.9, 19.2, 29.0, 31.7, 48.8, 52.5, 53.9, 67.7, 70.7, 169.8; $\nu_{max}$ (film) 2959, 2870, 1736, 1437, 1160, 1116, 1017, 707 (Found: C, 56.7; H, 8.7. $C_{11}H_{20}O_5$ requires C, 56.88; H, 8.68%).

**Dimethyl 2-methylheptylmalonate 5ea.** Oil; $\delta_H$ 0.87 (3 H, t, *J* 7.0, Me), 0.88 (3 H, d, *J* 6.5, *Me*CH), 1.0–1.5 (9 H, 4 $CH_2$ and 1 CH), 1.67 (1 H, ddd, *J* 14.5, 7.9 and 6.6, CH $CH^AH^B$), 1.96 (1 H, ddd, *J* 14.5, 8.6 and 5.5, CH $CH^AH^B$), 3.47 [1 H, dd, *J* 8.6 and 6.6, $CH(CO_2Me)_2$], 3.72(5) (3 H, s, OMe), 3.72(9) (3 H, s, OMe); $\delta_C$ 14.1, 19.2, 22.6, 26.3, 30.8, 32.0. 35.9, 36.6, 49.8, 52.4 52.5, 170.1, 170.2; $\nu_{max}$ (film) 2956, 2857, 1739, 1437, 1331, 1247, 1200, 1154, 1015, 976 (Found: C, 63.8; H, 10.0. $C_{13}H_{24}O_4$ requires C, 63.91; H, 9.90%).

**Dimethyl 3-acetoxy-2-methylpropylmalonate 5fa.** Oil; $\delta_H$ 0.95 (3 H, d, *J* 6.4, Me), 1.79 (2 H, m, $CH_2$), 2.04 (1 H, m, CH), 2.05 (3 H, s, Ac), 3.50 [1 H, dd, *J* 8.4 and 6.8, CHC(O)], 3.73 ( 6H, s, 2 MeO), 3.91 (2 H, ddd, *J* 13.7, 11.0 and 5.5, $OCH_2$); $\delta_C$ 16.5, 20.8, 30.6, 32.6, 49.4, 52.6 (2 C), 68.6, 169.6, 169.8, 171.0; $\nu_{max}$ (film) 2959, 1738, 1439, 1369, 1242, 1157, 1038, 911 (Found: C, 53.7; H, 7.4. $C_{11}H_{18}O_6$ requires C, 53.65; H, 7.37%).

**(2-Acetoxypropyl)triphenylsilane 6.** Mp 61–62 °C; $\delta_H$ 1.21 (3 H, d, *J* 6.1, *Me*CH), 1.68 (3 H, s, Ac), 1.73 (1 H, dd, *J* 14.9 and 6.4, $SiCH^A$), 1.98 (1 H, dd, *J* 14.9 and 8.0, $SiCH^B$), 5.16 (1 H, m, C*H*OAc), 7.31–7.62 (15 H, m, 3 Ph); $\delta_C$ 20.9, 21.9, 23.5, 69.2, 127.9, 129.5, 134.6, 135.6, 170.3; $\nu_{max}$ (mull) 1720, 1247, 1109, 948 (Found: C, 76.6; H, 6.6. $C_{23}H_{24}O_2Si$ requires C, 76.62; H, 6.71%).

**5-[2,2-Bis(methoxycarbonyl)ethyl]tetrahydrofuran-2-one 8.** Oil; yield 72%; $\delta_H$ 1.90 (1 H, m, $CHCH^AH^BCH$), 2.15 (1 H, ddd, *J* 15.1, 9.7 and 5.3, $CHCH^AH^BCH$), 2.23 (2 H, m, 4-H), 2.53 (2 H, m, 3-H), 3.66 [1 H, dd, *J* 9.4 and 5.3, CHC(O)], 3.73 (3 H, s, $OMe^A$), 3.75 (3 H, s, $OMe^B$), 4.52 (1 H, m, OCH); $\delta_C$ 27.9, 28.4, 34.7, 48.2, 52.8, 77.8, 169.1, 173.3; $\nu_{max}$ (film) 2957, 1735, 1740, 1438, 1180, 1043, 926, 652 (Found: C, 52.3; H, 6.2. $C_{10}H_{14}O_6$ requires C, 52.17; H, 6.13%).

**5-Triphenylsilylmethyltetrahydrofuran-2-one 9.** Mp 96–98 °C; $\delta_H$ 1.65 (1 H, m, 4-$H^A$), 1.80 (1 H, dd, *J* 14.4 and 9.5, $SiCH^A$), 1.97 (1 H, m, 3-$H^A$), 2.23 (1 H, dd, *J* 14.4 and 5.0, $SiCH^B$), 2.40 (2 H, m, 4-$H^B$ and 3-$H^B$ ), 4.72 (1 H, m, OCH), 7.3–7.6 (15 H, m, 3 Ph); $\delta_C$ 21.5, 29.5, 30.8, 79.5, 128.1, 129.9, 133.7, 135.6, 176.8; $\nu_{max}$ (mull) 1736, 1105, 968, 725 (Found: C, 77.2; H, 6.3. $C_{23}H_{22}O_2Si$ requires C, 77.06; H, 6.19%).

### Enantioselective reactions

Enantioselective reductive alkylation reactions were carried out in refluxing benzene, using the general method described above, with DLP as the initiator (10 mol% based on alkene) and one of the homochiral thiols **15**–**18** as catalyst (10 mol%). The optical

rotations and the corresponding ees of the products are given in Table 2; the characteristics of the racemic adducts, obtained using TPST (10 mol%) as catalyst, are given below.

**5,5-Dimethyl-6-[2,2-bis(methoxycarbonyl)ethyl]tetrahydropyran-2-one 11aa.** Oil; yield 62%; $\delta_H$ 0.95 (3 H, s, $CMe^A$), 1.01 (3 H, s, $CMe^B$), 1.60 (2H, m, 4-$CH_2$), 1.98 (1 H, m, OCHC$H^A$), 2.25 (1 H, m, OCHC$H^B$), 2.52 (2 H, m, 3-H), 3.73 (6 H, s, 2 OMe), 3.74 [1 H, dd, *J* 10.4 and 4.0, CHC(O)], 4.00 (1H, dd, *J* 11.2, 1.6, 6-H); $\delta_C$ 19.3, 26.2, 27.3, 29.6, 31.9, 34.3, 47.8, 52.7, 52.8, 84.6, 169.4, 169.7, 170.7; $\nu_{max}$ (film) 1779, 1737, 1438, 1350, 1260, 1162 (Found: C, 57.0; H, 7.5. $C_{13}H_{20}O_6$ requires C, 57.33; H, 7.40%). The ee was determined by $^1$H NMR analysis.

**5,5-Dimethyl-6-[2-(methoxycarbonyl)ethyl]tetrahydropyran-2-one 11ab.** Oil; yield 87%; $\delta_H$ 0.93 (3 H, s, $Me^A$), 1.00 (3 H, s, $Me^B$), 1.60 (1 H, m, OCHC$H^AH^B$), 1.69 (2 H, m, 4-H), 1.92 (1 H, m, OCHCH$^A$C$H^B$), 2.40–2.70 [4 H, m, 3-H and $CH_2C(O)$], 3.65 (3 H, s, OMe), 3.97 (1 H, dd, *J* 11.2 and 1.6, 6-H); $\delta_C$ 19.4, 25.2, 26.4, 27.4, 30.0, 32.0, 34.4, 51.7, 86.4, 171.3, 173.7; $\nu_{max}$ (film) 1737, 1440, 1352, 1168, 1056 (Found: C, 61.6; H, 8.4. $C_{11}H_{18}O_4$ requires C, 61.66; H, 8.47%). The ee was determined by $^1$H NMR analysis.

**6-(2-Phenylsulfonylethyl)-5,5-dimethyltetrahydropyran-2-one 11af.** Mp 127–128 °C; yield 72%; $\delta_H$ 0.93 (3 H, s, Me), 1.01 (3 H, s, Me), 1.61 (1 H, m, OCHC$H^AH^B$), 1.70 (1 H, m, OCHCH$^A$C$H^B$), 1.91 (1 H, m, 4-H$^A$), 2.15 (1 H, m, 3-H$^A$), 2.51 ( 2 H, 4-H$^B$ and 3-H$^B$), 3.14 (1 H, ddd, *J* 14.0, 9.8 and 5.6, $SO_2CH^AH^B$), 3.41 (1 H, ddd, *J* 14.0, 9.8 and 5.2, $SO_2CH^AH^B$), 4.07 (1 H, dd, *J* 11.2 and 2.0, 6-H), 7.58 (2 H, m, aromatic), 7.67 (1 H, m, aromatic), 7.91 (2 H, m, aromatic); $\delta_C$ 19.0, 23.0, 26.2, 27.2, 32.0, 34.3, 52.9, 85.4, 127.8, 129.3, 133.8, 139.1, 170.7; $\nu_{max}$ (mull) 1732, 1211 1050, 753 (Found: C, 60.8; H, 6.7. $C_{15}H_{20}O_4S$ requires C, 60.79; H, 6.80%). The ee was determined by HPLC (eluent 20% isopropyl alcohol; $t_R$ 6.7 and 8.9 min).

**6-[2,2,2-Tris(ethoxycarbonyl)ethyl]-5,5-dimethyltetrahydropyran-2-one 11ai.** Oil; which partially solidified on standing at room temperature, yield 57%; $\delta_H$ 0.96 (3H, s, $CMe^A$), 1.06 (3H, s, $CMe^B$), 1.26 (9 H, t, *J* 7.2, $OCH_2CH_3$), 1.60 (1H, ddd, *J* 13.6, 7.2 and 5.6, 4-H$^A$), 1.70 (1 H, m, 4-H$^B$), 2.15 (1 H, dd, *J* 14.8 and 1.6, OCHC$H^A$), 2.28 (1 H, dd, *J* 14.8 and 10.0, OCHC$H^B$), 2.51 (2 H, m, 3-H), 4.26 (6H, q, *J* 7.2, $OCH_2CH_3$), 4.55 (1H, dd, *J* 10.0 and 1.6, 6-H); $\delta_C$ 13.9, 19.7, 26.3, 27.3, 32.3, 34.2(8), 34.3(4), 62.4, 63.0, 82.5, 166.7, 170.4; $\nu_{max}$ (film) 1740, 1469, 1368, 1221, 1075 (Found: C, 58.2; H, 7.6, $C_{18}H_{28}O_8$ requires C, 58.05; H, 7.58%). The ee was determined by $^1$H NMR analysis. Careful repeated recrystallisation from hexane–dichloromethane gave enantiopure (*S*)-(−)-**11ai**, $[a]_D^{22} = -37.5$ (*c* 1.44, $CHCl_3$), mp 63–64 °C.

**6-[(2,2-Bis(methoxycarbonyl)ethyl]-5,5-diphenyltetrahydropyran-2-one 11ba.** Mp 130–131 °C; yield 92%; $\delta_H$ 1.68 (1 H, ddd, *J* 18.2, 7.9 and 6.7, OCHC$H^AH^B$), 2.10 (1 H, ddd, *J* 19.1, 11.8 and 7.0, 4-H$^A$), 2.22 (1 H, ddd, *J* 18.2, 11.5 and 6.6, OCHCH$^A$C$H^B$), 2.46 (1 H, m, 4-H$^B$), 2.59 (1 H, ddd, *J* 18.8, 6.1,and 1.8, 3-H$^A$), 2.87 (1 H, m, 3-H$^B$), 3.68 (3 H, s, OMe), 3.71 (1 H, dd, *J* 7.5 and 6.7, CH), 3.73 (3 H, s, OMe), 5.30 ( 1 H, ddd, *J* 9.3, 2.2 and 2.0, 6-H), 7.10–7.40 (10 H, m, Ph); $\delta_C$ 26.7, 27.3, 31.8, 47.6, 48.3, 52.7, 52.9, 81.9, 126.9, 127.1, 127.2, 127.3, 128.8 (2 C), 143.4, 143.6, 169.1, 169.7; $\nu_{max}$ (mull) 1746, 1597, 1268, 1180, 1057, 933, 760 (Found: C, 69.5; H, 6.0. $C_{23}H_{24}O_6$ requires C, 69.68; H, 6.10%). The ee was determined by $^1$H NMR analysis.

**6-[2-(Methoxycarbonyl)ethyl]-5,5-diphenyltetrahydropyran-2-one 11bb.** Mp 143–144 °C; yield 75%; $\delta_H$ 1.43 (1 H, dddd, *J* 14.6, 12.1, 7.6 and 2.6, OCHC$H^AH^B$), 1.89 (1 H, dddd, *J* 14.6, 11.3, 6.7 and 4.6, OCHCH$^A$C$H^B$), 2.12 (1 H, ddd, *J* 18.7, 11.4 and 6.7, 4-H$^A$), 2.44 (2 H, m, 3-H$^A$ and $CH^ACO_2$), 2.56 (2 H, m, 4-H$^B$ and $CH^BCO_2$), 2.85 (1 H, m, 3-H$^B$), 3.63 ( 3 H, s, OMe), 5.21 (1 H, ddd, *J* 11.3, 2.3 and 2.0, 6-H), 7.0–7.4 (10 H, m, 2 Ph); $\delta_C$ 26.9, 27.4, 27.6, 30.3, 47.8, 51.7, 83.4, 126.8, 127.0, 127.1, 127.4, 128.7, 128.8, 143.8, 143.9, 169.6, 173.4; $\nu_{max}$ (mull) 1720, 1560, 1287, 1053, 950, 755 (Found: C, 74.4; H, 6.4. $C_{21}H_{22}O_4$ requires C, 74.54; H, 6.55%). The ee was determined by $^1$H NMR analysis.

**6-[2-(1-Adamantyloxycarbonyl)ethyl]-5,5-diphenyltetrahydropyran-2-one 11bd.** Mp 163–164 °C; yield 52%; $\delta_H$ 1.38 ( 1 H, m, OCHC$H^AH^B$), 1.81 ( 1 H, m, OCHCH$^A$C$H^B$), 2.04 (6 H, br d, *J* 2.8, 3 $CH_2$ of Ad), 2.10 (1 H, m, 4-H$^A$), 2.13 (3 H, br s, 3 CH of Ad), 2.32 ( 1 H, m, 4-H$^B$), 2.48 [2 H, m, $CH_2C(O)$], 2.59 ( 1 H, ddd, *J* 18.5, 6.1 and 1.8, 3-H$^A$), 2.89 (1 H, m, 3-H$^B$), 5.20 (1 H, m, 6-H), 7.10–7.40 (10 H, m, 2 Ph); $\delta_C$ 26.9, 27.5, 27.6, 30.8, 31.6, 36.1, 41.3, 47.9, 80.6, 83.4, 126.8, 126.9, 127.2, 127.5, 128.7, 128.8, 143.9, 144.0, 167.7, 171.9; $\nu_{max}$ (mull) 1699, 1652, 1176, 1057, 701 (Found: C, 78.4; H, 7.5. $C_{30}H_{34}O_4$ requires C, 78.57; H, 7.47%). The ee was determined by HPLC (eluent 15% isopropyl alcohol; $t_R$ 10.4 and 13.0 min).

**6-(1-Adamantyl-1-oxo-propyl)-5,5-diphenyltetrahydropyran-2-one 11be.** Mp 145–147 °C; yield 57%; $\delta_H$ 1.38 (1 H, m, OCHC$H^AH^B$), 1.80 (1 H, m, OCHCH$^A$C$H^B$), 1.60–2.02 (15 H, m, Ad), 2.11 (1H, ddd, *J* 19.1, 11.8 and 7.0, 4-H$^A$), 2.45 (1 H, m, 4-H$^B$ ), 2.57 [2 H, m, $CH_2C(O)$], 2.73 (1 H, ddd, *J* 19.1, 7.8 and 5.4, 3-H$^A$), 2.89 (1 H, 3-H$^B$), 5.16 (1 H, m, 6-H), 7.10–7.40 (10 H, m, 2 Ph); $\delta_C$ 26.2, 26.9, 27.5, 27.9, 32.3, 36.5, 38.2, 46.2, 47.9, 83.5, 126.8, 126.9, 127.2, 127.5, 128.7, 128.8, 144.0, 144.1, 170.0, 214.9; $\nu_{max}$ (mull) 1736, 1055, 701 (Found: C, 81.3; H, 7.7. $C_{30}H_{34}O_3$ requires C, 81.41; H, 7.74%). The ee was determined by HPLC (eluent 15% isopropyl alcohol; $t_R$ 11.5 and 25.4 min).

**6-[2-(Phenylsulfonyl)ethyl]-5,5-diphenyltetrahydropyran-2-one 11bf.** Mp 192–194 °C; yield 70%; $\delta_H$ 1.62 ( 1 H, m, OCHC$H^AH^B$), 2.00 (1 H, m, OCHCH$^A$C$H^B$), 2.13 ( 1 H, ddd, *J* 18.7, 11.6 and 7.2, 4-H$^A$), 2.46 (1 H, m, 4-H$^B$), 2.55 (1 H, ddd, *J* 18.7, 5.6 and 2.5, 3-H$^A$), 2.75 (1 H, m, 3-H$^B$), 3.15 (1 H, ddd, *J* 14.1, 9.1 and 6.3, $SO_2CH^A$), 3.32 (1 H, ddd, *J* 14.1, 9.1 and 5.3, $SO_2CH^B$), 5.24 (1 H, ddd, *J* 11.2, 2.0 and 1.9, 6-H), 7.0–7.7 (15 H, m, 3 Ph); $\delta_C$ 25.8, 27.0, 27.4, 47.8, 52.7, 82.4, 127.0, 127.2, 127.3 (2C), 127.8, 128.8(5), 128.9(1), 129.2, 133.7, 138.7, 143.1, 143.4, 169.1; $\nu_{max}$ (mull) 1739, 1053, 930, 745, 702 (Found: C, 71.2; H, 5.7. $C_{25}H_{24}O_4S$ requires C, 71.41; H, 5.75%). The ee was determined by HPLC (eluent 20% isopropyl alcohol; $t_R$ 11.3 and 14.4 min).

**6-(4,4-Dimethyl-3-oxopentyl)-5,5-diphenyltetrahydropyran-2-one 11bg.** Mp 112 °C; yield 78%; $\delta_H$ 1.11 (9 H, s, Bu$^t$), 1.39 (1 H, dddd, *J* 14.9, 12.4, 7.6 and 2.5, OCHC$H^AH^B$), 1.80 (1 H, m, OCHC$H^BH^A$), 2.11 (1 H, ddd, *J* 19.1, 12.1 and 7.3, 4-H$^A$), 2.46 (1 H, m, 4-H$^B$), 2.60 [2 H, m, $CH_2C(O)$], 2.77 ( 1 H, ddd, *J* 18.5, 7.9 and 5.3, 3-H$^A$), 2.88 (1 H, m, 3-H$^B$), 5.17 ( 1 H, m, 6-H), 7.10–7.40 (10 H, m, 2 Ph); $\delta_C$ 26.5, 26.9, 27.5(1), 27.5(3), 32.7, 44.0, 47.9, 83.5, 126.8, 127.0, 127.2, 127.5, 128.7, 128.8, 143.9, 144.0, 169.9, 215.2; $\nu_{max}$ (mull) 1735, 1699, 1651, 1182, 1056, 761 (Found: C, 78.8; H, 7.8. $C_{24}H_{28}O_3$ requires C, 79.09; H, 7.74%). The ee was determined by $^1$H NMR analysis. Careful repeated recrystallisation from hexane–dichloromethane gave enantiopure (*S*)-(−)-**11bg**, $[a]_D^{20} = -266.0$ (*c* 1.35, $CHCl_3$), mp 170–172 °C.

**6-[2,2-Bis(*tert*-butoxycarbonyl)ethyl]-5,5-diphenyltetrahydropyran-2-one 11bh.** Mp 84–85 °C; yield 62%; $\delta_H$ 1.34 (9 H, s, Bu$^t$), 1.42 (9 H, s, Bu$^t$), 1.61 (1 H, ddd, *J* 14.6, 9.5 and 2.4, OCHC$H^AH^B$), 2.11 (2 H, m, 4-H$^A$ and OCHCH$^A$C$H^B$), 2.47 (1 H, m, 4-H$^B$), 2.60 (1H, m, 3-H$^A$), 2.87 (1 H, m, 3-H$^B$), 3.53 [1 H, dd, *J* 9.5 and 4.8, CHC(O)], 5.26 (1 H, m, 6-H), 7.10–7.50 (10 H, 2 Ph); $\delta_C$ 26.9, 27.4, 27.8, 27.9, 31.4, 47.8, 50.2, 81.8, 83.5, 126.8, 127.0, 127.2, 127.4, 128.8(0), 128.8(2), 143.6, 143.8, 168.2, 168.4, 169.4; $\nu_{max}$ (mull) 1730, 1699, 1651, 1272, 758 (Found:

C, 72.4; H, 7.3. $C_{29}H_{36}O_6$ requires C, 72.48; H, 7.55%). The ee was determined by $^1$H NMR analysis.

**6-[(2-*tert*-Butoxycarbonyl)ethyl]-5,5-diphenyltetrahydropyran-2-one 11bj.** Mp 110–112 °C; yield 83%; $\delta_H$ 1.34 (9 H, s, Bu$^t$), 1.40 (1 H, m, OCHC$H^A$H$^B$), 1.82 (1 H, m, OCHCH$^A H^B$), 2.12 [1 H, ddd, *J* 18.9, 11.6 and 6.8, CH$^A$C(O)], 2.32 [1 H, m, CH$^B$C(O)], 2.40–2.52 ( 2 H, m, 3-H$^A$ and 4-H$^A$), 2.59 (1 H, ddd, *J* 18.7, 6.1 and 2.0, 4-H$^B$), 2.86 (1 H, m, 3-H$^B$), 5.19 (1 H, ddd, *J* 11.2, 2.3 and 2.0, 6-H) 7.10–7.35 (10 H, m, 2 Ph); $\delta_C$ 26.9, 27.4, 27.6, 28.1, 31.6, 47.9, 80.5, 83.4, 126.8, 127.0, 127.2, 127.5, 128.8 (2C), 144.0 (2C), 169.8, 172.2; $\nu_{max}$ (mull) 1721, 1278, 1060, 954, 755 (Found: C, 75.5; H, 7.3. $C_{24}H_{28}O_4$ requires C, 75.76; H, 7.42%). The ee was determined by $^1$H NMR analysis.

**4,4-Dimethyl-5-[2,2-bis(methoxycarbonyl)ethyl]-1,3-dioxolan-2-one 14a.** Oil; yield 71%; $\delta_H$ 1.40 (3 H, s, Me), 1.50 (3 H, s, Me), 2.15 (1 H, ddd, *J* 17.3, 11.0 and 4.8, C$H^A$H$^B$), 2.20 (1 H, ddd, *J* 17.3, 9.8 and 2.6, CH$^A H^B$), 3.65 [1 H, dd, *J* 9.8 and 4.8, CHC(O)], 3.76 (3 H, s, OMe), 3.78 (3 H, s, OMe), 4.31 (1 H, dd, *J* 11.0 and 2.6, 5-H); $\delta_C$ 21.1, 26.0, 28.7, 47.8, 52.9(6), 53.0(2), 82.3, 83.8, 153.3, 168.7, 168.8; $\nu_{max}$ (film) 2957, 1794, 1732, 1437, 1346, 1047, 776, 763 (Found: C, 48.5; H, 6.5. $C_{10}H_{16}O_7$ requires C, 48.39; H, 6.50%). The ee was determined by HPLC (eluent 15% isopropyl alcohol; $t_R$ 5.4 and 7.5 min with detection at 224 nm).

**4,4-Dimethyl-5-(2-phenylsulfonylethyl)-1,3-dioxolan-2-one 14b.** Oil; yield 55%; $\delta_H$ 1.32 (3 H, s, Me$^A$), 1.44 (3 H, s, Me$^B$), 1.99–2.07 (2 H, m, $SO_2CH_2$), 3.11–3.20 (1 H, m, $CH_2^A$), 3.22–3.31 (1 H, m, $CH_2^B$), 4.35 (1 H, dd, *J* 2.8 and 10.8, OCH), 7.53–7.87 (5 H, m, Ph); $\delta_C$ 21.2, 23.0, 26.2, 52.6, 82.9, 84.0, 127.9, 129.6, 134.3, 138.7, 153.3; $\nu_{max}$ (film) 1790, 1448, 1308, 1279, 1147 (Found: C, 55.2; H, 5.6; S, 11.3. $C_{13}H_{16}O_5S$ requires C, 54.92; H, 5.67; S, 11.28%).

### X-Ray crystallography

All measurements were made on a Stoe-Siemens AED 2 diffractometer with Cu-Kα radiation ($\lambda = 1.54184$ Å). For (*S*)-**11ai**, a Bede Scientific Microsource X-ray tube was employed using an 8 μm filter to remove Cu-Kβ radiation. For (*S*)-**11bg**, the source was a conventional sealed X-ray tube and the radiation was monochromated by a graphite crystal. All machine control calculations were performed with standard Stoe DIF4 software. Intensities were measured with $\omega/\theta$ scans and on-line profile fitting.[22] Data were obtained at low temperature using a Cryostream cooler[23] and were corrected for Lorentz and polarisation effects, crystal decay, and (by $\psi$-scans) for absorption. The structures were solved by direct methods and refined by full-matrix-least-squares on $F^2$.[24] CCDC reference number 207/343. See http://www.rsc.org/suppdata/p1/1999/2061 for crystallographic files in .cif format.

**Crystal data for (*S*)-(−)-6-[2,2,2-tris(ethoxycarbonyl)ethyl]-5,5-dimethyltetrahydropyran-2-one 11ai.** $C_{18}H_{28}O_8$, $M = 372.40$, monoclinic, $a = 10.0392(8)$, $b = 7.6254(6)$, $c = 13.2278(11)$ Å, $\beta = 107.559(7)°$, $V = 965.44(13)$ Å$^3$ [from $2\theta$ values of 42 reflections measured at $\pm\omega$ ($43° < 2\theta < 50°$)], space group $P2_1$, $Z = 2$, $\mu$(Cu-Kα) = 0.843 mm$^{-1}$, transmission range 0.891 to 0.708, $T = 160$ K, 3630 reflections measured to $2\theta_{max} = 135°$, 2956 unique ($R_{int} = 0.0267$). Final $wR = 0.1101$ for all data, conventional $R = 0.0409$ [for 2898 reflections with $F^2 > 2\sigma(F^2)$]. The absolute configuration was determined with a Flack parameter $x = 0.1(2)$. The final electron density map was featureless.

**Crystal data for (*S*)-(−)-6-(4,4-dimethyl-3-oxopentyl)-5,5-diphenyltetrahydropyran-2-one 11bg.** $C_{24}H_{28}O_3$, $M = 364.46$, monoclinic, $a = 9.8331(10)$, $b = 10.3392(10)$, $c = 10.5216(12)$ Å, $\beta = 99.957(12)°$, $V = 1053.58(19)$ Å$^3$ [from $2\theta$ values of 43 reflections measured at $\pm\omega$ ($45° < 2\theta < 50°$)], space group $P2_1$, $Z = 2$, $\mu$(Cu-Kα) = 0.586 mm$^{-1}$, transmission range 0.664 to 0.525, $T = 200$ K (the structure undergoes a phase transition at around 175 K as the temperature is lowered giving a unit cell with three times the volume and three molecules in the asymmetric unit), 3660 reflections measured to $2\theta_{max} = 135°$, 3467 unique ($R_{int} = 0.0436$). Final $wR = 0.1269$ for all data, conventional $R = 0.0450$ [for 3435 reflections with $F^2 > 2\sigma(F^2)$]. The absolute configuration was determined with a Flack parameter $x = 0.1(3)$. The final electron density map was featureless.

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