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The unprecedented reaction of dimethylsulfonium methylide with Michael acceptors: synthesis of 1-substituted vinyl silanes and styrenes†

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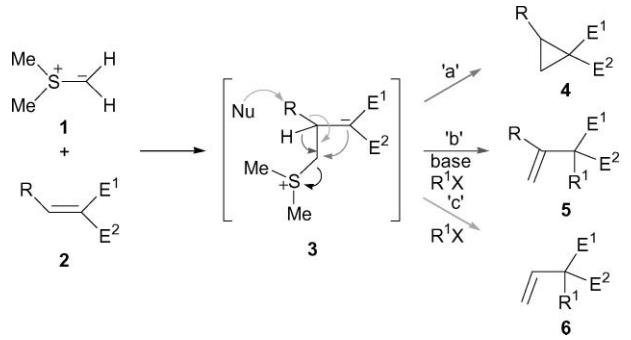
Rather than the usual cyclopropanation, conditions for an unprecedented elimination reaction from the adduct of dimethylsulfonium methylide and various Michael acceptors have been established leading to functionalized 1-substituted alkenes. In silyl substituted substrates (**2a** and **2h**), where a facile Peterson-type olefination is possible from the adduct; elimination took place instead to give functionalized 1-substituted vinyl silanes. Aryl substituted Michael acceptors (**2b–e**, **2g** and **2i–k**) also underwent a similar kind of olefination to give 1-substituted styrene derivatives with moderate yields along with a side product, which arose by nucleophilic demethylation from the adduct of dimethylsulfonium methylide and arylidene malonates. Hammett studies revealed that selectivity for olefination *vs.* demethylation increases as the aryl substituent becomes more electron deficient. Alkylidene malonates (**2f** and **2l**) with a β-alkyl substituent did not favour the olefination process. Sequential addition of Michael acceptors and alkyl halides to a mixture of dimethylsulfonium methylide and sodium dimsylate provided olefination followed by alkylation on the active methine group. A mechanistic pathway has been formulated from the studies of a few sulfonium methylides.

Introduction

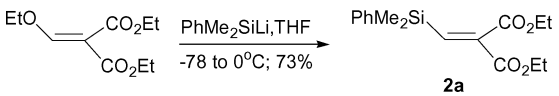
The Corey–Chaykovsky reagent, dimethylsulfonium methylide **1**, generated from a trimethylsulfonium salt and a base is known to react with an aldehyde or a ketone to give an epoxide by an overall methylene insertion.[1] Excess reagent could lead to the formation of allylic alcohol by further addition of the ylide on the epoxide.[2] In line with the carbonyl compounds, imines give aziridines with **1**.[1] The ylide can be used for the conversion of halides and mesylates to one-carbon homologated terminal alkenes.[3] It has been commonly used to add on Michael acceptors in a 1,4-fashion to provide cyclopropanes.[1] Thus, the reaction of ylide **1** with the Michael acceptor **2** gives a betaine intermediate **3** which in principle can undergo various reactions (Scheme 1), the driving force in all cases being the elimination of Me_2S. The most well known amongst these is the formation of cyclopropane **4** (path 'a', Scheme 1). The other possible mode of reaction which could be envisioned from intermediate **3** is the loss of a proton and Me_2S in the presence of excess base resulting in the formation of an olefin **5** (path 'b'). An additional possibility, Peterson-type olefination is plausible in the case of substrates with the R group being a silyl substituent leading to olefin **6** (path 'c'). The formation of cyclopropane **4** has been well studied while that of olefin **5** or **6** has not been observed. This paper details the development of specific reaction conditions and selection of the substituents (R, E_1 and E_2) on **2** for the formation of **5**. In addition, a one-pot sequential olefination–alkylation protocol was devised by quenching the reaction with various alkyl halides leading to functionalised 1-substituted olefins. A mechanistic pathway has also been formulated from studies of a few sulfonium methylides. A communication[4] on a part of this work has already been published.



Scheme 1

Results and discussion

Recently, we have developed a method for the preparation of the 2-silyl alkylidene malonate **2a** by a high yielding reaction of $PhMe_2SiLi$ with diethyl ethoxymethylenemalonate (Scheme 2) and used it as a Michael acceptor in the preparation of a functionalised β-silyl ketone.[5] When **2a** was reacted with **1**, generated from Me_3SI[1] and sodium dimsylate (1 equiv) in DMSO–THF (70 : 30) at 0 °C, we obtained the anticipated product, cyclopropane **4a** (Table 1; entry 1) in moderate yield. Remarkably, when the amount of base was increased (1.5 equiv), the formation of vinyl silane **5a** was also found in addition to cyclopropane **4a** (entry 2). The formation of **5a** was highly dependent upon the number of equivalents of base present as shown in Table 1. The solvent composition also has a significant effect in product selectivity (Table 1; entries 2, 4–6) besides improving the combined yield (entries 3 and 8). The best condition for the olefination was to use a combination of DMSO–THF (30 : 70) and 2.5 equivalents of sodium dimsylate in addition to 1.2 equivalents of Me_3SI. Under these conditions (Table 1; entry 8), **5a** was isolated in 66% yield. It was also gratifying to note that **5a** was formed exclusively from the adduct **3** (Scheme 1; R = $PhMe_2Si$, E_1 = E_2 = CO_2Et) where



Scheme 2

† Dedicated to Professor Ian Fleming F. R. S. of Cambridge University on his 70th birthday.

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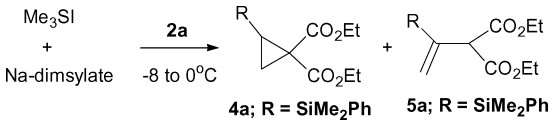
Table 1 Effect of solvent and base on selectivity (cyclopropanation/olefination)

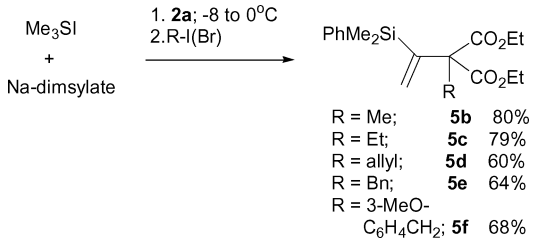


4a; R = $SiMe_2Ph$ **5a; R = $SiMe_2Ph$**

Entry	DMSO–THF	Equiv base[a]	**4a**–**5a**[b]	Yield (%)[c]
1	70 : 30	1.0	100 : 0	55
2	70 : 30	1.5	98 : 2	40
3	70 : 30	2.5	0 : 100	27
4	60 : 40	1.5	96 : 4	51
5	40 : 60	1.5	87 : 13	55
6	30 : 70	1.5	76 : 24	60
7	30 : 70	1.0	100 : 0	36
8	30 : 70	2.5	0 : 100	66

[a] Equivalent with respect to Me_3SI. [b] Ratio determined by GC. [c] Combined isolated yield of **4a** and **5a**.

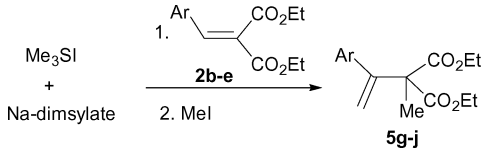
the elimination of a proton and dimethylsulfide was favored over the loss of a silyl group in a Peterson-type elimination. In addition, a one-pot olefination–alkylation protocol was devised using 1.2 equivalents of Me_3SI and 2.5 equivalents of sodium dimsylate, and quenching the reaction with alkyl halides leading to functionalised vinyl silanes **5b–f** in good yields as shown in Scheme 3. It is worth mentioning that these types of vinyl silanes are important intermediates in organic syntheses[6–11] and there has been no reported general access to 1-substituted vinyl silanes.[12]



Scheme 3

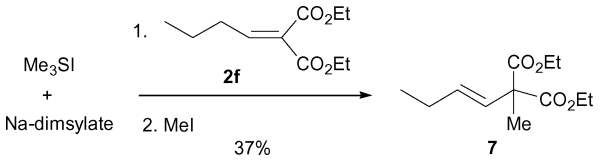
At this stage we were not convinced whether the silyl ($PhMe_2Si$) substitution in **2a** was responsible for this preferred elimination over cyclopropanation. Therefore, this one-pot protocol (olefination–alkylation) was attempted using a series of arylidene malonates **2b–e**. We were pleased to observe that the above elimination process was general and furnished the styrene derivatives **5g–i** exclusively in moderate to good yields as shown in Table 2. The poor yield of the styrene **5j** could be due to the degradation of the substrate as well as the product under the reaction conditions as was evident from the generation of a substantial amount of colored polar material. No cyclopropanation product was observed in any of these cases. When 2-alkylidene malonate **2f** was subjected to the same reaction conditions, desired product was not formed; instead, methylated isomerised product **7** was obtained in 37% yield (Scheme 4).

Table 2 Preparation of substituted styrenes



5g-j

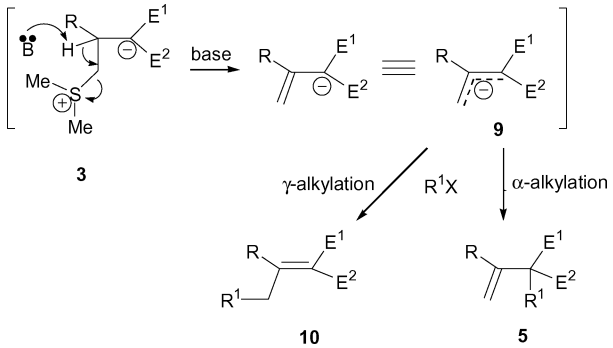
Entry	Ar	Substrate	Product	Yield (%)
1	Ph	**2b**	**5g**	73
2	4-MeO–C_6H_4	**2c**	**5h**	57
3	4-Br–C_6H_4	**2d**	**5i**	69
4	4-NO_2–C_6H_4	**2e**	**5j**	20



Scheme 4

Our next interest was to study the influence of activating groups present in the Michael acceptor **2** on olefination reaction. The substrate with a phosphonate activating group **2g** upon olefination–methylation gave exclusively the desired styrene derivative **5k** in 50% yield (Table 3). The silyl substituted alkylidene cyanoacetate **2h** when subjected to similar conditions gave exclusively the desired vinyl silane **5l** (Table 3). Contrary to silyl substitution, the arylidene cyanoacetate **2i** gave the desired product **5m** along with a double methylation product **8** in a ratio of 6 : 4. The *cis*-relationship between the Me and the Ar in **8** was confirmed by 1D-NOE study (7.5% NOE enhancement was observed between the olefinic proton and the C-1 Me). The selectivity (**5m** *vs.* **8**) could not be improved by changing the cation from Na to K. Fortunately, the reaction could be driven in the desired direction to give styrene **5m** albeit in poor yield by the addition of $MgBr_2$[13] into the reaction medium prior to the addition of methyl iodide.

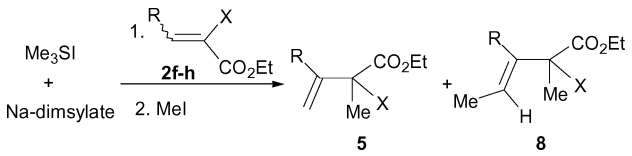
Even though the stabilized allylic anion **9** (Scheme 5) could provide two regioisomeric alkylation products, **5** by α-alkylation and **10** by γ-alkylation; the present olefination–alkylation protocol using malonates exclusively gave the α-alkylated products **5b–5l**. Base induced γ-deprotonation in alkylidene malonates and cyanoacetates followed by alkylation exclusively at the α-position has been documented by Cope and co-workers.[14] We were therefore inquisitive to know whether the same level of regioselectivity would be obtained upon olefination–protonation instead of alkylation; although in the case of silylated substrate **2a**, the protonation exclusively took place at the α-position to give **5a** (Table 1).



Scheme 5

Therefore, this olefination was attempted with a series of 2-substituted arylidene malonates **2b–e** and **2j–k**. Indeed we observed a very high level of selectivity for α-protonation and not a trace amount of γ-protonated product was formed. Unexpectedly, in addition to the olefination products **5n–s**, small amounts of side products **11b–e** and **11j–k** were also formed (Table 4). When 2-alkylidene malonate **2l** was subjected to the same reaction conditions, instead of the desired olefination, product **12** was formed due to isomerization of the starting material along with the thiomethylmethyl addition product **11l** (Scheme 6).

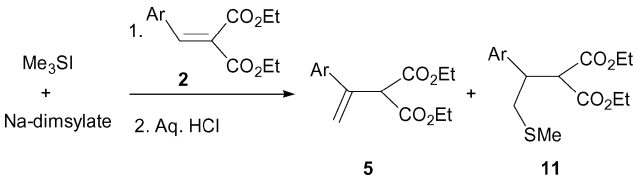
Table 3 Effect of activating group on the one-pot olefination–alkylation reaction



Entry	X	R	Substrate	Product(s)	**5m**/**8**	Yield (%)
1	$P(O)(OEt)_2$	4-MeO–C_6H_4–	**2g**	**5k**	—	50
2	CN	$PhMe_2Si$–	**2h**	**5l**	—	28
3	CN	4-MeO–C_6H_4–	**2i**	**5m**; **8**	64 : 36	60
4	CN	4-MeO–C_6H_4–	**2i**	**5m**; **8**	65 : 35	55[a]
5	CN	4-MeO–C_6H_4–	**2i**	**5m**; **8**	100 : 0	17[b]

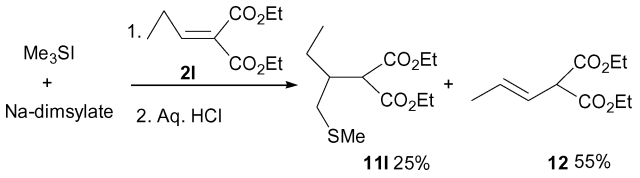
[a] Potassium dimsylate was used instead of sodium dimsylate. [b] $MgBr_2$ was added prior to the addition of MeI.

Table 4 Effect of aryl substituent on olefination



Entry	Ar	Substrate	**5**/**11**[a]	Product **5** (% yield)	Product **11** (% yield)	σ	$\log(sel_{Ar}/sel_{Ph})$
1	Ph	**2b**	77 : 23	**5n** (65)	**11b** (15)	0	0
2	4-MeO–C_6H_4–	**2c**	70 : 30	**5o** (61)	**11c** (20)	−0.268	−0.157
3	4-Br–C_6H_4–	**2d**	82 : 18	**5p** (68)	**11d** (7)	0.232	0.134
4	4-NO_2–C_6H_4–	**2e**	82 : 18	**5q** (46)	**11e** (8)	0.778	0.134
5	3-MeO–C_6H_4–	**2j**	80 : 20	**5r** (68)	**11j** (11)	0.115	0.077
6	3-Cl–C_6H_4–	**2k**	85 : 15	**5s** (70)	**11k** (8)	0.373	0.228

[a] Ratio determined from crude product by ^1H NMR.



Scheme 6

The formation of products **11** from **2** *via* intermediate **3** (Scheme 1) could be rationalized as follows. Abstraction of a proton (path b, Scheme 1) by sodium dimsylate followed by loss of Me_2S results in the formation of olefins **5**. A nucleophilic attack of Na-dimsylate on the methyl group of the dimethylsulfonium substituent in an intermediate of type **3** competes with proton abstraction resulting in the formation of products **11** (Table 4). To gain insight into the electronic dependence of the selectivity of olefination *vs.* demethylation from intermediate **3**, a Hammett plot[15] (Fig. 1) was constructed by plotting the log of the selectivity (olefination/demethylation) ratios *vs.* σ with the results obtained from a few arylidene malonates (Table 4); where the aryl ring embodied substituents having Hammett values in the range of $-0.3 \leq \sigma \leq 0.8$. Detailed examination of the selectivities of olefination *i.e.* the ratio of olefination product **5** to demethylation product **11** for electron-rich and electron-poor arylidene malonates revealed a clear trend in selectivity. Taking an unsubstituted phenyl ring as a reference point, the selectivity increased as the aryl ring became more and more electron poor. The plot was linear over the entire domain of tested compounds ($\rho \approx 0.6$, $R^2 = 0.999$) with the exception of 4-NO_2 ($\sigma = 0.778$), where a significant deviation was found. The positive slope of the Hammett plot is indicative that an electron withdrawing aryl ring improves olefination. A

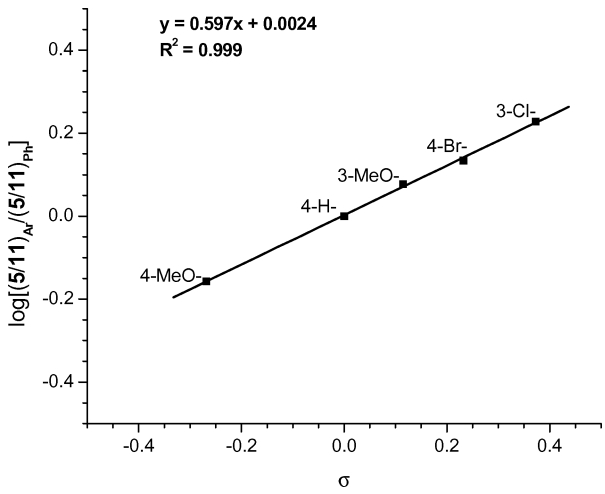
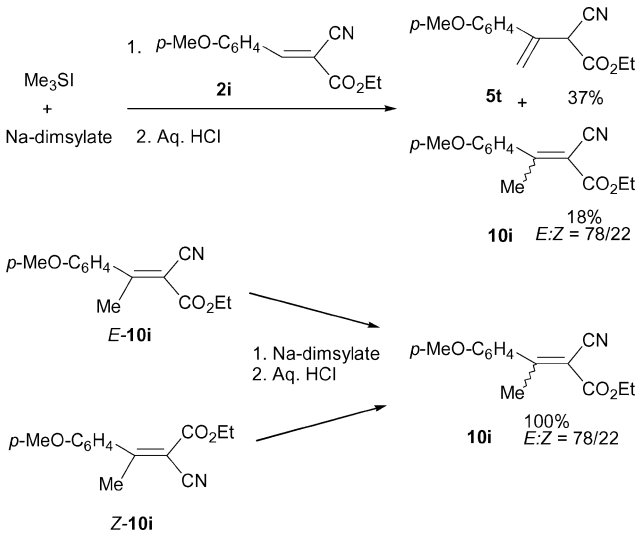


Fig. 1 Hammett correlation of the log of relative selectivity for olefination *versus* Hammett value, σ (taken from ref. 15).

possible explanation for the improved rates of olefination of arylidene malonates where the aryl substituent is embodied with electron-withdrawing groups is that these substituents lower the pK_a of the benzylic protons in intermediate **3**, effectively increasing the ease of proton abstraction by a base. The aryl ring with 4-NO_2 substitution followed the same trend although the magnitude was much less than expected. This anomaly is due to the degradation of the substrate as well as the products under the reaction conditions as reflected in the isolated yields. In the case of 2-alkylidene malonate **2l**, no olefination product was observed. The intermediate of type **3** generated after conjugate addition of dimethylsulfonium methylide to **2l** is unable to

undergo a proton loss due to the high pK_a of its β-proton. Instead, loss of a methyl group from the dimethylsulfonium substituent by nucleophilic attack of dimsylate resulted in the formation of **11l** (Scheme 6). In the case of 2-silylalkylidene malonate **2a**, the exclusive formation of olefination product **5a** (Table 1, entry 8) could be attributed to a much easier loss of the CH proton α to the $SiMe_2Ph$ group.

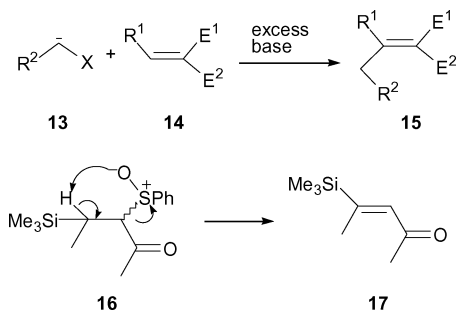
The only exception to exclusive α-methylation was found with arylidene cyanoacetate **2i** as shown in Table 3 (entries 3 and 4). This substrate gave both α-methylation product **5m** and γ-methylation product **8** (**5m**/**8** = 65 : 35). In order to probe the mechanism of the formation of **8**, we carried out a few experiments. First, the arylidene cyanoacetate **2i** was subjected to the optimized conditions for olefination and quenched with aqueous acid which gave a mixture of desired olefination product **5t** and arylidene cyano acetate **10i** (**5t**/**10i** = 65 : 35) predominantly as the *E*-isomer (*E*/*Z* = 78 : 22) (Scheme 7). The products were separated, individually treated with Na-dimsylate and quenched with aq. HCl. The olefination product **5t** was recovered unchanged whereas pure (*E*)- or pure (*Z*)-**10i** underwent isomerization to provide a mixture of (*E*)- and (*Z*)-**10i** (*E*/*Z* = 78 : 22) quantitatively. These observations infer that olefin **5i** and olefin **10j** are formed independently and are not interconvertible under the reaction conditions. In addition to this, olefin **5b** also remained unaltered when treated with Na-dimsylate followed by aqueous or anhydrous acid.



Scheme 7

Plausible pathway for the formation of the 1-substituted olefins

Makosza and Kwast[16] have shown that carbanion **13** containing a leaving group reacts, in the presence of excess base, with electrophilic alkene **14** giving product **15** in which vinylic hydrogen is replaced with a carbanion moiety (Scheme 8). It has been proposed that such vicarious nucleophilic substitution

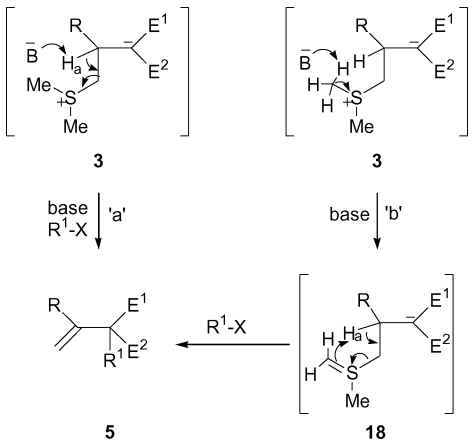


Scheme 8

occurs first by Michael addition of a carbanion on an electrophilic alkene, followed by abstraction of the vinylic proton by excess base and β-elimination of the leaving group leading to an allylic anion which on protonation provides the olefinic product. This kind of reaction does not take place in the case of arylidene malonates, instead normal Michael addition products were isolated. In some specific cases, this overall substitution process goes *via* cyclization leading to a cyclopropane ring which undergoes ring opening to give the product.

It has also been observed by Fleming *et al.*[17] that β-silylethyl sulfoxide having α-carbonyl substituent(s) **16** prefers elimination of the β-hydrogen instead of the silyl group to give the β-silyl substituted α,β-unsaturated carbonyl compound **17** (Scheme 8). The reason for this is that silicon stabilizes the alpha carbanion making the loss of hydrogen more facile as well as the carbonyl group increasing the electrophilicity of the carbon adjacent to it and hence a push–pull kind of mechanism operates.

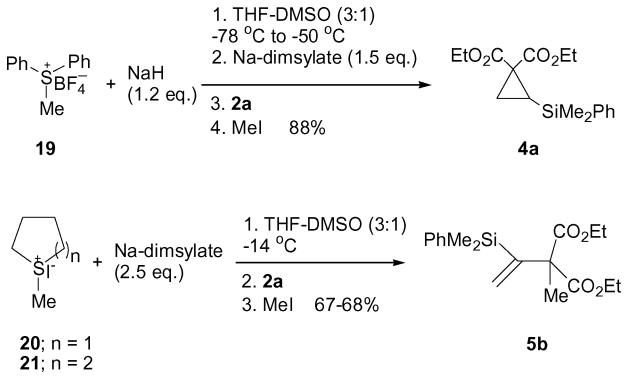
In the present work, the isolation of cyclopropane **4a** when substrate **2a** was treated with one equivalent of ylide **1** showed that it first undergoes a Michael type addition to the activated olefin **2a** to give a reactive intermediate **3** which undergoes rapid eliminative cyclisation (Scheme 1). This product **4a** on treatment with an excess of sodium dimsylate did not give the olefin **5a**, therefore, precludes its intermediacy in this olefination. The formation of the olefin **5a** when the reaction was carried out in the presence of excess base (sodium dimsylate) showed that the base has a significant role in the removal of H_a and Me_2S. The two alternative pathways in the presence of excess base are shown in Scheme 9. In path 'a', analogous to Makosza's mechanism, the base takes the proton H_a from **3** with concomitant elimination of Me_2S leading to olefin **5** after alkylation with alkyl halides. In the second pathway, in parallel with Fleming's observation, the base takes a proton from one of the methyl groups attached to sulfur and generates a new ylide/ylene **18** which then undergoes cycloelimination of H_a and Me_2S to give the olefin **5**.



Scheme 9

The substantial clue supporting pathway 'b' came from studies using different sulfonium methylides. The results are presented in Scheme 10. The diphenylsulfonium methylide generated *in situ* from diphenylmethylsulfonium tetrafluoroborate **19** ‡ in the presence of excess base on reaction with olefin **2a** provided only cyclopropane **4a**. On the contrary, cyclic sulfonium methylides generated *in situ* from sulfonium iodides **20** and **21**, respectively, gave the desired olefination product **5b**. The former ylide lacks the protons for generation of an intermediate of type **18** (Scheme 7) after its addition to the activated olefin **2a**, thus only cyclopropanation takes place, whereas the latter cases

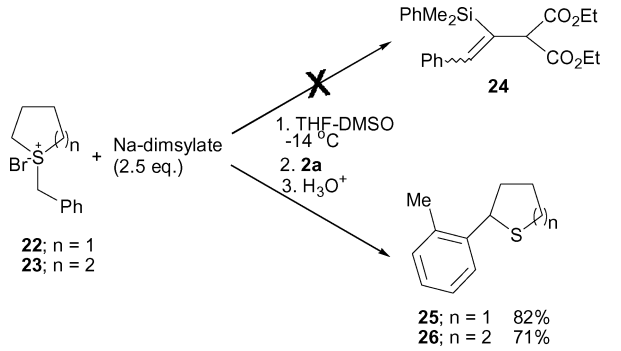
‡ This salt did not work well under our standard olefination procedure. A modified procedure (*vide* experimental) was therefore introduced. Under these modified conditions, Me_3SI also gave the desired olefination product **5b** when reacted with **2a**.



Scheme 10

have methylenes and readily generate ylides[18] of type **18** in the presence of base thus providing the desired product.

Having established the olefination protocol with dimethylsulfonium methylide and various Michael acceptors, we explored the possibility to extend this methodology for the synthesis of trisubstituted olefins. We performed this reaction using benzyl sulfonium salts **22** and **23** with **2a**, however no olefination product **24** was detected. Instead, the generated ylides underwent a Sommelet–Hauser rearrangement[18,19] under the reaction conditions used to give rearranged products **25** and **26** only (Scheme 11).



Scheme 11

In conclusion, we have developed a novel application of dimethylsulfonium methylide for the general preparation of non-readily accessible and synthetically valuable 1-substituted vinyl silanes, and styrene derivatives from easily available activated olefins. The additional feature of these silanes and styrenes is that they have a β,γ-unsaturated diester moiety in their framework which is not always easy to obtain by other methods. This study also demonstrated that by varying conditions, the reactions could be tuned in either direction to give an olefin or cyclopropane exclusively. The limitation of this olefination protocol is that it works with sulfonium methylides only and does not work for β-alkyl substituted Michael acceptors. The mechanistic studies on the formation of vinyl silanes and styrenes confirmed the intermediacy of ylide **18** which underwent cycloelimination to provide the olefination products.

Experimental

General methods

The ester **2a** was prepared following the published procedure.[5] Compounds **2b–2f** and **2i–l** were prepared by standard Knoevenagel condensation between different aromatic aldehydes and diethyl malonate or ethyl cyanoacetate. Ethyl ethoxymethylenecyanoacetate,[20] compound **2g**,[21] and diphenylmethylsulfonium tetrafluoroborate **19** (Ph_2SMe^+ BF_4^-)[22] were prepared following the literature procedures. Sulfonium salts **20** and **21** were prepared by mixing excess iodomethane with tetrahydrothiophene and pentamethylene sulfide, respectively, and standing at room temperature overnight followed by crystallization from EtOH. The benzyl sulfonium salts **22** and **23** were also prepared by heating a solution of benzyl bromide and tetrahydrothiophene or pentamethylene sulfide in hexanes followed by crystallization from EtOH–EtOAc.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 200 MHz spectrometer. Spectra were referenced to residual chloroform (δ 7.26 ppm, ^{1}H; 77.00 ppm, ^{13}C). Chemical shifts are reported in ppm (δ); multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), quint (pentet), m (multiplet) and br (broad). Coupling constants, J, are reported in Hertz. Mass spectra were recorded on a Fissons VG Quatro II mass spectrometer (EI 70 V; CI 30 V). HRMS were recorded in a Waters Micromass Q-TOF Mass Spectrometer. Infrared spectra (IR) were recorded on a Nicolet Impact 410 FT IR spectrophotometer in NaCl cells or in KBr discs. Peaks are reported in cm^{-1}. Melting points (mp) were determined on a Fischer John's melting point apparatus and are uncorrected. Analytical thin-layer chromatography was performed using home made Acme silica gel plates (about 0.5 mm).

Ethyl (*Z*)-2-cyano-3-dimethyl(phenyl)silyl-2-propenoate 2h

A solution of ethyl ethoxymethylenecyanoacetate (5.6 gm, 33.3 mmol) in THF (100 cm^3) was added to a stirred solution of dimethyl(phenyl)silyllithium[23] (0.95 M solution in THF) (35 cm^3, 33.4 mmol) dropwise at −78 °C. After the addition was over, the reaction mixture was stirred for 15 min and the cold bath was removed. The reaction mixture was allowed to attain room temperature (about 25 min) and was then poured into a saturated ammonium chloride solution and extracted with Et_2O. The organic extract was washed with water and with brine, dried ($MgSO_4$) and evaporated. The residue was purified by column chromatography on silica using hexane–EtOAc (95 : 5) as eluent to give the cyanoester **2h** (0.9 g, 24%) as a colorless oil; R_f 0.57 (hexane–EtOAc, 95 : 5); ν_{max}(neat)/cm^{-1} 3070 (HC=C), 2227 (CN), 1732 (CO), 1587 (C=C), 1234 (SiMe) and 1115 (SiAr); δ_H(200 MHz, $CDCl_3$) 0.64 (6 H, s, 2 × SiMe), 1.36 (3 H, t, J = 7.1 Hz, $MeCH_2OCO$), 4.32 (2 H, q, J = 7.1 Hz, $MeCH_2OCO$), 7.40–7.60 (5 H, m, Ar) and 8.07 (1 H, s, C=CHSi); δ_C(50 MHz, $CDCl_3$) −3.47 (2 C), 14.01, 62.77, 115.30, 120.74, 128.24 (2 C), 130.14, 133.84 (2 C), 134.42, 160.88 and 163.74; m/z (EI) 259 (M$^+$, 4%), 258 (10), 244 (14), 230 (73), 216 (74), 188 (41.5), 186 (50), 145 (60.4), 137 (45.5), 135 (65.3), 105 (100), 103 (65.3), 91 (32.7), 75 (94).

Diethyl 2-dimethyl(phenyl)silylcyclopropane-1,1-dicarboxylate 4a

A solution of sodium dimsylate (1 mmol) in DMSO (4 cm^3) was prepared. The solution was diluted with THF (1 cm^3) and cooled to 0 °C. Solid trimethylsulfonium iodide (205 mg, 1 mmol) was introduced into the flask and the reaction mixture was stirred under the same conditions for 15 min. A solution of **2a** (0.306 gm, 1 mmol) in dry THF (0.75 cm^3) was rapidly added to the reaction mixture. It was slowly brought to room temperature (about 1 h) and stirred for 1 h. The reaction mixture was diluted with water and extracted with ether. The organic extract was washed with brine, dried ($MgSO_4$) and evaporated. The residue was purified by column chromatography on silica using hexane–EtOAc (95 : 5) as eluent to give the cyclopropane **4a** (173 mg, 55%) (found: C, 63.36; H, 7.88. $C_{17}H_{24}O_4Si$ requires C, 63.72; H, 7.55%); R_f 0.32 (hexane–EtOAc, 95 : 5); ν_{max}(neat)/cm^{-1} 1731 (C=O), 1249 (SiMe) and 1116 (SiPh); δ_H(200 MHz, $CDCl_3$) 0.25 (3 H, s, SiMe), 0.34 (3 H, s, SiMe), 1.10 (1 H, dd, J = 9.5, 11 Hz, SiCH), 1.18 (3 H, t, J = 7.1 Hz, $MeCH_2OCO$), 1.26 (3 H, t, J = 7 Hz, $MeCH_2OCO$), 1.41 (1 H, dd, J = 3.4, 9.5 Hz, CH_AH_BCHSi), 1.52 (1 H, dd, J = 3.4, 11 Hz, CH_AH_BCHSi), 3.80–4.30 (4 H, m, 2 × $MeCH_2OCO$) and 7.30–7.75 (5 H, m, Ar); δ_C(50 MHz, $CDCl_3$) −3.32, −3.16, 13.80, 14.00, 15.35,

18.38, 33.31, 61.16, 61.56, 127.71 (2 C), 129.12, 133.78 (2 C), 137.86, 169.07 and 170.98; *m/z* (EI) 305 ($M^+ - Me$, 100%), 275 (11), 243 (70.3), 231 (90), 215 (21), 187 (76), 169 (73), 159 (27), 135 (41) and 105 (29).

This compound was also prepared using diphenylmethylsulfonium tetrafluoroborate (Ph_2SMe^+ BF_4^-) (**19**). For this, a solution of the sulfonium salt **19** (173 mg, 0.6 mmol, 1.2 equiv) in THF–DMSO (1 : 1) (1 cm^3) was added to a stirred suspension of sodium hydride (55% in oil) (27 mg, 0.6 mmol, 1.2 equiv) (freed from oil by washing with dry hexane and dried) in THF (1.5 cm^3) at −78 °C. The temperature of the bath was raised to −50 °C, and sodium dimsylate (1 cm^3 of a 0.75 M solution in DMSO, 0.75 mmol, 1.5 equiv) was added into the reaction mixture followed by a solution of the ester **2a** (153 mg, 0.5 mmol, 1 equiv) in dry THF (1 cm^3). The reaction mixture was allowed to attain room temperature and was stirred for 45 min, cooled on an ice–water bath and MeI (0.16 cm^3, 2.5 mmol, 5 equiv) was added. After 14 h at room temperature, the reaction mixture was diluted with water and extracted with ether. The organic extract was washed with brine, dried ($MgSO_4$) and evaporated. The residue was purified by column chromatography on silica using hexane–EtOAc (95 : 5) as eluent to give the cyclopropane **4a** (140 mg, 88%).

Diethyl (1-dimethyl[phenyl]silylvinyl)malonate 5a

A solution of sodium dimsylate (2.5 mmol) in DMSO (2.5 cm^3) was prepared. The solution was diluted with THF (4 cm^3) and cooled on an ice–salt bath (−8 °C). Solid trimethylsulfonium iodide (245 mg, 1.2 mmol) was introduced into the flask and the reaction mixture was stirred under the same conditions for 15 min. A solution of **2a** (0.306 gm, 1 mmol) in dry THF (2 cm^3) was rapidly added to the reaction mixture. It was slowly brought to room temperature (about 1 h) and stirred for 1 h. The reaction mixture was diluted with water and extracted with ether. The organic extract was washed with brine, dried ($MgSO_4$) and evaporated. The residue was purified by column chromatography on silica using hexane–EtOAc (95 : 5) as eluent to give the vinyl silane **5a** (210 mg, 66%) (found: C, 63.44; H, 7.90. $C_{17}H_{24}O_4Si$ requires C, 63.72; H, 7.55%); R_f 0.30 (hexane–EtOAc, 95 : 5); ν_{max}(neat)/cm^{-1} 1732 (C=O), 1250 (SiMe) and 1112 (SiPh); δ_H(200 MHz, $CDCl_3$) 0.41 (6 H, s, 2 × SiMe), 1.20 (6 H, t, $J = 7.1$ Hz, 2 × *Me*CH_2OCO), 4.10 (4 H, q, $J = 7.1$ Hz, 2 × Me*CH*$_2$OCO), 4.14 (1 H, br s, *H*C$(CO_2Et)_2$), 5.76 (1 H, d, $J = 1.4$ Hz, SiC=CH), 6.03 (1 H, t, br, $J = 1.1$ Hz, SiC=CH) and 7.32–7.55 (5 H, m, Ar); δ_C(50 MHz, $CDCl_3$) −2.81 (2 C), 13.79 (2 C), 56.82, 61.24 (2 C), 127.59 (2 C), 129.06, 132.21, 133.97 (2 C), 136.99, 141.83 and 168.10 (2 C); *m/z* (EI) 305 ($M^+ - Me$, 99%), 275 (9), 247 (16), 243 (100), 231 (41), 215 (21), 187 (58), 169 (40), 161 (42), 159 (22), 137 (47), 135 (88), 125 (36) and 105 (78).

Diethyl (1-dimethyl[phenyl]silylvinyl)methylmalonate 5b. A solution of sodium dimsylate (7.5 mmol) in DMSO (7.5 cm^3) was prepared. The solution was diluted with THF (9 cm^3) and cooled on an ice–salt bath (−8 °C). Solid trimethylsulfonium iodide (735 mg, 3.6 mmol) was introduced into the flask and the reaction mixture was stirred under the same conditions for 15 min. A solution of the 2-silyl alkylidene malonate **2a** (0.92 gm, 3 mmol) in dry THF (9 cm^3) was rapidly added to the reaction mixture. It was slowly brought to room temperature (about 2.5 h) and stirred for 45 min. The reaction mixture was cooled on an ice–water bath and MeI (0.94 cm^3, 15 mmol) was added. After 14 h at room temperature, the reaction mixture was diluted with water and extracted with ether. The organic extract was washed with brine, dried ($MgSO_4$) and evaporated. The residue was purified by column chromatography on silica using hexane–EtOAc (95 : 5) as eluent to give the vinyl silane **5b** (800 mg, 80%) (found: C, 64.21; H, 8.10. $C_{18}H_{26}O_4Si$ requires C, 64.63; H, 7.84%); R_f 0.46 (hexane–EtOAc, 95 : 5); ν_{max}(neat)/cm^{-1} 1731 (C=O), 1259 (SiMe) and 1110 (SiPh); δ_H(200 MHz, $CDCl_3$) 0.42 (6 H, s, 2 × SiMe), 1.22 (6 H, t, $J = 7.1$ Hz, 2 × *Me*CH_2OCO), 1.59 (3 H, s, *Me*C$(CO_2Et)_2$), 4.04–4.25 (4 H, m, 2 × Me*CH*$_2$OCO), 5.61 (1 H, s, SiC=CH), 5.82 (1 H, s, SiC=CH) and 7.31–7.58 (5 H, m, Ar); δ_C(50 MHz, $CDCl_3$) −0.59 (2 C), 13.76 (2 C), 21.84, 59.92, 61.20 (2 C), 127.41 (2 C), 128.61, 129.07, 133.87 (2 C), 139.29, 148.50 and 171.41 (2 C); *m/z* (EI) 319 ($M^+ - Me$, 100%), 289 (7), 262 (27), 261 (27), 257 (93), 245 (40), 229 (9), 201 (18), 173 (38), 169 (8), 135 (48), 111 (20) and 105 (29).

This compound **5b** was also prepared using sulfonium salts **20** and **21** instead of trimethylsulfonium iodide in 67% and 68% yields, respectively.

Diethyl (1-dimethyl[phenyl]silylvinyl)ethylmalonate 5c. Procedure as described for the preparation of **5b**; yield 79% (found: C, 65.22; H, 8.27. $C_{19}H_{28}O_4Si$ requires C, 65.48; H, 8.10%); R_f 0.48 (hexane–EtOAc, 95 : 5); ν_{max}(neat)/cm^{-1} 1731 (C=O), 1244 (SiMe) and 1110 (SiPh); δ_H(200 MHz, $CDCl_3$) 0.43 (6 H, s, 2 × SiMe), 0.89 (3 H, t, $J = 7.4$ Hz, *Me*CH_2), 1.20 (6 H, t, $J = 7.1$ Hz, 2 × *Me*CH_2OCO), 2.10 (2 H, q, $J = 7.4$ Hz, Me*CH*$_2$), 4.11 (2 H, q, $J = 7.1$ Hz, Me*CH*$_2$OCO), 4.12 (2 H, q, $J = 7.1$ Hz, Me*CH*$_2$OCO), 5.67 (1 H, s, SiC=CH), 5.91 (1 H, s, SiC=CH) and 7.30–7.58 (5 H, m, Ar); δ_C(50 MHz, $CDCl_3$) −0.32 (2 C), 9.44, 13.92 (2 C), 28.57, 61.07 (2 C), 63.72, 127.42 (2 C), 128.53, 130.80, 134.02 (2 C), 140.09, 147.52 and 171.00 (2 C); *m/z* (EI) 333 ($M^+ - Me$, 33%), 303 (5), 275 (16), 271 (59), 259 (13), 233 (12), 215 (32), 187 (42), 159 (87), 153 (48), 135 (100), 141 (33), 125 (46), 121 (22), 107 (20), 105 (71), 95 (38), 91 (30), 77 (33) and 75 (73).

Diethyl allyl(1-dimethyl[phenyl]silylvinyl)malonate 5d

Procedure as described for the preparation of **5b** except 1.5 equiv of allyl bromide were used; yield 60% (found: C, 66.71; H, 8.11. $C_{20}H_{28}O_4Si$ requires C, 66.63; H, 7.83%); R_f 0.32 (hexane–EtOAc, 98 : 2); ν_{max}(neat)/cm^{-1} 1731 (C=O), 1245 (SiMe) and 1111 (SiPh); δ_H(200 MHz, $CDCl_3$) 0.42 (6 H, s, 2 × SiMe), 1.19 (6 H, t, $J = 7.1$ Hz, 2 × *Me*CH_2OCO), 2.82 (2 H, d, $J = 7.1$ Hz, CH_2=CH*CH*$_2$), 3.97–4.19 (4 H, m, 2 × Me*CH*$_2$OCO), 5.00 (1 H, s, C$H_A$$H_B$=CH$CH_2$), 5.06 (1 H, d, $J = 5$ Hz, $CH_A$$H_B$=CH$CH_2$), 5.68 (1 H, s, SiC=CH), 5.68–5.94 (1 H, m, $CH_A$$H_B$=*CH*$CH_2$), 5.94 (1 H, s, SiC=CH) and 7.30–7.57 (5 H, m, Ar); δ_C(50 MHz, $CDCl_3$) −0.32 (2 C), 13.92 (2 C), 40.12, 61.24 (2 C), 63.36, 117.99, 127.46 (2 C), 128.60, 131.04, 133.83, 134.05 (2 C), 139.92, 147.46 and 170.52 (2 C); *m/z* (EI) 345 ($M^+ - Me$, 100%), 319 (5.5), 287 (10), 285 (11), 283 (82), 271 (29), 244 (8), 227 (13), 209 (28), 199 (21), 165 (14), 135 (60), 121 (22) and 105 (27).

Diethyl benzyl(1-dimethyl[phenyl]silylvinyl)malonate 5e. Procedure as described for the preparation of **5b** except 2.5 equiv of benzyl bromide were used; yield 64% (found: C, 70.45; H, 7.68. $C_{24}H_{30}O_4Si$ requires C, 70.20; H, 7.36%); R_f 0.37 (hexane–EtOAc, 98 : 2); ν_{max}(neat)/cm^{-1} 1732 (C=O), 1248 (SiMe) and 1111 (SiPh); δ_H(200 MHz, $CDCl_3$) 0.23 (6 H, s, 2 × SiMe), 1.11 (6 H, t, $J = 7.1$ Hz, 2 × *Me*CH_2OCO), 3.43 (2 H, s, Ph*CH*$_2$), 4.03 (4 H, q, $J = 7.1$ Hz, 2 × Me*CH*$_2$OCO), 5.73 (1 H, s, SiC=CH), 6.06 (1 H, s, SiC=CH) and 7.10–7.50 (10 H, m, Ar); δ_C(50 MHz, $CDCl_3$) −0.60 (2 C), 13.74 (2 C), 42.55, 61.24 (2 C), 64.76, 126.76, 127.34 (2 C), 127.87 (2 C), 128.35, 130.73 (2 C), 132.02, 134.03 (2 C), 136.56, 140.53, 148.48 and 170.49 (2 C); *m/z* (EI) 395 ($M^+ - Me$, 0.5%), 333 (24), 215 (31), 199 (20), 158 (15), 137 (29), 135 (58), 129 (20), 128 (16), 105 (35), 91 (100), 77 (13) and 75 (22).

Diethyl (1-dimethyl[phenyl]silylvinyl)(3-methoxybenzyl)malonate 5f. Procedure as described for the preparation of **5b** except 2.5 equiv of 3-methoxy benzyl bromide were used; yield 68% (found: C, 67.85; H, 7.54. $C_{25}H_{32}O_5Si$ requires C, 68.15; H, 7.32%; Found: $M^+ + Na$, 463.1933, $C_{25}H_{32}O_5SiNa$ requires ($M^+ + Na$), 463.1917) $R_f = 0.33$ (hexane–EtOAc, 5 : 95); ν_{max}(neat)/cm^{-1} 1729 (C=O), 1260 (SiMe) and 1111 (SiPh);

δ_H(200 MHz, $CDCl_3$) 0.24 (6 H, s, 2 × SiMe), 1.13 (6 H, t, J = 7.2 Hz, 2 × *Me*CH_2OCO), 3.41 (2 H, s, Ar*CH*$_2$), 3.76 (3 H, s, OMe), 4.05 (4 H, q, J = 7.2 Hz, 2 × Me*CH*$_2$OCO), 5.73 (1 H, s, SiC=CH), 6.06 (1 H, s, SiC=CH), 6.70–6.78 (3 H, m, Ar), 7.14 (1 H, t, J = 8 Hz, Ar), 7.27–7.36 (3 H, m, Ar), 7.45–7.50 (2 H, m, Ar); δ_C(50 MHz, $CDCl_3$) −0.6 (2 C), 13.74 (2 C), 42.53, 55.06, 61.24 (2 C), 64.67, 112.27, 116.37, 123.11, 127.31 (2 C), 128.31, 128.76, 131.99, 133.99 (2 C), 137.98, 140.52, 148.42, 159.13, 170.41 (2 C); *m*/*z* (ESI) 463 (M^+ + Na, 61%), 363 (100), 317 (18), 245 (9).

Diethyl methyl(1-phenylvinyl)malonate 5g. Procedure as described for the preparation of **5b**; yield 73% (found: C, 69.30; H, 7.52. $C_{16}H_{20}O_4$ requires C, 69.55; H, 7.30%); R_f 0.40 (hexane–EtOAc, 95 : 5); ν_{max}(neat)/cm^{-1} 1728 (C=O); δ_H(200 MHz, $CDCl_3$) 1.20 (6 H, t, J = 7.1 Hz, 2 × *Me*CH_2OCO), 1.60 (3 H, s, *Me*C(CO_2Et)$_2$), 4.18 (4 H, q, J = 7.1 Hz, 2 × Me*CH*$_2$OCO), 5.34 (2 H, s, ArC=*CH*$_2$) and 7.36 (5 H, br s, Ar); δ_C(50 MHz, $CDCl_3$) 13.82 (2 C), 22.26, 60.03, 61.59 (2 C), 118.03, 127.34, 127.82 (2 C), 128.24 (2 C), 140.76, 147.78 and 171.33 (2 C); *m*/*z* (EI) 276 (M^+, 0.5%), 231 (0.5), 203 (100), 185 (11), 175 (89), 147 (16), 129 (64), 115 (33) and 91 (27).

Diethyl (1-[4-methoxyphenyl]vinyl)methylmalonate 5h. Procedure as described for the preparation of **5b**; yield 57% (found: C, 66.22; H, 7.41. $C_{17}H_{22}O_5$ requires C, 66.65; H, 7.24%); R_f 0.24 (hexane–EtOAc, 95 : 5); ν_{max}(neat)/cm^{-1} 1731 (C=O) and 1609 (C=C); δ_H(200 MHz, $CDCl_3$) 1.20 (6 H, t, J = 7.1 Hz, 2 × *Me*CH_2OCO), 1.58 (3 H, s, *Me*C(CO_2Et)$_2$), 3.77 (3 H, s, *Me*OAr), 4.17 (4 H, q, J = 7.1 Hz, 2 × Me*CH*$_2$OCO), 5.26 (1 H, s, ArC=C*H*), 5.29 (1 H, s, ArC=C*H*), 6.79 (2 H, d, J = 8.6 Hz, Ar) and 7.18 (2 H, d, J = 8.6 Hz, Ar); δ_C(50 MHz, $CDCl_3$) 13.79 (2 C), 22.15, 55.09, 60.09, 61.50 (2 C), 113.10 (2 C), 117.24, 129.35 (2 C), 133.03, 147.26, 158.84 and 171.35 (2 C); *m*/*z* (EI) 307 (M^+ + 1, 2.5%), 306 (2.5), 261 (2), 233 (100), 205 (80), 187 (11), 177 (25), 159 (46), 145 (17), 115 (21) and 91 (20).

Diethyl (1-[4-bromophenyl]vinyl)methylmalonate 5i. Procedure as described for the preparation of **5b**; yield 69% (found: C, 53.88; H, 5.40. $C_{16}H_{19}BrO_4$ requires C, 54.10; H, 5.39%); R_f 0.40 (hexane–EtOAc, 95 : 5); ν_{max}(neat)/cm^{-1} 1732 (C=O);δ_H(200 MHz, $CDCl_3$) 1.21 (6 H, t, J = 7.1 Hz, 2 × *Me*CH_2OCO), 1.59 (3 H, s, *Me*C(CO_2Et)$_2$), 4.17 (4 H, q, J = 7.1 Hz, 2 × Me*CH*$_2$OCO), 5.33 (1 H, s, ArC=C*H*), 5.36 (1 H, s, ArC=C*H*), 7.16 (2 H, d, J = 8.4 Hz, Ar) and 7.40 (2 H, d, J = 8.4 Hz, Ar); δ_C(50 MHz, $CDCl_3$) 13.84 (2 C), 22.21, 59.85, 61.71 (2 C), 118.65, 121.52, 130.05 (2 C), 130.94 (2 C), 139.77, 146.79 and 171.11 (2 C); *m*/*z* (EI) 356 ($C_{16}H_{19}O_4{}^{81}Br$, M^+, 0.2%), 354 ($C_{16}H_{19}O_4{}^{79}Br$, M^+, 0.25), 311 (0.5), 309 (0.6), 283 (76), 281 (78), 255 (67), 253 (69), 227 (8), 225 (8), 207 (11), 207 (12), 146 (15), 130 (42), 129 (44), 128 (100), 127 (41), 115 (30) and 102 (26).

Diethyl methyl(1-[4-nitrophenyl]vinyl)malonate 5j. Procedure as described for the preparation of **5b**; yield 20% (found: C, 60.06; H, 6.00; N, 4.11. $C_{16}H_{19}NO_6$ requires C, 59.81; H, 5.96; N, 4.36%); R_f 0.36 (hexane–EtOAc, 90 : 10); ν_{max}(neat)/cm^{-1} 1728 (C=O), 1598 (C=C) and 1521 (NO_2); δ_H(200 MHz, $CDCl_3$) 1.20 (6 H, t, J = 7.1 Hz, 2 × *Me*CH_2OCO), 1.65 (3 H, s, *Me*C(CO_2Et)$_2$), 4.17 (4 H, q, J = 7.1 Hz, 2 × Me*CH*$_2$OCO), 5.43 (1 H, s, ArC=C*H*), 5.51 (1 H, s, ArC=C*H*), 7.48 (2 H, d, J = 8.6 Hz, Ar) and 8.15 (2 H, d, J = 8.6 Hz, Ar); δ_C(50 MHz, $CDCl_3$) 13.74 (2 C), 22.22, 59.57, 61.80 (2 C), 120.19, 122.97 (2 C), 129.20 (2 C), 146.22, 147.01, 147.75 and 170.67 (2 C); *m*/*z* (EI) 276 (M^+ − OEt, 0.5%), 248 (80), 220 (100), 174 (19), 129 (26), 128 (41) and 115 (18).

Diethyl (*E*)-(1-butenyl)methylmalonate 7[24]. Procedure as described for the preparation of **5b**; yield 37%, R_f 0.4 (hexane–EtOAc, 95 : 5); ν_{max}(neat)/cm^{-1} 1733 (C=O), 970 (*trans*-C=C); δ_H(200 MHz, $CDCl_3$) 0.98 (3 H, t, J = 7.4 Hz, *Me*CH_2CH=CH), 1.23 (6 H, t, J = 7 Hz, 2 × *Me*CH_2OCO), 1.51 (3 H, s, *Me*C(CO_2Et)$_2$), 1.95–2.15 (2 H, m, Me*CH*$_2$CH=CH), 4.18 (4 H, q, J = 7 Hz, 2 × Me*CH*$_2$OCO), 5.60 (1 H, td, J = 6 and 16 Hz, $MeCH_2$*CH*=CH), 5.88 (1 H, d, J = 16 Hz, $MeCH_2$CH=*CH*); δ_C(50 MHz, $CDCl_3$) 13.29, 13.95 (2 C), 20.32, 25.60, 55.32, 61.35 (2 C), 126.86, 133.60, 171.51 (2 C).

Ethyl 2-diethylphosphonato-2-methyl-3-(4-methoxyphenyl)but-3-enoate 5k. Procedure as described for the preparation of **5b**; yield 50%, R_f 0.5 (hexane–EtOAc, 70 : 30); ν_{max}(neat)/cm^{-1} 1731 (C=O), 1608 (C=C), 1247 (P=O) and 1028 (P–O); δ_H(200 MHz, $CDCl_3$) 1.02 (3 H, t, J = 7.1 Hz, *Me*CH_2OCO), 1.26 (3 H, t, J = 6.9 Hz, *Me*CH_2OP), 1.29 (3 H, t, J = 6.8 Hz, *Me*CH_2OP), 1.64 (3 H, d, J = 15.7 Hz, *Me*C(CO_2Et)(EtO)$_2$P(O)), 3.74 (3 H, s, *Me*OAr), 3.85–4.05 (2 H, m, Me*CH*$_2$OP), 4.05–4.26 (4 H, m, Me*CH*$_2$OP and Me*CH*$_2$OCO), 5.28 (1 H, d, J = 4.4 Hz, ArC=CH), 5.61 (1 H, d, J = 4.2 Hz, ArC=CH), 6.76 (2 H, d, J = 8.4 Hz, Ar) and 7.22 (2 H, d, J = 8.4 Hz, Ar); δ_C(50 MHz, $CDCl_3$) 13.48, 16.25 (2 C, d, J = 5.5 Hz), 21.63 (d, J = 5 Hz), 54.39 (d, J = 140 Hz), 55.02, 61.23, 62.89 (2 C, d, J = 4.3 Hz), 112.80 (2 C), 119.09 (d, J = 8.1 Hz), 129.34 (2 C), 133.82 (d, J = 4.9 Hz), 145.79 (d, J = 7 Hz), 158.63 and 170.98; *m*/*z* (EI) 370 (M^+, 0.1%), 325 (0.5), 297 (16), 233 100), 205 (46), 159 (30), 145 (11) and 121 (20).

Ethyl 2-cyano-3-dimethyl(phenyl)silyl-2-methylbut-3-enoate 5l. Procedure as described for the preparation of **5b**; yield 28% (found: C, 66.95; H, 7.55; N, 4.45. $C_{16}H_{21}NO_2Si$ requires C, 66.86; H, 7.36; N, 4.87%). R_f 0.42 (hexane–EtOAc, 98 : 2); ν_{max}(neat)/cm^{-1} 2241 (CN), 1745 (C=O), 1251 (SiMe) and 1113 (SiAr); δ_H(200 MHz, $CDCl_3$) 0.49 (3 H, s, SiMe), 0.52 (3 H, s, SiMe), 1.19 (3 H, t, J = 7.1 Hz, *Me*CH_2OCO), 1.65 (3 H, s, *Me*C(CO_2Et)(CN)), 3.77–4.10 (2 H, m, Me*CH*$_2$OCO), 5.78 (1 H, s, SiC=CH), 6.24 (1 H, s, SiC=CH) and 7.33–7.55 (5 H, m, Ar); δ_C(50 MHz, $CDCl_3$) −1.46, −1.37, 13.67, 24.13, 49.36, 62.77, 119.52, 127.79 (2 C), 129.43, 131.34, 134.04 (2 C), 136.72, 145.20 and 168.01; *m*/*z* (EI) 272 (M^+ − Me, 29%), 244 (13), 210 (47), 200 (67), 173 (84), 135 (100) and 111 (51).

Ethyl 2-cyano-2-methyl-3-(4-methoxyphenyl)but-3-enoate 5m and ethyl (*Z*)-2-cyano-2-methyl-3-(4-methoxyphenyl)pent-3-enoate 8. Procedure as described for the preparation of **5b**; yield 60%; ratio of **5m**/**8** = 65 : 35; the individual components could not be separated from the mixture. Data for **8**: δ_H(200 MHz, $CDCl_3$) (recognizable peaks) 1.25 (3 H, t, J = 6.7 Hz, *Me*CH_2OCO), 1.50 (3 H, d, J = 6.7 Hz, *Me*CH=C), 1.66 (3 H, s, *Me*C(CO_2Et)(CN)), 3.81 (3 H, s, *Me*OAr), 4.18 (2 H, q, J = 6.7 Hz, Me*CH*$_2$OCO) and 6.18 (1 H, q, J = 6.7 Hz, ArC=C*H*).

Ethyl 2-cyano-2-methyl-3-(4-methoxyphenyl)but-3-enoate 5m

A solution of sodium dimsylate (2.5 mmol, 2.5 equiv) in DMSO (2.5 cm^3) was prepared. The solution was diluted with THF (3 cm^3) and cooled on an ice–salt bath (−8 °C). Solid trimethylsulfonium iodide (245 mg, 1.2 mmol, 1.2 equiv) was introduced into the flask and the reaction mixture was stirred under the same conditions for 15 min. A solution of the arylidene cyanoacetate **2i** (0.231 gm, 1 mmol, 1 equiv) in dry THF (3 cm^3) was rapidly added to the reaction mixture. It was slowly brought to room temperature (about 2.5 h) and stirred for 45 min. The reaction mixture was cooled on an ice–water bath and a warm solution of $MgBr_2$ (920 mg, 5 mmol) in THF (10 cm^3) was added into the reaction mixture. After 15 min, MeI (0.5 cm^3, 8 mmol, 8 equiv) was added to the above slurry and allowed to attain room temperature. After 14 h at room temperature, the reaction mixture was diluted with water and extracted with ether. The organic extract was washed with brine, dried ($MgSO_4$) and evaporated. The residue was purified by column chromatography on silica using hexane–EtOAc (95 : 5) as eluent to give the styrene **5m** (44 mg, 17%) (found: C, 69.22; H, 6.87; N, 5.12. $C_{15}H_{17}O_3N$ requires C, 69.48; H, 6.61; N, 5.40%); R_f 0.37 (hexane–EtOAc, 98 : 2); ν_{max}(neat)/cm^{-1} 2240 (CN), 1746

(C=O) and 1608 (C=C); δ_H(200 MHz, $CDCl_3$) 1.22 (3 H, t, J = 7.2 Hz, *Me*CH_2OCO), 1.79 (3 H, s, *Me*C(CO_2Et)(CN)), 3.81 (3 H, s, *Me*OAr), 4.21 (2 H, q, J = 7.2 Hz, Me*CH_2*OCO), 5.42 (1 H, s, ArC=CH), 5.63 (1 H, s, ArC=CH), 6.85 (2 H, d, J = 8.7 Hz, Ar) and 7.22 (2 H, d, J = 8.7 Hz, Ar); δ_C(50 MHz, $CDCl_3$) 13.76, 23.19, 48.87, 55.24, 63.08, 113.62 (2 C), 118.10, 119.41, 129.20 (2 C), 130.39, 143.92, 159.60 and 167.85; *m/z* (EI) 260 (M^+ + 1, 3.8%), 259 (20), 244 (3), 233 (4), 186 (17), 172 (10), 144 (13), 135 (28), 133 (100), 121 (28), 108 (24), 91 (10), 89 (12) and 77 (22).

Diethyl (1-[phenyl]vinyl)malonate 5n. Procedure as described for the preparation of **5a**. After the usual workup, the residue was purified by column chromatography on silica using hexane–EtOAc (95 : 5) as eluent to give the styrene **5n** (65%) and diethyl (1-phenyl-2-thiomethyl)ethylmalonate **11b** (15%).

*Data for diethyl (1-[phenyl]vinyl)malonate **5n**.* (Found: M^+ + Na, 285.1101. $C_{15}H_{18}O_4Na$ requires M^+ + Na, 285.1103); R_f 0.55 (hexane–EtOAc, 90 : 10); ν_{max}(neat)/cm^{-1} 1736 (C=O) and 1631 (Ar); δ_H(200 MHz, $CDCl_3$) 1.24 (6 H, t, J = 7.2 Hz, 2 × *Me*CH_2OCO), 4.21 (4 H, q, J = 7.2 Hz, 2 × Me*CH_2*OCO), 4.62 (1 H, s, *H*C(CO_2Et)$_2$), 5.42 (1 H, s, PhC=C*H*), 5.64 (1 H, s, PhC=C*H*) and 7.28–7.44 (m, 5 H, Ph); δ_C(50 MHz, $CDCl_3$) 13.66 (2 C), 56.88, 61.47 (2 C), 117.35, 125.96 (2 C), 127.69, 128.17 (2 C), 139.89, 140.47 and 167.61 (2 C); *m/z* (ESI) 285 (M^+ + Na, 100%), 115 (74) and 99 (28).

*Data for diethyl (1-phenyl-2-thiomethyl)ethylmalonate **11b**.* (Found: M^+ + Na, 333.1126. $C_{16}H_{22}O_4SNa$ requires M^+ + Na, 333.1137); R_f 0.50 (hexane–EtOAc, 90 : 10); ν_{max}(neat)/cm^{-1} 1732 (C=O); δ_H(200 MHz, $CDCl_3$) 0.93 (3 H, t, J = 7.2 Hz, *Me*CH_2OCO), 1.26 (3 H, t, J = 7.2 Hz, *Me*CH_2OCO), 1.96 (3 H, s, SMe), 2.78 (1 H, dd, J = 8.8 and 13.2 Hz, C*H_A*H_BSMe), 2.92 (1 H, dd, J = 4.6 and 13.2 Hz, CH_A*H_B*SMe), 3.63 (1 H, dt, J = 4.6 and 10.2 Hz, C*H*Ph), 3.77 (1 H, d, J = 10.4 Hz, *H*C(CO_2Et)$_2$), 3.88 (2 H, q, J = 7.2 Hz, Me*CH_2*OCO), 4.22 (2 H, q, J = 7.2 Hz, Me*CH_2*OCO) and 7.20–7.32 (m, 5 H, Ph); δ_C(50 MHz, $CDCl_3$) 13.57, 13.94, 15.85, 38.68, 44.96, 57.25, 61.19, 61.59, 127.26, 128.25 (2 C), 129.31 (2 C), 139.61, 167.37, 168.05; *m/z* (ESI) 333 (M^+ + Na, 100%), 161 (23), 124 (79), and 77 (68).

Diethyl (1-[4-methoxyphenyl]vinyl)malonate 5o. Procedure as described for the preparation of **5a**. After the usual workup, the residue was purified by column chromatography on silica using hexane–EtOAc (95 : 5) as eluent to give the vinyl silane **50** (61%) and diethyl (1-[4-methoxyphenyl]-2-thiomethyl)ethylmalonate **11c** (20%).

*Data for diethyl (1-[4-methoxyphenyl]vinyl)malonate **5o**.* (Found: M^+ + Na, 315.1219. $C_{16}H_{20}O_5Na$ requires M^+ + Na, 315.1208); R_f 0.45 (hexane–EtOAc, 90 : 10); ν_{max}(neat)/cm^{-1} 1734 (C=O) and 1608 (Ar); δ_H(200 MHz, $CDCl_3$) 1.24 (6 H, t, J = 7.2 Hz, 2 × *Me*CH_2OCO), 3.80 (3 H, s, –OCH_3), 4.21 (4 H, q, J = 7.2 Hz, 2 × Me*CH_2*OCO), 4.59 (1 H, s, *H*C(CO_2Et)$_2$), 5.31 (1 H, s, ArC=C*H*), 5.56 (1 H, s, ArC=C*H*), 6.86 (2 H, d, J = 8.8 Hz, Ar) and 7.34 (2 H, d, J = 8.8 Hz, Ar); δ_C(50 MHz, $CDCl_3$) 13.77 (2 C), 55.02, 57.08, 61.52 (2 C), 113.56 (2 C), 115.85, 127.22 (2 C), 132.32, 139.95, 159.26 and 167.79 (2 C); *m/z* (ESI) 315 (M^+ + Na, 8%) and 99 (100).

*Data for diethyl (1-[4-methoxyphenyl]-2-thiomethyl)ethylmalonate **11c**.* (Found: M^+ + Na, 363.1246. $C_{17}H_{24}O_5SNa$ requires M^+ + Na, 363.1242); R_f 0.38 (hexane–EtOAc, 90 : 10); ν_{max}(neat)/cm^{-1} 1743 (C=O); δ_H(200 MHz, $CDCl_3$) 0.99 (3 H, t, J = 7 Hz, *Me*CH_2OCO), 1.28 (3 H, t, J = 7.2 Hz, *Me*CH_2OCO), 1.98 (3 H, s, SMe), 2.75(1 H, dd, J = 4 and 13.2 Hz, C*H_A*H_BSMe), 2.90 (1 H, dd, J = 4.4 and 13.2 Hz, CH_A*H_B*SMe), 3.62 (1 H, dt, J = 6.6 and 10 Hz, C*H*Ar), 3.74 (1 H, d, J = 10 Hz, *H*C(CO_2Et)$_2$), 3.77 (3 H, s, ArO*Me*), 3.92 (2 H, q, J = 7 Hz, Me*CH_2*OCO), 4.22 (2 H, q, J = 7.2 Hz, Me*CH_2*OCO), 6.83 (2 H, d, J = 8.6 Hz, Ar) and 7.16 (2 H, d, J = 8.6 Hz, Ar); δ_C(50 MHz, $CDCl_3$) 13.76, 14.05, 15.96, 38.92, 44.25, 55.15, 57.54, 61.28, 61.66, 113.71 (2 C), 129.39 (2 C), 131.61, 158.73, 167.54, 168.21; *m/z* (ESI) 363 (M^+ + Na, 70%), 181 (100), 159 (15) and 79 (8).

Diethyl (1-[4-bromophenyl]vinyl)malonate 5p. Procedure as described for the preparation of **5a**. After the usual workup, the residue was purified by column chromatography on silica using hexane–EtOAc (95 : 5) as eluent to give the styrene **5p** (66%) and diethyl (1-[4-bromophenyl]-2-thiomethyl)ethylmalonate **11d** (7%).

*Data for diethyl (1-[4-bromophenyl]vinyl)malonate **5p**.* (Found: M^+ + Na, 363.0210. $C_{15}H_{17}O_4BrNa$ requires M^+ + Na, 363.0208); ν_{max}(neat)/cm^{-1} 1734 (C=O); δ_H(200 MHz, $CDCl_3$) 1.23 (6 H, t, J = 7.2 Hz, 2 × *Me*CH_2OCO), 4.20 (4 H, q, J = 7.2 Hz, 2 × Me*CH_2*OCO), 4.55 (1 H, s, *H*C(CO_2Et)$_2$), 5.43 (1 H, s, ArC=C*H*), 5.61 (1 H, s, ArC=C*H*), 7.27 (2 H, d, J = 8.5 Hz, Ar) and 7.45 (2 H, d, J = 8.5 Hz, Ar); δ_C(50 MHz, $CDCl_3$) 13.86 (2 C), 57.00, 61.79 (2 C), 118.38, 121.95, 127.93 (2 C), 131.43 (2 C), 138.96, 139.69 and 167.59 (2 C); *m/z* (ESI) 365 (^{81}Br M^+ + Na, 60%), 363 (^{79}Br M^+ + Na, 54) and 99 (100).

*Data for diethyl (1-[4-bromophenyl]-2-thiomethyl)ethylmalonate **11d**.* (Found: M^+ + Na, 411.0258. $C_{16}H_{21}O_4BrSNa$ requires M^+ + Na, 411.0242); R_f 0.30 (hexane–EtOAc, 95 : 5); ν_{max}(neat)/cm^{-1} 1730 (C=O); δ_H(200 MHz, $CDCl_3$) 1.00 (3 H, t, J = 7 Hz, *Me*CH_2OCO), 1.28 (3 H, t, J = 7 Hz, *Me*CH_2OCO), 1.99 (3 H, s, SMe), 2.74 (1 H, dd, J = 9 and 13 Hz, C*H_A*H_BSMe), 2.91 (1 H, dd, J = 4.4 and 13 Hz, CH_A*H_B*SMe), 3.62 (1 H, dt, J = 4.4 and 9 Hz, C*H*Ar), 3.74 (1 H, d, J = 10.2 Hz, *H*C(CO_2Et)$_2$), 3.93 (2 H, q, J = 7 Hz, Me*CH_2*OCO), 4.23 (2 H, q, J = 7 Hz, Me*CH_2*OCO), 7.13 (2 H, d, J = 8.4 Hz, Ar) and 7.43 (2 H, d, J = 8.4 Hz, Ar); δ_C(50 MHz, $CDCl_3$) 13.67, 13.98, 15.92, 38.45, 44.36, 56.96, 61.40, 61.75, 121.22, 130.10 (2 C), 131.41 (2 C), 138.73, 167.21, 167.82; *m/z* (ESI) 413 (^{81}Br M^+ + Na, 36%), 411 (^{79}Br M^+ + Na, 42), 231 (24), 239 (36), 156 (21), 124 (27), 99 (100) and 77 (36).

Diethyl (1-[4-nitrophenyl]vinyl)malonate 5q. Procedure as described for the preparation of **5a**. After the usual workup, the residue was purified by column chromatography on silica using hexane–EtOAc (95 : 5) as eluent to give the styrene **5q** (46%) and diethyl (1-[4-nitrophenyl]-2-thiomethyl)ethylmalonate **11e** (8%).

*Data for diethyl (1-[4-nitrophenyl]vinyl)malonate **5q**.* (Found: M^+ + Na, 330. 0953. $C_{15}H_{17}O_6NNa$ requires M^+ + Na, 330.0954); R_f 0.46 (hexane–EtOAc, 90 : 10); ν_{max}(neat)/cm^{-1} 1740 (C=O); δ_H(200 MHz, $CDCl_3$) 1.24 (6 H, t, J = 7.2 Hz, 2 × *Me*CH_2OCO), 4.22 (4 H, q, J = 7.2 Hz, 2 × Me*CH_2*OCO), 4.59 (1 H, s, *H*C(CO_2Et)$_2$), 5.61 (1 H, s, ArC=C*H*), 5.75 (1 H, s, ArC=C*H*), 7.57 (2 H, d, J = 8.8 Hz, Ar) and 8.19 (2 H, d, J = 8.8 Hz, Ar); δ_C(50 MHz, $CDCl_3$) 13.71 (2 C), 56.73, 61.85 (2 C), 121.16, 123.46 (2 C), 127.16 (2 C), 139.07, 146.35, 147.09, 167.17 (2 C); *m/z* (ESI) 330 (M^+ + Na, 100%), 308 (41), 262 (33), 216 (75), 159 (12), 156 (41) and 79 (12).

*Data for diethyl (1-[4-nitrophenyl]-2-thiomethyl)ethylmalonate **11e**.* (Found: M^+ + Na, 378.0982. $C_{16}H_{21}O_6NSNa$ requires M^+ + Na, 378.0987); R_f 0.35 (hexane–EtOAc, 90 : 10); ν_{max}(neat)/cm^{-1} 1737 (C=O); δ_H(200 MHz, $CDCl_3$) 1.01 (3 H, t, J = 7 Hz, *Me*CH_2OCO), 1.29 (3 H, t, J = 7.2 Hz, *Me*CH_2OCO), 2.02 (3 H, s, SMe), 2.79 (1 H, dd, J = 7.6 and 13 Hz, C*H_A*H_BSMe), 2.95 (1 H, d, J = 13 Hz, CH_A*H_B*SMe), 3.73–3.83 (2 H, m, C*H*Ar and *H*C(CO_2Et)$_2$), 3.95 (2 H, q, J = 7.2 Hz, Me*CH_2*OCO), 4.25 (2 H, q, J = 7 Hz, Me*CH_2*OCO), 7.44 (2 H, d, J = 8.6 Hz, Ar) and 8.18 (2 H, d, J = 8.6 Hz, Ar); δ_C(50 MHz, $CDCl_3$) 13.73, 13.99, 15.96, 38.23, 44.60, 56.61, 61.64, 62.00, 123.51 (2 C), 129.44 (2 C), 147.15, 147.54, 166.97, 167.53; *m/z* (ESI) 378 (M^+ + Na, 1%), 164 (23) and 104 (100).).

Diethyl (1-[3-methoxyphenyl]vinyl)malonate 5r. Procedure as described for the preparation of **5a**. After the usual workup, the residue was purified by column chromatography on silica using hexane–EtOAc (95 : 5) as eluent to give the styrene **5r** (46%) and diethyl (1-[3-methoxyphenyl]-2-thiomethyl)ethylmalonate **11j** (8%).

Data for diethyl (1-[3-methoxyphenyl]vinyl)malonate ***5r***. (Found: $M^+ + Na$, 315.1206. $C_{16}H_{20}O_5Na$ requires $M^+ + Na$, 315.1208); R_f 0.46 (hexane–EtOAc, 90 : 10); ν_{max}(neat)/cm^{-1} 1734 (C=O); δ_H(200 MHz, $CDCl_3$) 1.24 (6 H, t, $J = 7.2$ Hz, 2 × *Me*CH_2OCO), 3.81 (3 H, s, OMe), 4.21 (4 H, q, $J = 7.2$ Hz, 2 × Me*CH*$_2$OCO), 4.60 (1 H, s, *H*C($CO_2Et)_2$), 5.42 (1 H, s, ArC=C*H*), 5.64 (1 H, s, ArC=C*H*), 6.84 (1 H, dd, $J = 2$ and 7.8 Hz, Ar), 6.96 (1 H, d, $J = 1.2$ Hz, Ar), 6.98 (1 H, d, $J = 7.7$ Hz, Ar), and 7.24 (1 H, t, $J = 7.8$ Hz, Ar); δ_C(50 MHz, $CDCl_3$) 13.93 (2 C), 55.19, 57.12, 61.75 (2 C), 112.05, 113.39, 117.78, 118.64, 129.38, 140.53, 141.68, 159.55, 167.85 (2 C); *m/z* (ESI) 315 ($M^+ + Na$, 31%), 201 (100), 173 (70), and 145 (84).

Data for diethyl (1-[3-methoxyphenyl]-2-thiomethyl)ethylmalonate ***11j***. (Found: $M^+ + Na$, 363.1237. $C_{17}H_{24}O_5SNa$ requires $M^+ + Na$, 363.1242); R_f 0.35 (hexane–EtOAc, 90 : 10); ν_{max}(neat)/cm^{-1} 1738 (C=O); δ_H(200 MHz, $CDCl_3$) 0.98 (3 H, t, $J = 7.2$ Hz, *Me*CH_2OCO), 1.27 (3 H, t, $J = 7.2$ Hz, *Me*CH_2OCO), 1.98 (3 H, s, SMe), 2.72–2.98 (2 H, m, CH_2SMe), 3.55–3.67 (1 H, m, C*H*Ar), 3.75 (1 H, d, $J = 8$ Hz, *H*C($CO_2Et)_2$), 3.78 (3 H, s, ArO*Me*), 3.92 (2 H, q, $J = 7.2$ Hz, Me*CH*$_2$OCO), 4.22 (2 H, q, $J = 7$ Hz, Me*CH*$_2$OCO), 6.75–6.85 (3 H, m, Ar) and 7.18 (1 H, d, $J = 8.8$ Hz, Ar); δ_C(50 MHz, $CDCl_3$) 13.62, 13.95, 15.91, 38.61, 44.95, 55.04, 57.21, 61.22, 61.60, 112.50, 114.24, 120.56, 129.22, 141.26, 159.39, 167.36, 168.04; *m/z* (ESI) 363 ($M^+ + Na$, 79%), 319 (13), 249 (90), 181 (100), 179 (20) and 134 (13).

Diethyl (1-[3-chlorophenyl]vinyl)malonate 5s. Procedure as described for the preparation of **5a**. After the usual workup, the residue was purified by column chromatography on silica using hexane–EtOAc (95 : 5) as eluent to give the styrene **5s** (46%) and diethyl (1-[3-chlorophenyl]-2-thiomethyl)ethylmalonate **11k** (8%).

Data for diethyl (1-[3-chlorophenyl]vinyl)malonate ***5s***. (Found: $M^+ + Na$, 319.0717. $C_{15}H_{17}O_4ClNa$ requires $M^+ + Na$, 319.0713); ν_{max}(neat)/cm^{-1} 1733 (C=O); δ_H(200 MHz, $CDCl_3$) 1.24 (6 H, t, $J = 7.2$ Hz, 2 × *Me*CH_2OCO), 4.22 (4 H, q, $J = 7.2$ Hz, 2 × Me*CH*$_2$OCO), 4.55 (1 H, s, *H*C($CO_2Et)_2$), 5.46 (1 H, s, ArC=C*H*), 5.63 (1 H, s, ArC=C*H*), 7.27 (3 H, s, broad, Ar), 7.40 (1 H, s, Ar); δ_C(50 MHz, $CDCl_3$) 13.85 (2 C), 56.98, 61.80 (2 C), 118.93, 124.45, 126.54, 127.89, 129.58, 134.25, 139.57, 141.97, 167.51 (2 C); *m/z* (ESI) 319 ($M^+ + Na$, 11%), 205 (100), 177 (28), and 149 (20).

Data for diethyl (1-[3-chlorophenyl]-2-thiomethyl)ethylmalonate ***11k***. (Found: $M^+ + Na$, 367.0752. $C_{16}H_{21}O_4ClSNa$ requires $M^+ + Na$, 367.0747); ν_{max}(neat)/cm^{-1} 1740 (C=O); δ_H(200 MHz, $CDCl_3$) 1.00 (3 H, t, $J = 7$ Hz, *Me*CH_2OCO), 1.28 (3 H, t, $J = 7.2$ Hz, *Me*CH_2OCO), 2.00 (3 H, s, SMe), 2.77 (1 H, dd, $J = 8.8$ and 13.2 Hz, CH_AH$_B$SMe), 2.92 (1 H, dd, $J = 4.4$ and 13.2 Hz, CH$_A$*H*$_B$SMe), 3.58–3.72 (1 H, m, C*H*Ar), 3.75 (1 H, d, $J = 10$ Hz, *H*C($CO_2Et)_2$), 3.91 (2 H, q, $J = 7$ Hz, Me*CH*$_2$OCO), 4.23 (2 H, q, $J = 7.2$ Hz, Me*CH*$_2$OCO) and 7.14–7.26 (4 H, m, Ar); δ_C(50 MHz, $CDCl_3$) 13.57, 13.91, 15.84, 38.35, 44.57, 56.87, 61.32, 61.67, 126.62, 127.41, 128.50, 129.48, 133.99, 141.79, 167.11, 167.72; *m/z* (ESI) 367 ($M^+ + Na$, 5%), 255 (11), 253 (100) and 185 (55).

Diethyl 2-(1-thiomethyl)butylmalonate 11l. Procedure as described for the preparation of **5a**. After the usual workup, the residue was purified by column chromatography on silica using hexane–EtOAc (95 : 5) as eluent. The residue on short path distillation gave diethyl (*E*)-1-propenylmalonate **12** (55%) and diethyl 2-(1-thiomethyl)butylmalonate **11l** (25%).

*Data for diethyl (E)-1-propenylmalonate****12***. Bp 100 °C (bath)/0.3 mmHg; (found: $M^+ + Na$, 223.0941. $C_{10}H_{16}O_4Na$ requires $M^+ + Na$, 223.0946); R_f 0.35 (hexane–EtOAc, 95 : 5); ν_{max}(neat)/cm^{-1} 1734 (C=O) and 972 (*trans* C=C); δ_H(200 MHz, $CDCl_3$) 1.29 (6 H, t, $J = 7.2$ Hz, 2 × *Me*CH_2OCO), 1.74 (3 H, d, $J = 4.4$ Hz, *Me*CH=CH), 3.96 (1 H, dd, $J = 5.8$, 2.4 Hz, *H*C($CO_2Et)_2$), 4.19 (4 H, q, $J = 7.2$ Hz, 2 × Me*CH*$_2$OCO), 5.55–5.77 (2 H, m, CH=CH); δ_C(50 MHz, $CDCl_3$) 14.00 (2 C), 17.98, 55.72, 61.54 (2 C), 122.51, 131.67, 168.47 (2 C); *m/z* (ESI) 223 ($M^+ + Na$, 100%), 166 (15) and 164 (50).

Data for diethyl 2-(1-thiomethyl)butylmalonate ***11l***. Bp 125–130 °C (bath)/0.3 mmHg; (found: $M^+ + Na$, 285.1145. $C_{12}H_{22}O_4SNa$ requires $M^+ + Na$, 285.1137); R_f 0.35 (hexane–EtOAc, 95 : 5); ν_{max}(neat)/cm^{-1} 1733 (C=O); δ_H(200 MHz, $CDCl_3$) 0.92 (3 H, t, $J = 7.4$ Hz, *Me*CH_2), 1.26 (6 H, t, $J = 7.2$ Hz, 2 × *Me*CH_2OCO), 1.46–1.62 (2 H, m, Me*CH*$_2$), 2.08 (3 H, s, SMe), 2.18–2.34 (1 H, m, MeCH$_2$*CH*), 2.50–2.70 (2 H, m, *CH*$_2$SMe), 3.65 (1 H, d, $J = 6.6$ Hz, *H*C($CO_2Et)_2$), 4.19 (4 H, q, $J = 7.2$ Hz, 2 × Me*CH*$_2$OCO); δ_C(50 MHz, $CDCl_3$) 11.14, 14.03 (2 C), 15.89, 23.33, 35.83, 39.43, 53.77, 61.21 (2 C), 168.77 (2 C); *m/z* (ESI) 285 ($M^+ + Na$, 31%), 200 (12), 168 (24), 166 (35), 164 (100), 159 (32), 104 (15), 99 (38) and 73 (84).

Ethyl 2-cyano-3-(4-methoxyphenyl)-but-3-enoate 5t. Procedure as described for the preparation of **5a**. After the usual workup, the residue was purified by column chromatography on silica using hexane–EtOAc (95 : 5) as eluent to give ethyl 2-cyano-3-(4-methoxyphenyl)-but-3-enoate **5t** (37%), ethyl (*E*)-2-cyano-3-(4-methoxyphenyl)-but-2-enoate *E*-**10i** (14%) and ethyl (*Z*)-2-cyano-3-(4-methoxyphenyl)-but-2-enoate *Z*-**10i** (4%).

Data for ethyl 2-cyano-3-(4-methoxyphenyl)-but-3-enoate ***5t***. (Found: $M^+ + H$, 246.1126. $C_{14}H_{16}O_3N$ requires $M^+ + H$, 246.1130); R_f 0.45 (hexane–EtOAc, 90 : 10); δ_H(200 MHz, $CDCl_3$) 1.23 (3 H, t, $J = 7$ Hz, *Me*CH_2OCO), 3.79 (3 H, s, OMe), 4.20 (2 H, q, $J = 7$ Hz, Me*CH*$_2$OCO), 4.59 (1 H, s, *H*C(CO_2Et)CN), 5.31 (1 H, s, ArC=CH), 5.55 (1 H, s, ArC=CH), 6.85 (2 H, d, $J = 8.8$ Hz, Ar), 7.34 (2 H, d, $J = 8.8$ Hz, Ar); δ_C(50 MHz, $CDCl_3$) 13.92, 55.21, 57.23, 61.69, 113.70 (2 C), 116.07, 127.37 (2 C), 132.50, 140.04, 159.36, 167.96 (2 C); *m/z* (ESI) 246 ($M^+ + H$, 3%), 201 (68), 200 (100) and 158 (13).

Data for ethyl (E)-2-cyano-3-(4-methoxyphenyl)-but-2-enoate ***E-10i***. (Found: $M^+ + Na$, 268.0940. $C_{14}H_{15}O_3NNa$ requires $M^+ + Na$, 268.0950); R_f 0.35 (hexane–EtOAc, 90 : 10); ν_{max}(neat)/cm^{-1} 2222 (CN), 1726 (C=O) and 1605 (C=C); δ_H(200 MHz, $CDCl_3$) 1.37 (3 H, t, $J = 7.2$ Hz, *Me*CH_2OCO), 2.67 (3 H, s, C=CMe), 3.84 (3 H, s, OMe), 4.32 (2 H, q, $J = 7.2$ Hz, Me*CH*$_2$OCO), 6.95 (2 H, d, $J = 8.8$ Hz, Ar), 7.46 (2 H, d, $J = 8.8$ Hz, Ar); δ_C(50 MHz, $CDCl_3$) 13.63, 22.60, 54.89, 61.34, 102.88, 113.49 (2 C), 116.47, 128.99 (2 C), 131.65, 161.09, 162.12, 171.46; *m/z* (ESI) 268 ($M^+ + Na$, 100%), 200 (77) and 99 (58).

Data for ethyl (Z)-2-cyano-3-(4-methoxyphenyl)-but-2-enoate ***Z-10i***. R_f 0.30 (hexane–EtOAc, 90 : 10); ν_{max}(neat)/cm^{-1} 2221 (CN), 1735 (C=O) and 1605 (C=C); δ_H(200 MHz, $CDCl_3$) 1.18 (3 H, t, $J = 7.2$ Hz, *Me*CH_2OCO), 2.53 (3 H, s, C=CMe), 3.82 (3 H, s, OMe), 4.13 (2 H, q, $J = 7.2$ Hz, Me*CH*$_2$OCO), 6.89 (2 H, d, $J = 8.8$ Hz, Ar), 7.17 (2 H, d, $J = 8.8$ Hz, Ar); δ_C(50 MHz, $CDCl_3$) 13.47, 26.05, 54.98, 61.45, 104.19, 113.28 (2 C), 115.78, 128.37 (2 C), 130.30, 160.73, 161.60, 168.74.

2-(2-Methylphenyl)tetrahydrothiophene 25[19]**.** Procedure as described for the preparation of **5a** except sulfonium bromide **22** was used instead of Me_3SI. Yield: 82%; R_f 0.20 (hexane); δ_H(200 MHz, $CDCl_3$) 1.86–2.14 (2 H, m, CH_2), 2.20–2.40 (2 H, m, CH_2), 2.38 (3 H, s, Ar*Me*), 2.95–3.05 (1 H, m, SCH_AH$_B$), 3.06–3.25 (1 H, m, SCH$_A$*H*$_B$), 4.74 (1 H, t, $J = 7.5$ Hz, SC*H*Ar), 7.11–7.24 (3 H, m, Ar), 7.60 (1 H, d, $J = 7.3$ Hz, Ar).

2-(2-Methylphenyl)tetrahydro-2*H*-thiopyran 26[19]**.** Procedure as described for the preparation of **5a** except sulfonium bromide **23** was used instead of Me_3SI. Yield: 71%; R_f 0.30 (hexane); δ_H(200 MHz, $CDCl_3$) 1.42–1.85 (2 H, m, CH_2), 1.95–2.12 (4 H, m, 2 × CH_2), 2.42 (3 H, s, Ar*Me*), 2.67 (1 H, d, broad, $J = 14$ Hz, SCH_AH$_B$), 2.90 (1 H, dt, $J = 2.2$ and 12 Hz, SCH$_A$*H*$_B$), 4.01 (1 H, dd, $J = 3.2$ and 10 Hz, SC*H*Ar), 7.08–7.24 (3 H, m, Ar), 7.39 (1 H, d, $J = 6.8$ Hz, Ar); δ_C(50 MHz, $CDCl_3$) 19.17, 26.94, 27.41, 31.01, 34.38, 43.36, 126.30, 126.60, 126.88, 130.32, 135.41, 140.74.

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