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A novel reaction of dimethylsulfonium methylide with Michael acceptors: application to the synthesis of difficultly accessible vinyl silanes and styrenes†

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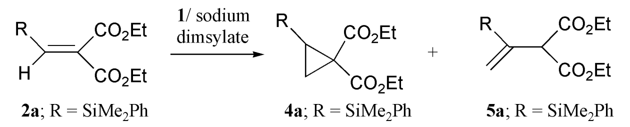
Rather than the usual cyclopropanation and Peterson-type olefination, conditions for a novel elimination reaction from the adduct of dimethylsulfonium methylide and 2-silylalkylidene/arylidene malonate/cyanoacetate/phosphonoacetate leading to geminally substituted vinyl silanes or styrenes, respectively, have been established.

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 can also add to Michael acceptors in 1,4-fashion to provide cyclopropanes.[1] Thus, the reaction of the 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 modes of reaction of intermediate **3** are elimination with a loss of proton resulting in formation of an olefin **5** (path 'b'), and a Peterson-type olefination (R = silyl group) with loss of the silyl group 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. We found that under specific reaction conditions and depending upon the substituents (R, E_1 and E_2) on **2**, the formation of **5** could be made exclusive.

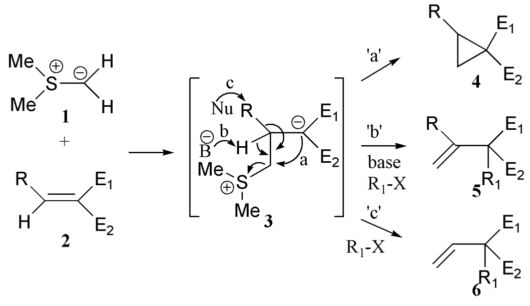
Recently, we have developed a method for the preparation of the 2-silyl alkylidene malonate **2a** and used as a Michael acceptor in the preparation of a functionalised β-silyl ketone.[4] When **2a** was reacted with **1**, generated from trimethylsulfonium iodide[1] and sodium dimsylate (1 equiv.) in DMSO–THF (70:30) at 0 °C, we obtained the anticipated product, cyclopropane **4a** (Table 1; entry 1). Surprisingly, when the amount of base was increased (1.5 equiv.), the formation of vinyl silane **5a** could be found in addition to cyclopropane **4a** (entry 2). The formation of **5a** was highly solvent dependent as shown in Table 1. With increasing the amount of THF into the reaction mixture, the formation of **5a** also proportionately increased and the reactions became cleaner as indicated by the combined isolated yields of **4a** and **5a**. Interestingly, using a combination of DMSO–THF (30:70) and 2.5 equiv. of sodium dimsylate (entry 8), **5a** was the sole product, isolated in 66% yield. It was also gratifying to note that **5a** formed exclusively from the adduct **3** (Scheme 1; R = $PhMe_2Si$, E_1 = E_2 = CO_2Et) where the elimination of a proton and dimethyl sulfide was favored over the loss of a silyl group in a Peterson-type elimination. In addition, one-pot olefination–alkylation protocol was devised using 1.2 equiv. of trimethylsulfonium iodide and 2.5 equiv. of sodium dimsylate, and quenching the reaction with alkyl halides leading to functionalised vinyl silanes **5b–e** in good yields as shown in Scheme 2. It is worth mentioning that these type of vinyl silanes are important intermediates in organic syntheses[5–8] and there has been no reported general access to 1,1-disubstituted vinyl silanes.[9]

Table 1 Effect of solvent and base on cyclopropanation



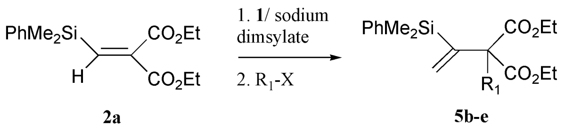
Entry	DMSO/THF	Equiv. base	4a/5a[a]	% Yield[b]
1	70:30	1.0	>99:0	55
2	70:30	1.5	98:2	40
3	70:30	2.5	0:>99	27
4	60:40	1.5	96:4	51
5	40:60	1.5	87:13	55
6	30:70	1.5	76:24	60
7	30:70	1.0	>99:0	36
8	30:70	2.5	0:>99	66

[a] Ratio determined by GC. [b] Combined isolated yield of **4a** and **5a**.



Scheme 1

At this stage we were not convinced whether the silyl ($PhMe_2Si$) substitution in **2a** was responsible for this preferred elimination over cyclopropanation. Therefore, the 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 **5f–i** exclusively in moderate to good yields as shown in Table 2. The poor yield of the styrene **5i** could be



R_1-X	Product	% Yield
Me-I	**5b**	80
Et-Br	**5c**	79
Allyl-Br	**5d**	60
Bn-Br	**5e**	64

Scheme 2

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† Electronic supporting information (ESI) available: general experimental. See http://www.rsc.org/suppdata/cc/b2/b211279e/

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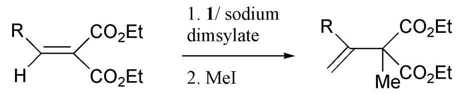
Table 2 Preparation of substituted styrenes



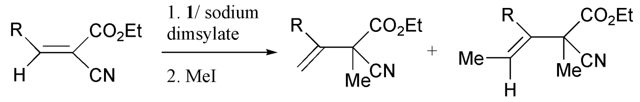
2b-e **5f-i**

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

due to the polymerization of the substrate **2e** 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.

Our next interest was to study the influence of activating groups on the Michael acceptor **2**. The silyl substituted alkylidene cyanoacetate **2f** was prepared and subjected under similar protocol to give exclusively the desired vinyl silane **5j** (Table 3). Contrary to silyl substitution, the arylidene cyanoacetate **2g** gave the desired product **5k** along with a double alkylation product **7b** in a ratio of 6:4. The formation of **7b** could be explained as shown in Scheme 3. Due to the presence of CN group, the negative charge could delocalise between C-2 and C-4 in **8**.[10] Methylation at C-2 gave the styrene derivative **5k** while that at C-4 provided an intermediate **9**. The latter in the presence of excess base underwent allylic deprotonation, which on isomerization[11] followed by reaction with methyl iodide yielded **7b**. The *cis*-relationship between the Me and the Ar in **7b** was confirmed by 1D-NOE study (7.5% NOE enhancement was observed between olefinic proton and the C-2 Me). The selectivity (**5k** *vs.* **7b**) 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 **5k** albeit in poor yield by the addition of $MgBr_2$ into the reaction medium prior to the addition of methyl iodide. The reaction yields with the cyanoacetates **2f** and **2g** were modest possibly due to the polymerisation of the substrates. However, the polymeric materials being polar, the desired products could be isolated very easily. The substrate with a phosphonate activating group such as **2h** gave exclusively the desired styrene derivative **5l** in 50% yield by this method.

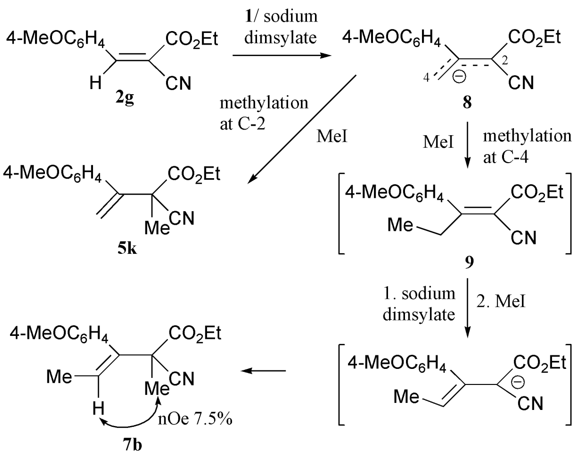
Table 3 Effect of activating group on the one-pot olefination–alkylation reaction



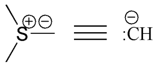
2 **5** **6**

X	R	Substrate	Products	Ratio **5/7**	%Yield
CN	$PhMe_2Si$	**2f**	**5j; 7a**	>99:0	28
CN	4-MeO-C_6H_4	**2g**	**5k; 7b**	64:36	60
CN	4-MeO-C_6H_4	**2g**	**5k; 7b**	65:35	55[a]
CN	4-MeO-C_6H_4	**2g**	**5k; 7b**	>99:0	17[b]
$P(O)(OEt)_2$	4-MeO-C_6H_4	**2h**	**5l; 7c**	>99:0	50

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



Scheme 3



1 **10**

Fig. 1

In conclusion, we have developed a novel application of dimethylsulfonium methylide for the general preparation of not readily accessible and synthetically valuable 1,1-disubstituted vinyl silanes, and substituted styrene derivatives from easily available activated olefins. This study also demonstrated that by varying conditions, the reactions could be tuned in either direction to give the vinyl silane or the cyclopropane exclusively. In these reactions, dimethylsulfonium methylide (**1**) acts as a synthetic equivalent of carbene anion **10** (Fig. 1). Since convenient methods for the generation of substituted sulfur ylides are known,[12] the present methodology might be extended for the preparation of highly substituted vinyl silanes and styrene derivatives.

Note added in proof. β-Silylethyl sulfoxides having β-carbonyl functionalities are known to give vinyl silanes. See ref. 13.

Notes and references

‡ Polar residue was not characterised.

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