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LETTERS

[2,3]-Sigmatropic rearrangement of allylic sulfur ylides derived from trimethylsilyldiazomethane (TMSD)

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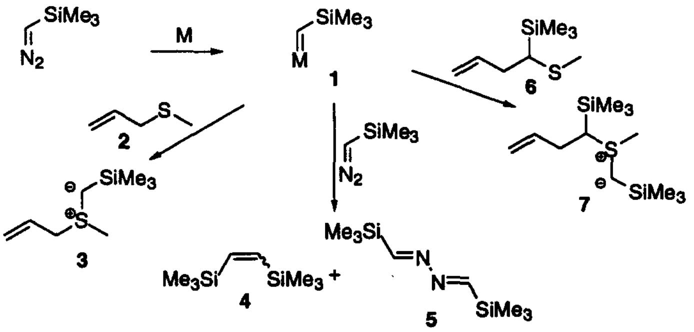
Abstract

Trimethylsilyldiazomethane reacts with allylic sulfides in the presence of catalytic quantities of $Rh_2(OAc)_4$ (1 mol%) to give homoallylic sulfides in good yields and with high diastereoselectivity. © 1999 Published by Elsevier Science Ltd. All rights reserved.

The [2,3]-sigmatropic rearrangement of sulfur ylides is a powerful synthetic method for creating new C–C bonds often with control of stereochemistry and alkene geometry.[1–3] There are two general methods for preparing sulfur ylides: deprotonation of the corresponding sulfonium salt or reaction of a sulfide with a diazocompound. In the latter method, most studies have used diazoesters due to their commercial availability, stability and potential for further manipulation of the ester moiety.[4] As trimethylsilyldiazomethane (TMSD)[5] has recently become commercially available, is also stable and has a useful functional handle for further manipulation, we decided to explore its potential for sulfur ylide formation and subsequent rearrangement. During the course of this work, van Vranken described a related study in which the focus of his work was to compare reactions of TMSD with ethyl diazoacetate (EDA).[6] In this paper we describe a simple method for the formation of silyl-substituted sulfur ylides using TMSD and the diastereo- and enantioselectivity of subsequent [2,3]-sigmatropic rearrangements.



Scheme 1.

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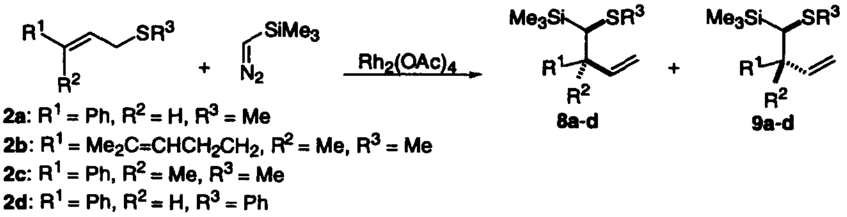


2a: $R^1 = Ph, R^2 = H, R^3 = Me$
2b: $R^1 = Me_2C{=}CHCH_2CH_2, R^2 = Me, R^3 = Me$
2c: $R^1 = Ph, R^2 = Me, R^3 = Me$
2d: $R^1 = Ph, R^2 = H, R^3 = Ph$

Scheme 2.

Table 1
Reaction of allyl sulfides with TMSD and $Rh_2(OAc)_4$

Entry	Allylic Sulfide	Amount of $Rh_2(OAc)_4$ (mol%)	Amount of TMSD (eq.)	Conditions	Yield (%)	**8**:**9**
1	**2a**	1	1.7	50°C, 2.5 h	58	90:10
2	**2a**	5	4.5	r.t., 5 d	90	91:9
3	**2a**	1	4.5	50°C, 18 h	90	90:10
4	**2b**	1	4.5	50°C, 18 h	80[a]	94:6
5	**2c**	1	4.5	50°C, 19 h	69	83:17
6	**2d**	1	4.5	50°C, 18 h	74	85:15

a: Pure material was afforded in 37% yield together with a mixture containing product (43%) and starting material

Reactions of diazocompounds with allyl sulfides to form sulfur ylides mediated by transition metal catalysts are often plagued by a number of side reactions. The intermediate metal carbene **1** can react with the allyl sulfide **2** to give the ylide **3** (reaction of interest) or more diazocompound to give alkenes **4** and azine **5**,[7] or with the homoallylic sulfide **6** (deriving from rearrangement of **3**) to give a new ylide **7** (Scheme 1). To promote the required reaction, slow addition of the diazocompound and an excess of sulfide are normally employed.[8] Indeed, in reaction of allylic sulfides, van Vranken employed slow addition of TMSD to obtain homoallylic sulfides in moderate yield. In our independent studies we combined the sulfide **2a**,[9] TMSD and $Rh_2(OAc)_4$ together and varied temperature and stoichiometry of TMSD (Scheme 2) and our results are summarised in Table 1. It was found that reactions at room temperature were very slow even with 5 mol% $Rh_2(OAc)_4$ but acceptable rates could be achieved at 50°C using only 1 mol% $Rh_2(OAc)_4$ (entries 1 and 2). For almost complete consumption of starting material, 4.5 equiv. of TMSD were required (entry 3) and under these conditions a high yield of the homoallylic sulfide was obtained.[10] We were surprised at the slow rate of reaction and the fact that a large excess of TMSD could be employed at the start of the reaction without significantly competing with ylide formation. Clearly this is due to the remarkable electronic stability of the diazocompound afforded by the TMS moiety and its large size (hence its slow rate). These features should significantly retard the rate of dimerisation of the diazocompound to form the silene **4** and the azine **5** (Scheme 1), and furthermore, demonstrate that the intermediate metal carbene is more reactive towards the sulfide than towards TMSD (the contrary is true for other diazocompounds). The generality of this protocol was tested with a range of allyl sulfides (entries 4–6) and good yields and high diastereoselectivities were obtained in all cases (vide infra). The stereochemistry of the major isomer **8a** from entry 3 was determined by X-ray analysis of the corresponding sulfone (Fig. 1).[11] Rearrangements of silyl substituted sulfonium ylides bearing *Z*-alkenes, generated by base treatment of the corresponding sulfonium salts, have been reported previously and high selectivity was obtained.[12,13] Usually, *E*-alkenes show much lower selectivity than *Z*-alkenes in [2,3]-sigmatropic rearrangements[14] but evidently with silyl-substituted sulfonium ylides high selectivity can be obtained in both cases.

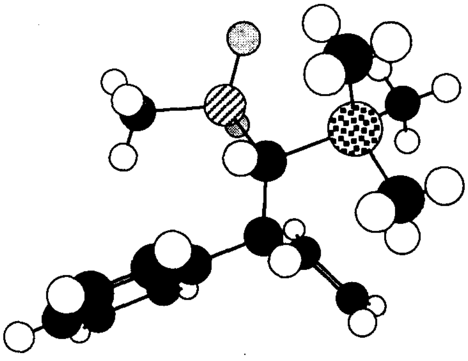


Figure 1.

The enantioselectivity of the rearrangement of substrate **2a** using chiral Rh/Cu catalysts was briefly examined (Table 2).[15] However, with all of the chiral catalysts only low enantioselectivity was observed (entries 2–6). Similarly, low enantioselectivity had been recently reported by Uemura[16] in [2,3]-sigmatropic rearrangements of allyl sulfides involving EDA although higher enantioselectivity has been reported by Katsuki[8] involving *t*-butyl diazoacetate and chiral salen-based cobalt catalysts. In contrast, high enantioselectivity has been achieved in rearrangements of allyl ethers involving EDA with chiral rhodium catalysts.[17] However, when we tested the reaction of *trans*-cinnamyl methyl ether with TMSD no reaction was observed with either $Rh_2(OAc)_4$ or $Rh_2(4S\text{-}MEOX)_4$ and $Rh_2(pfb)_4$ only gave the corresponding cyclopropane.[18] Evidently the allyl ether (which is less nucleophilic than the corresponding sulfide) is unable to react with the silyl-substituted metal carbene unless the carbene is made more electrophilic by using strongly electron withdrawing groups on the metal centre. Interestingly, the chemoselectivity of the reaction using $Rh_2(pfb)_4$ is opposite to that generally observed with $Rh_2(OAc)_4$ as cyclopropanation rather than ylide formation was observed. Using EDA and $Rh_2(OAc)_4$ with the same ether, a 73:27 ratio of products derived from ylide rearrangement and cyclopropanation was obtained.[17]

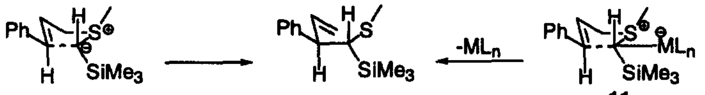
Comparing entries 1 and 2 (Table 2), it should be noted that there is a marked influence on the diastereoselectivity by the metal catalyst used. Similar observations have been made in rearrangements of allyl ethers with rhodium catalysts and imply that a metal-associated ylide is involved in the product forming step.[17] Our results show, for the first time, that metal-associated ylides are also involved in sulfur ylide rearrangements using rhodium catalysts (Scheme 3).[19] The diastereoselectivity can be rationalised by the envelope transition state **10**, in which the silyl group and the *E*-alkene substituent adopt pseudoequatorial positions (Scheme 3). Similar transition states have been invoked for [2,3]-

Table 2
Reaction of **2a** with TMSD and chiral catalysts

Entry	Catalyst[a]	Solvent	Conditions	Yield (%)	**8a**:**9a** [ee (%)]
1	$Rh_2(OAc)_4$	Toluene	50 °C, 18 h	90	90:10
2	$Rh_2(4S\text{-}MEOX)_4$	DCM	Reflux, 4.5 d	74	53(10):47(≤5)
3	$Rh_2(5S\text{-}MEPY)_4$	DCM	Reflux, 3.5 d	94	49(13):51(15)
4	$Rh_2(4S\text{-}MPPIM)_4$	DCM	Reflux, 4.5 d	73	68(≤5):32(≤5)
5	$Rh_2(S\text{-}DOSP)_4$	DCM	Reflux, 3.5 d	82	80(≤5):20(≤5)
6	$Cu(CH_3CN)_4PF_6$/Ox[b]	DCM	Reflux, 19 h	96	88(≤5):12(18)

a: 1 mol% of the metal catalyst and 4.5 eq. of TMSD were used in all reactions.
b: Ox = Isopropylidenebis[(4*S*)-4-*tert*-butyl-2-oxazoline]. 1.2 mol% of ligand used.

Wittig rearrangements and [2,3]-oxonium ylide rearrangements.[14] However, as we know that the metal is associated with the ylide, TS **11** might be a better representation of the species involved in the rearrangement.



10 **8a** **11**

Scheme 3.

In summary, we have discovered that TMSD is a suitable precursor for the formation of silyl-substituted sulfonium ylides and that, unlike other diazocompounds, no slow addition is required. High diastereoselectivity is obtained with a range of allyl sulfides but only low enantioselectivity is observed with a range of chiral metal catalysts.

Acknowledgements

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8. Using Co catalysts slow addition does not seem to be required: Fukuda, T.; Irie, R.; Katsuki, T. *Tetrahedron* **1999**, *55*, 649–664.
9. All the allylic sulfides were prepared from the corresponding halides by standard procedures. See, for example: Zheng, Y. F.; Dodd, D. S.; Oehlschager, A. C.; Hartman, P. G. *Tetrahedron* **1995**, *51*, 5255–5276.
10. Typical procedure: TMSD (1.23 mL of 1.8 M solution in hexanes, 2.2 mmol, 4.5 equiv.) was added to a solution of *trans*-cinnamyl methyl sulfide (81.1 mg, 0.49 mmol) and rhodium(II) acetate dimer (2.2 mg, 5 μmol, 0.01 equiv.) in toluene (1.75 mL). After stirring for 18 h at 50°C the solvent was removed under reduced pressure and the residue was purified by flash chromatography eluting with petroleum ether to give **8a** (99.4 mg, 81%) and **9a** (9.9 mg, 9%) as colourless liquids. **8a**: R_f 0.63 (5% ethyl acetate in petroleum ether); ν_{max} (CH_2Cl_2) 3080, 3028, 2957, 1600; δ_H (250 MHz; $CDCl_3$) 0.00 (9H, s), 1.55 (3H, s), 1.92 (1H, d, J=4.9), 3.70 (1H, dd, J=9.5, 4.9), 5.05–5.13 (2H, m), 6.31 (1H, ddd, J=16.8, 10.4, 9.5), 7.10–7.27 (5H, m); δ_C (63 MHz; $CDCl_3$) 1.7, 19.0, 43.1, 51.2, 116.1, 126.2, 127.9, 128.3, 139.7, 145.0; *m/z* (EI) 250 (M^+, 6), 133 (76), 130 (90), 129 (45), 105 (100), 73 (48) (Found: M^+, 250.1208. $C_{14}H_{22}SSi$ requires 250.1212). (Found: C, 67.27; H, 9.00. $C_{14}H_{22}SSi$ requires: C, 67.13; H, 8.85).
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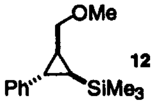
18. The cyclopropane **12** was obtained as the major product (35% yield) together with a significant amount of starting material from slow addition (2 d) of TMSD (4.5 equiv.) to a refluxing solution of the ether in DCM in the presence of 1 mol% of rhodium(II) perfluorobutyrate dimer [$Rh_2(pfb)_4$].



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19. In contrast, metal-free ylides are believed to be involved in sulfur ylide rearrangements using Co catalysts (Ref. 8) and the similar diastereoselectivity observed with a variety of Cu catalysts (Ref. 16) suggests that metal-free ylides are probably involved with this metal also.