SHORT PAPER

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$Sm/SmI_2/TiCl_4$(cat.) system promoted direct alkylidenating reaction of ketones with *gem*-dibromomethyl sulfones: a new method for preparation of alkylidene sulfones†

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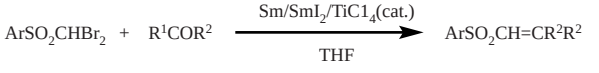
Alkylidene sulfones were prepared in moderate to good yields *via* direct alkylidenating reaction of ketones with geminal dibromomethyl sulfones promoted by the Sm/SmI_2 system in the presence of a catalytic amount of $TiCl_4$ under mild conditions.

Vinyl sulfones are important intermediates in various synthetic transformation.[1] Many methods have been developed for the preparation of vinyl sulfones, for example, the olefination of carbonyl compounds *via* the Wittig-Horner reaction[2] or the Peterson reaction,[3] selenosulfonation of olefins followed by the subsequent elimination,[4] the elimination reaction of β-halosulfones prepared from the addition of sulfonyl halides to olefins,[5] Knoevenagel condensation of aldehydes with sulfonylacetic acid esters followed by decarboxylation.[6] However, these methods suffer from some disadvantages in terms of the availability of the starting materials, reaction conditions, or laborious manipulation. Besides, some of these methods are limited to the preparation of arylidene sulfones only.

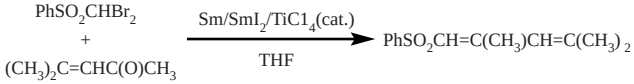
In last two decades, the reation of carbonyl groups with *gem*-dimetallic species has played a compensatory role in olefin synthesis.[7] It was reported that aldehyde-selective olefination could be performed by *gem*-dichromium reagents[8] and ester–carbonyl olefination was realized by the use of the Ti–Zn system.[9] However, to the best of our knowledge, there have been few reports on dimetallic reagents using lanthanoids as the key element. Most recently, Matsubara *et al*.[10] developed a convenient route for carbonyl olefination using the $Sm/SmI_2/CrCl_3$(cat.) system. Since low valent titanium is also an efficient reagent in forming olefins,[11] we tried to apply the $Sm/SmI_2/TiCl_4$(cat.) system to directly alkylidenate ketones with dibromomethyl sulfones. Fortuitously, the reaction gave alkylidene sulfones in moderate to good yields (Scheme 1). The reaction conditions and the results are summarized in Table 1.



1 **2** **3 (*E*/*Z*)**

Scheme 1

For efficent alkylidenation both low valent samarium and a titanium (IV) salt were indispensable. When only SmI_2 was used, the reaction gave β-arylsulfonyl alcohols while alkylidene sulfones were not detected (entry 1). Table 1 shows the combination of SmI_2 and Sm worked more effectively than the use of SmI_2 alone (by comparing entry **2** with **1**: Entry **4** with **3**). Treatment of *gem*-dibromomethyl sulfones with SmI_2 and Sm in the presence of $TiCl_4$ gave the best yield. Interestingly, when an α, β-unsaturated ketone 4-methyl-3-penten-2-one **4** was used, the reaction could also afford vinyl sulfone although the yield was not high (Scheme 2).



4 **5** (E/Z=70/30) Yield=40%.

Scheme 2

The mixtures of geometrical isomers from **3b** to **3i** could not be separated by TLC. However, the *E*/*Z* ratio of product was easily determined by ^1H NMR spectra since the characteristic chemical shift of C=C–CH_3 is about 2.10 ppm for *E* isomers while it is 1.85 ppm for *Z* isomers. For substrate **5**, two isomers could be well separated by TLC.

Although there are many methods for preparation of vinyl sulfones, little attention has been paid to synthesis of alkylidene sulfones. We herein provide a convenient route for preparation of alkylidene sulfones *via* direct alkylidenating reaction of ketones with *gem*-dibromo methyl sulfones promoted by the $Sm/SmI_2/TiCl_4$(cat.) system. The remarkable advantages of this procedure are its mild, neutral reaction conditions, easy availability of starting materials, simple operation and moderate to good yields.

Experimental section

Melting points are uncorrected. IR spectra were recorded on a PE-683 spectrometer, ^1H NMR spectra were obtained with a Bruker AC 80 MHz spectrometer (for compounds **3a** and **3j**) and a Bruker Avance 300 MHz spectrometer in $CDC1_3$ solution using TMS as the internal standard. Mass spectra were obtained on a HP 5989B mass spectrometer. Elemental analyses were performed on a Carlo Erba 1106 instrument. The reactions were performed in a Schlenk type glass apparatus under a nitrogen atmosphere. THF was freshly distilled from sodium-benzophenone ketyl prior to use.

General procedure for the synthesis of alkylidene sulfones: To a micture of Sm powder (0.30 g, 2.00 mmol), SmI_2 (0.1M in THF, 20 ml, 2.0 mmol), $TiC1_4$ (0.038g, 0.2mmol), was added a mixture of dibromomethyl sulfone (2.0 mmol) and ketone (1.0 mmol) in THF (4 ml) at room temperature under an inert atmosphere of nitrogen. The mixture was stirred for 2.5h at room temperature. The resulting mixture was treated with dilute HCl(0.1N, 5ml) and then extracted with ether (2 × 30ml) and dried over anhydrous $NaSO_4$. The solvent was removed *in vacuo*. The crude product was purified by preparative TLC on silica gel using cyclohexane-ethyl acetate (6:1) as eluent.

1-p-Tolysulfonyl methylidenecyclopentane **3a**: Oil. δ_H (ppm) 7.80 (d, 2H, *J*=8.0Hz, ArH), 7.31 (d, 2H, *J*=8.0Hz, ArH), 6.16 (s, 1H, C=CH), 2.40 (s, 3H, $ArCH_3$), 2.32–1.50 (m, 8H, 4×CH_2). ν_{max} (cm^{-1})

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† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1 Synthesis of alkylidene sulfones

Entry	Ar	R_1	R_2	Reagent (mmol)			Ratio	Yield(%)
				SmI_2	Sm	$TiC1_4$	(*E/Z*)[a]	
1	*p*-MeC_6H_4	$-(CH_2)_4-$		4	0	0		Not detected[c]
2	*p*-MeC_6H_4	$-(CH_2)_4-$		2	2	0		21
3	*p*-MeC_6H_4	$-(CH_2)_4-$		4	0	0.2		30
4	*p*-MeC_6H_4	$-(CH_2)_4-$		2	2	0.2		67(**3a**)
5	*p*-MeC_6H_4	Me	Et	2	2	0.2	60/40	81(**3b**)
6	*p*-MeC_6H_4	Me	*n*-Pr	2	2	0.2	63/37	75(**3c**)
7	*p*-MeC_6H_4	Me	*n*-Bu	2	2	0.2	65/35	72(**3d**)
8	*p*-MeC_6H_4	Me	*n*- C_5H_{11}	2	2	0.2	69/31	74(**3e**)
9	Ph	Me	Et	2	2	0.2	65/35	80(**3f**)
10	Ph	Me	*n*-Pr	2	2	0.2	66/34	73(**3g**)
11	Ph	Me	*n*-Bu	2	2	0.2	68/32	75(**3h**)
12	Ph	Me	*n*- C_5H_{11}	2	2	0.2	70/30	74(**3i**)
13	Ph	$-(CH_2)_4-$		2	2	0.2		65(**3j**)

[a]Ratio determined by ^1H NMR (300 MHz). [b]Isolated yields. [c]1-(Bromo-*p*-tolysulfonyl) methyl cyclopentanol was isolated in 50% yield.

3050, 1640. *m/z*, 236(M^+). Anal. calcd. for $C_{13}H_{16}O_2S$: C66.07; H 6.82. Found: C 66.30; H 6.88.

2-Methyl-1-p-tolysulfonyl-1-butene **3b**: Oil. δ_H (ppm) 7.76 (d, 2H, *J*=8.1Hz, ArH), 7.30 (d, 2H, *J*=8.1Hz, ArH), 6.12 (m, 1H, C=CH), 2.57(q, 0.4×2H, *J*=7.50Hz, Z-CH_2), 2.41 (s, 3H, $ArCH_3$), 2.16–2.09 (m, 0.60×2H+0.60×3H, *E*–CH_2, *E*–CH_3), 1.83 (s, 0.40×3H, Z-CH_3), 0.99 (t. 3H, *J*=7.50Hz, CH_3). ν_{max} (cm^{-1}) 3060, 1635. *m/z*, 224(M^+). Anal. calcd. for $C_{12}H_{16}O_2S$: C 64.25; H 7.19. Found: C 64.05; H 7.08.

2-Methyl-1-p-tolysulfonyl-1-pentene **3c**: Oil. δ_H (ppm) 7.77 (d, 2H, *J*=8.1Hz, ArH), 7.30 (d, 2H, *J*=8.1Hz, ArH), 6.15 (m, 1H, C=CH), 2.54(q, 0.37×2H, *J*=7.50Hz, Z-CH_2), 2.42 (s, 3H, $ArCH_3$), 2.09–2.05 (m, 0.63×2H+0.63×3H, *E*-CH_2, *E*-CH_3), 1.84 (s, 0.37×3H, Z-CH_3), 1.47–1.42 (m, 2H, CH_2), (t. 3H, J=7.50Hz, CH_3). ν_{max} (cm^{-1}) 3060, 1640. *m/z*, 238 (M^+). Anal. calcd. for $C_{13}H_{18}O_2S$: C 65.51; H 7.61. Found: C 65.22; H 7.48.

2-Methyl-1-p-tolysulfonyl-1-hexene **3d**: Oil. δ_H (ppm) 7.77 (d, 2H, *J*=8.1Hz, ArH), 7.32 (d, 2H, *J*=8.1Hz, ArH), 6.14 (m, 1H, C=CH), 2.53(q, 0.35x2H, *J*=7.50Hz, *Z*-CH_2), 2.42 (s, 3H, $ArCH_3$), 2.12–2.07 (m, 0.65×2H+0.65×3H, *E*-CH_2, E-CH_3), 1.85 (s, 0.35×3H, *Z*-CH_3), 1.48–1.24 (m, 4H, 2×CH_2), 0.90 (t. 3H, *J*=7.50 Hz, CH_3). ν_{max} (cm^{-1}) 3060, 1640. *m/z*, 252 (M^+). Anal. calcd. for $C_{14}H_{20}O_2S$: C 66.63; H 7.99. Found: C 66.73; H 7.88.

2-Methyl-1-p-tolysulfonyl-1-heptene **3e**: Oil. δ_H (ppm) 7.76 (d, 2H, *J*=8.1Hz, ArH), 7.31 (d, 2H, *J*=8.1Hz, ArH), 6.12 (m, 1H, C=CH), 2.53(q, 0.31×2H, *J*=7.50Hz, Z-CH_2), 2.42 (s, 3H, $ArCH_3$), 2.13–2.07 (m, 0.69×2H+0.69×3H, *E*-CH_2, *E*-CH_3), 1.84 (s, 0.37×3H, *Z*-CH_3), 1.50–1.15 (m, 6H, 3×CH_2), 0.90 (t. 3H, J=7.50 Hz, CH_3). ν_{max} (cm^{-1}) 3065, 1640. *m/z*, 266 (M^+). Anal. calcd. for $C_{15}H_{22}O_2S$: C 67.63; H 8.32. Found: C 67.42; H 8.45.

2-Methyl-1-phenylsulfonyl-1-butene **3f**: Oil. δ_H (ppm) 8.01–7.88 (m, 2H, ArH), 7.60-7.50 (m, 3H, ArH), 6.17 (m, 1H, C=CH), 2.60(q, 0.35×2H, J=7.50Hz, Z-CH_2), 2.17-2.13 (m, 0.65×2H+0.65x3H, *E*-CH_2, *E*-CH_3), 1.87 (s, 0.35×3H, *Z*-CH_3), 1.00 (t, 3H, *J*=7.50Hz, CH_3). ν_{max} (cm^{-1}) 3060, 1635. *m/z*, 210 (M^+). Anal. calcd. for $C_{11}H_{14}O_2S$: C 62.83; H 6.71. Found: C 62.62; H 6.80.

2-Methyl-1-phenylsulfonyl-1-pentene **3g**: Oil. δ_H (ppm) 7.98–7.87 (m, 2H, ArH), 7.60-7.51 (m, 3H, ArH), 6.17 (m, 1H, C=CH), 2.54(q, 0.34×2H, *J*=7.50Hz, *Z*-CH_2), 2.11–2.07 (m, 0.66×2H+0.66×3H, *E*-CH_2, *E*-CH_3), 1.86 (s, 0.34×3H, *Z*-CH_3), 1.49–1.43 (m, 2H, CH_2), 0.90 (t, 3H, *J*=7.50Hz, CH_3). ν_{max} (cm^{-1}) 3055, 1635. *m/z*, 224 (M^+). Anal. calcd. for $C_{12}H_{16}O_2S$: C 64.25; H 7.19. Found: C 64.48; H 7.26.

2-Methyl-1-phenylsulfonyl-1-hexene **3h**: Oil. δ_H (ppm) 7.98–7.87 (m, 2H, ArH), 7.60–7.50 (m, 3H, ArH), 6.17 (m, 1H, C=CH), 2.54(q, 0.32×2H, *J*=7.50Hz, *Z*-CH_2), 2.12–2.06 (m, 0.68×2H+0.68×3H, *E*-CH_2, E-CH_3), 1.87 (s, 0.34x3H, Z-CH_3), 1.48-1.24 (m, 4H, 2xCH_2), 0.90 (t, 3H, *J*=7.50Hz, CH_3). ν_{max} (cm^{-1}) 3060, 1640. *m/z*, 238 (M^+). Anal. calcd. for $C_{13}H_{18}O_2S$: C 65.51; H 7.61. Found: C 65.83; H 7.49.

2-Methyl-1-phenylsulfonyl-1-heptene **3i**: Oil. δ_H (ppm) 7.97–7.87 (m, 2H, ArH), 7.60–7.50 (m, 3H, ArH), 6.15 (m, 1H, C=CH), 2.53(q, 0.30x2H, J=7.50Hz, *Z*-CH_2), 2.14–2.08 (m, 0.70×2H+0.70×3H, *E*-CH_2, *E*-CH_3), 1.86 (s, 0.30×3H, *Z*-CH_3), 1.50–1.15 (m, 6H, 3×CH_2), 0.88 (t, 3H, *J*=7.50Hz, CH_3). ν_{max} (cm^{-1}) 3065, 1640. *m/z*, 252 (M^+). Anal. calcd. for $C_{14}H_{20}O_2S$: C 66.63; H 7.99. Found: C 66.38; H 7.88.

1-Phenylsulfonyl methylidenecyclopentane **3j**: Oil. δ_H (ppm) 7.88–7.58 (m, 2H, ArH), 7.52–7.28 (m, 3H, ArH), 5.92 (s, 1H, C=CH), 2.24-1.50 (m, 8H, 4xCH_2). ν_{max} (cm^{-1}) 3060, 1635. m/z, 222 (M^+). Anal. calcd. for $C_{12}H_{12}O_2S$: C 64.84; H 6.35. Found: C 65.14; H 6.28.

2,4-dimethyl-1-phenylsulfonyl-penta-1,3-diene **5**: δ_H (ppm) E isomer:7.98-7.88 (m, 2H, ArH), 7.62–7.50 (m, 3H, ArH), 6.08 (s, 1H, =CH), 5.60 (s, 1H, =CH), 2.12 (s, 3H, CH_3), 1.83 (s, 3H, CH_3); Z isomer: 7.88–7.78 (m, 2H, ArH), 7.54–7.42 (m, 3H, ArH), 6.12 (s, 1H, =CH), 5.20 (s, 1H, =CH), 1.91 (s, 3H, CH_3), 1.74(s, 3H, CH_3), 1.42 (s, 3H, CH_3), ν_{max} (cm^{-1}) E isomer: 3112, 3025, 1662, 1642, 1632; Z isomer: 3100, 3020, 1650, 1630, 1605. m/z, 238 (M^+). Anal. calcd. for $C_{13}H_{16}O_2S$: C 66.07; H 6.82. Found: C 66.22; H 6.77.

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