

PII: S0040-4039(96)01110-0

## Phosphazene Base P2-Et Mediated Isomerization of Vinyl Sulfones to Allyl Sulfones<sup>1</sup>

Zhendong Jin, Seong Heon Kim, and P. L. Fuchs\*
Department of Chemistry, Purdue University, West Lafayette, IN 47907

**Abstract**: Treatment of vinyl sulfones with 0.1-0.2 eq of Phosphazene base, P<sub>2</sub>-Et in THF at 25°C affords the corresponding allyl sulfones in high yield. P<sub>2</sub>-Et has shown clear superiority to both DBU and KO-t-Bu in these reactions. Copyright © 1996 Elsevier Science Ltd

In conjunction with a project in our laboratories we wished to effect the conversion of vinyl sulfone 1 to allyl sulfone 2. It is well known that allyl sulfones are more thermodynamically stable than the corresponding vinyl sulfones, and that DBU or KO-t-Bu is usually the choice of the base employed in these reactions.<sup>2</sup> Unfortunately, neither of these was satisfactory in our case. The reaction was very slow even in neat DBU, and the work-up was tedious, which resulted in a moderate yield (see Table 1 entry 1). When the reaction was run in the presence of a catalytic amount of KO-t-Bu in THF, it generated a plethora of products presumably due to  $\beta$ -elimination of the benzylic ether bond, and no desired product 2 was isolated (see Table 1 entry 2).

Synthetic reagents termed phosphazene bases have opened a new era for base chemistry.<sup>3</sup> They are extremely strong, neutral nitrogen bases. One of the phosphazene bases,  $P_2$ -Et is about 13,000 times more reactive than DBU in elimination reactions.<sup>3</sup> Because of these unique properties,  $P_2$ -Et was examined in the isomerization reaction. Treatment of vinyl sulfone 1 with 0.1 eq of  $P_2$ -Et in THF at 25°C for 30 min. gave allyl sulfone 2 in 95% yield. The reaction was clean and no  $\beta$ -elimination product was observed (Table 1, entry 3). The subsequent table shows additional examples of  $P_2$ -Et mediated isomerization of vinyl sulfones to allyl sulfones where both DBU and KO-t-Bu failed to give satisfactory results (see Table 2 entries 1-7).

Table 1.

Entry	Vinyl Sulfone	Conditions	Allyl Sulfone	Yield
1	1	DBU (neat), 25°C, 48 hr	2	75%
2	1	KO-t-Bu (10%), 25°C, THF	No desired product 2 was isolated	0%
3	1	P <sub>2</sub> -Et (0.1 eq) THF, 25°C, 30 min.	2	95%

Ta	ы	A	2

#	Vinyl Sulfone	Conditions§	Allyl Sulfone	A:V ratio*	Yield
	(CH <sub>2</sub> ) <sub>n</sub> SO <sub>2</sub> Ph	P <sub>2</sub> -Et (0.1 eq) THF, 25°C	(CH <sub>2</sub> ) <sub>n</sub> SO <sub>2</sub> Ph		
1 2 3	4 n = 1 5 n = 2 6 n = 3	1 hr 4 or 14hr 4 or 14hr	7 n = 1 8 n = 2 9 n = 3	100:0 45:55 <sup>†</sup> 13:87 <sup>†</sup>	99%⁴ 96% 99%
	SO₂Ph (CH₂)n OCH₃	P <sub>2</sub> -Et (0.2 eq) THF, 50-55°C	SO₂Ph (CH₂)n OCH₃		
4 5 6	10 n = 1 11 n = 2 12 n = 3	70 hr 15hr 7hr	13 n = 1 14 n ≠ 2 15 n ≠ 3	100:0 100:0 100:0	92% <sup>4</sup> 95% 99%
	PhO <sub>2</sub> S OTBS	P <sub>2</sub> -Et (0.1 eq) THF, 25°C,	PhO <sub>2</sub> S <sub>N</sub> ,		
7	16 OTBS	20 hr	17 OTBS	70:30†	98%

§ The concentration of these reactions is ~0.05-0.1 M. \*Allyl sulfone/vinyl sulfone ratio.

†This reaction is an equilibrium mixture.

## References and Notes

<sup>1</sup> Syntheses via vinyl sulfones 64.

PhO<sub>2</sub>S 18

OMe

SO<sub>2</sub>Ph 19

(Received in USA 23 January 1996; revised 30 May 1996; accepted 31 May 1996)

<sup>&</sup>lt;sup>2</sup> (a) Hine, J., Skoglund, M. J. *J. Org. Chem.* **1982**, *47*, 4766; (b) Hine, J.; Linden, S.-M., Wang, A., Thiagarajan, V. *J. Org. Chem.* **1980**, *45*, 2821.

<sup>&</sup>lt;sup>3</sup> (a) Schwesinger, R., Schlemper, H. *Angew. Chem.* 1987, 99, 1212; (b) Schwesinger, R. *Chimia.* 1985, 39, 269; (c) Pietzonka, T., Seebach, D. *Chem. Ber.* 1991, 124, 1837; (d) Schwesinger, R., Willaredt, J., Schlemper, H., Keller, M., Schmitt, D., Fritz H. *Chem. Ber.* 1994, 127, 2435 and references cited therein.

<sup>&</sup>lt;sup>4</sup> The only product isolated from the reaction of **4** with catalytic amount of KO-t-Bu was compound **18**. This is consistent with our observation that 5 membered-ring vinyl sulfones are good Michael acceptors. The major product isolated from the reaction of **10** with a catalytic amount of KO-tBu was compound **19**. For additional examples of this reaction, see Jin, Z., Fuchs, P. L. *J. Am. Chem. Soc.* **1995**, *117*, 3022; and Kim, S. H., Jin, Z. Fuchs, P. L. *Tetrahedron Lett.* **1995**, *36*, 4537.