

Stereochemistry of the Conversion of  $\gamma$ -Substituted (E)-Vinylsulfones  
to the Corresponding Allylsulfones.

Determination of the Relative Degree of "Syn-Effect"

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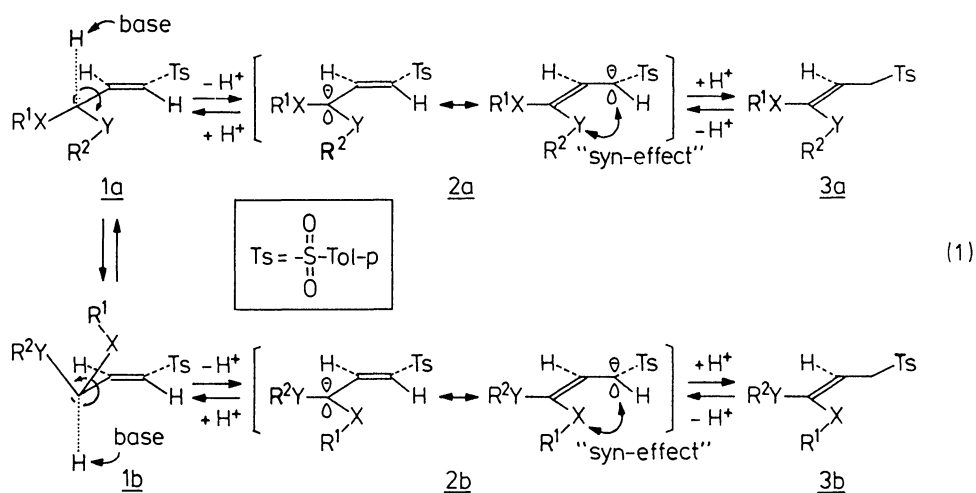
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The relative degree of "syn-effect" for the  $\gamma$ -substituted vinylsulfones in their conversion to the corresponding allylsulfones with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was determined by observing E/Z ratios of the resulting allylsulfones as follows:  $\text{CH}_3\text{O}- \geq \text{AcO}- > \text{CH}_3- > -\text{CH}_2- \gg \text{t-Bu}-$  and  $\text{Ph}-$ .

In connection with our interest in extending the synthetic utility of sulfones, we have so far investigated the syntheses and reactions of vinyl- and allylsulfones.<sup>1)</sup> In the previous paper,<sup>2)</sup> we reported the regio- and stereo-selective syntheses of (E)- and (Z)-vinylsulfones and their conversion to the corresponding allylsulfones under mild basic conditions, and it was found that (E)-vinylsulfone preferentially affords (Z)-allylsulfone as a kinetically-controlled product, while (Z)-vinylsulfone gives (E)-allylsulfone exclusively. Such experimental results were rationalized by the new concept "conformational acidity" (a sort of kinetic acidity),<sup>2)</sup> which essentially depends on a "syn-effect"<sup>3)</sup> within the cases of the conversion discussed.

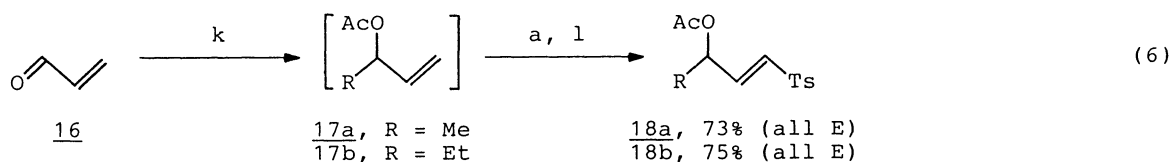
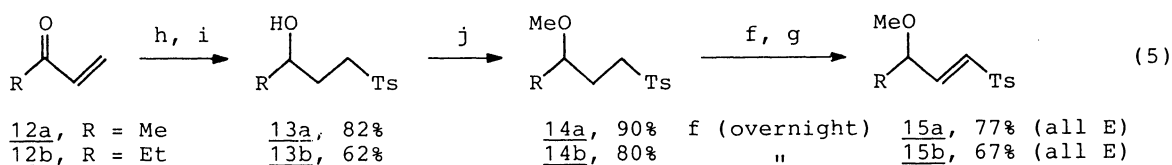
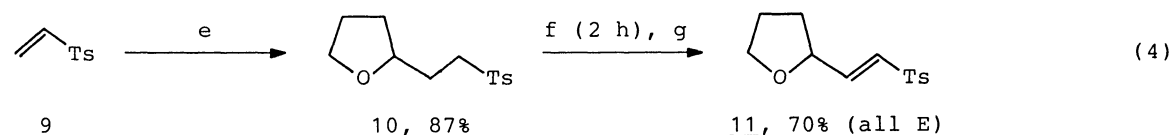
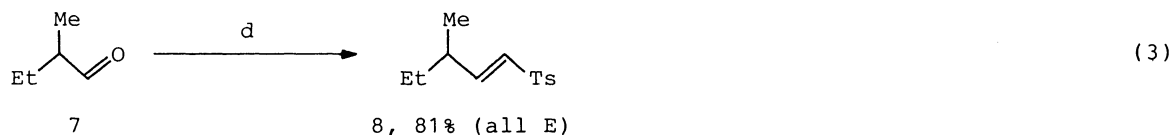
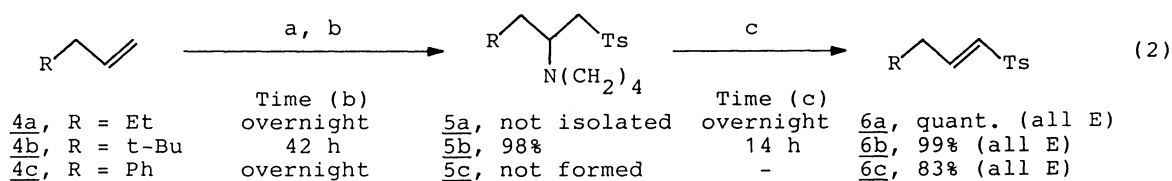
Several explanations for the "syn-effect" have been proposed,<sup>3b)</sup> namely (1)  $6\pi$ -electron homoaromaticity, (2)  $\sigma$ -orbital interactions, (3) dipole-dipole



interactions, and (4) chelations. In order to make sure which explanation is most suitable in the case of the conversion of vinylsulfones to allylsulfones, we herein revealed the relative degree of the "syn-effect" for the  $\gamma$ -substituted vinylsulfones by observing the E/Z ratios of the allylsulfones (3a,b) produced by treating (E)-vinylsulfones (1) with DBU (Eq. 1).

The stereochemically pure (E)-vinylsulfones used in the present experiments were prepared according to Eqs. 2-6. All of the products (6a-c, 8, 11, 15a,b, and 18a,b) were isolated by a preparative TLC (silica gel) as oily substances except 6c (Mp 120 °C, from i-PrOH), and their structures and purity were confirmed by IR, UV, mass, and 400 MHz  $^1\text{H-NMR}$  spectra.

The (E)-vinylsulfones thus prepared were treated with DBU in  $\text{CH}_3\text{CN}$  at ambient temperature (25 °C) to convert to the corresponding allylsulfones in the similar manner described in the previous paper.<sup>2)</sup> The results were summarized in Table 1. The structures of (E)- and (Z)- isomers of the resulting allylsulfones were confirmed by the measurement of NOE or determined based on the empirical rule<sup>4)</sup> that



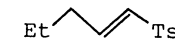
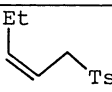
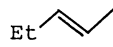
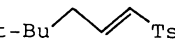
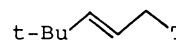
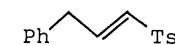
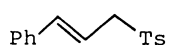
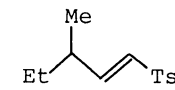
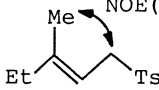
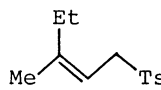
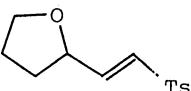
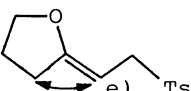
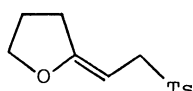
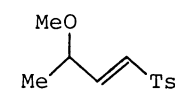
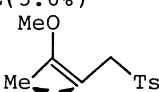
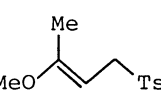
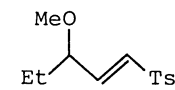
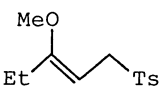
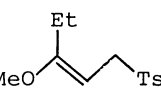
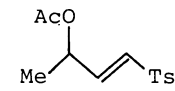
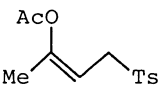
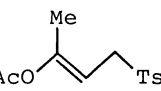
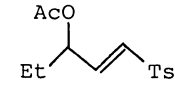
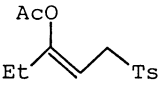
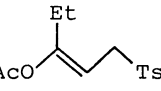
(a) p-TolSOONa $\cdot$ 4H<sub>2</sub>O (1.5 equiv.)/I<sub>2</sub> (1 equiv.) in AcOEt/H<sub>2</sub>O, r.t., 2 - 3 h. (b) pyrrolidine (3 equiv.) in CH<sub>3</sub>CN, r.t. (c) finely powdered Na<sub>2</sub>CO<sub>3</sub> (2 equiv.)/mCPBA (1.4 equiv.) in CH<sub>2</sub>Cl<sub>2</sub>, r.t. (d) TsCHLiPO(OEt)<sub>2</sub> prepared by the reaction of TsCH<sub>2</sub>PO(OEt)<sub>2</sub> (1 equiv.) and n-BuLi (1.1 equiv.) at -78 °C for 30 min, -78 °C - r.t., 3 h. (e) PhCOPh (0.05 equiv.) in THF, hv (300 W Hg-lamp), r.t., 1 h. (f) LDA (2 equiv.)/ (PhSe)<sub>2</sub> (1.1 equiv.) in THF, -78 °C - r.t. (g) 30% H<sub>2</sub>O<sub>2</sub> (5 equiv.) in THF/AcOEt, 0 °C - r.t., 1 - 1.5 h. (h) p-TolSOOH (1 equiv.) in aq. THF, r.t., 1 - 2 h. (i) NaBH<sub>4</sub> in EtOH, r.t. (j) Ag<sub>2</sub>O (5 equiv.)/MeI (10 equiv.) in DMF, r.t., 2 d in the dark. (k) i) RMgBr (1.1 equiv.) in THF, r.t., 30 min under N<sub>2</sub>. ii) AcCl (1.2 equiv.), r.t., 2 h. (l) Et<sub>3</sub>N (2 equiv.) in CH<sub>3</sub>CN, r.t., 2 h.

the protons of alkyl group syn to the tosylmethyl group in an allylsulfone appear at higher field in NMR spectrum than that anti to the tosylmethyl group.

Previously, we observed that the proportion of (Z)- and (E)-allylsulfones ( $RCH=CHCH_2Ts$ ) obtained from (E)-1-tosyl-1-alkene ( $RCH_2CH=CHTs$ ) with DBU was almost constant around 75/25 at 10 °C and 70/30 (see Run 1) at 25 °C after 12 h regardless of the substituent R (R = Et, n-Pr, n-Pen, n-Oc) except benzyl group.<sup>2b)</sup>

This result shows that the steric difference among the linear alkyl substituents R

Table 1. Conversion of (E)-Vinylsulfones to the Corresponding Allylsulfones

(E)-Vinylsulfone		DBU (2 equiv.) in $CH_3CN$ , 25 °C		(Z)- and (E)-Allylsulfones	Conversion yield/% <sup>b)</sup> (Recovery/%)
Run	Vinylsulfones	Time/h	Allylsulfones (Ratio) <sup>a)</sup>		
1	<u>6a</u> , 	12	 (66),	 (34)	95 (5)
2	<u>6b</u> , 	12	 (100)		69 (31)
3	<u>6b</u> , "	48	"		(100) 98 (2)
4	<u>6c</u> , 	1	 (100)		100 <sup>c)</sup>
5	<u>8</u> , 	6	 (70),	 (30)	72 (28)
6	<u>8</u> , "	18	"		(70), (30) 100
7	<u>11</u> , 	24	 (84),	 (16)	100
8	<u>15a</u> , 	12	 (79),	 (21)	91 (9)
9	<u>15a</u> , "	48	"		(80), (20) 100
10	<u>15b</u> , 	12	 (91),	 (9)	48 (52)
11	<u>15b</u> , "	48	"		(91), (9) 95 (5)
12	<u>18a</u> , 	4	 (71),	 (29)	100
13	<u>18a</u> , "	12	"		(70), (30) 100
14	<u>18b</u> , 	4	 (80),	 (20)	92 (8)
15	<u>18b</u> , "	12	"		(79), (21) 100

a) Determined by 400 MHz  $^1H$ -NMR spectra. b) Since the allylsulfones were not separable in general from the unaffected vinylsulfones on TLC, the recovery was estimated by 400 MHz  $^1H$ -NMR spectra. The detail of the time-course will be reported elsewhere. c) Mp 125 °C (from i-PrOH). d) Methyl group was irradiated. e) An olefinic proton was irradiated.

in  $\text{RCH}_2\text{CH}=\text{CHTs}$  is not so important when we determine the relative degree of "syn-effect" for  $\gamma$ -substituents. However, it should be noted that only (E)-allyl-sulfones were obtained (Runs 2-4 in Table 1) when R is t-butyl or phenyl group which precludes the possibility of syn-geometry by the steric congestion.

Runs 5 and 6 were performed to determine the difference of "syn-effect" between methyl and ethyl groups. The experimental result clearly showed that methyl group prefers syn-geometry more than ethyl group. The relative degree of the "syn-effect" for alkyl, aryl, alkoxy, and acetoxy groups was similarly examined as shown in Table 1, and revealed to be  $\text{CH}_3\text{O}- \succ \text{AcO}- \succ \text{CH}_3- \succ -\text{CH}_2- \gg \text{t-Bu}-$  and  $\text{Ph}-$ .

In order to confirm the structure of 2-ethyl-1-tosyl-1-butene (19,  $\text{Et}_2\text{C}=\text{CHTs}$ , Mp 62 °C, from cyclohexane), which has afforded exclusively (Z)-2-ethyl-1-tosyl-2-butene (20) by treating with DBU,<sup>2b)</sup> X-ray crystallography was performed (Fig. 1).<sup>5)</sup> It was found that C8, C9, C10, and C11 exist on a plane, and H4 and H5 are placed parallel to the axis of p-orbital on C8. This observation suggests as if "syn-effect" worked not only in the transition state of the conversion of 19 to 20, but also in the substrate (19) itself. This will be the first structural evidence to support  $6\pi$ -electron homoaromaticity as an explanation for the "syn-effect", if the long distance between C8 and the protons H4 and H5 is reasonable (C8-H4, 2.86 Å; C8-H5, 2.84 Å; C8-C11, 2.89 Å). Related works are further in progress in our laboratory.

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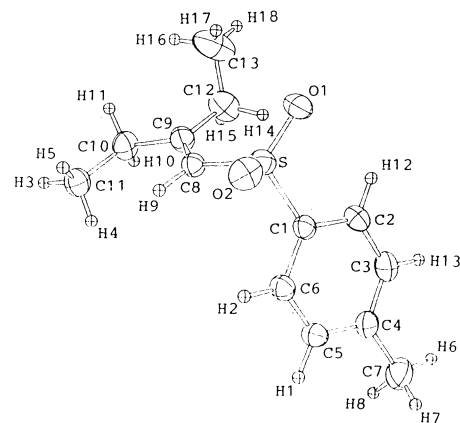


Fig. 1. ORTEP diagram of  $\text{Et}_2\text{C}=\text{CHTs}$  (19).

#### References

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- 2) a) K. Inomata, S. Sasaoka, T. Kobayashi, Y. Tanaka, S. Igarashi, T. Ohtani, H. Kinoshita, and H. Kotake, *Bull. Chem. Soc. Jpn.*, **60**, 1767 (1987); b) T. Kobayashi, Y. Tanaka, T. Ohtani, H. Kinoshita, K. Inomata, and H. Kotake, *Chem. Lett.*, **1987**, 1209.
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- 4) The rule was applicable to all allylsulfones prepared in our laboratory without exception.
- 5) Crystal data:  $\text{C}_{13}\text{H}_{18}\text{SO}_2$ , FW=238.3, monoclinic, space group  $\text{P}2_1/\text{n}$ ,  $a=7.9603(9)$ ,  $b=10.001(1)$ ,  $c=16.662(2)$  Å,  $\beta=102.361(8)^\circ$ ,  $U=1295.8(3)$  Å<sup>3</sup>,  $D_c=1.22$  g/cm<sup>3</sup>,  $F(000)=512$ ,  $(\text{Mo-K}\alpha)=2.32$  cm<sup>-1</sup>. Intensities were measured on a Rigaku AFC-5R diffractometer using Mo-K $\alpha$  radiation within  $2\theta=55^\circ$  and  $\theta-2\theta$  scan method. Observed independent reflections of 1675 with  $I>3\sigma(I)$  were used in the structure analysis and refinement applying TEXSAN program system. The final R factor was 0.052.

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