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Regio- and Stereoselective Synthesis of (E)- and (Z)-Vinylic Sulfones and Their Conversion to the Corresponding Allylic Sulfones

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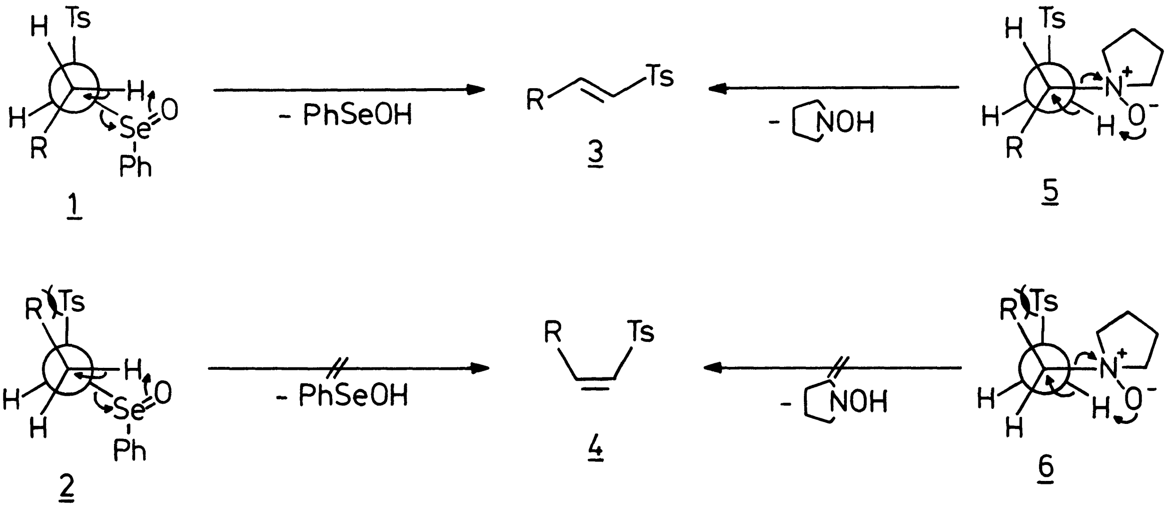
(E)- and (Z)-vinylic sulfones were prepared regio- and stereoselectively from 1-alkenes or 1-alkynes in high yields via iodosulfonization in AcOEt-H_2O. The vinylic sulfones thus prepared were converted to the corresponding allylic sulfones by treatment with DBU. Stereochemistry of the conversion was discussed.

In the previous paper,1) we reported a convenient method for the preparation of vinylic sulfones from alkenes via iodosulfonization. The vinylic sulfones thus prepared, however, were mixture of geometrical isomers. Although the sterically pure vinylic sulfones were required in connection with the studies on the stereochemistry of the conversion of the vinylic sulfones to allylic sulfones, the separation of each isomer from the mixture was unsuccessful. Such situation prompted us to develop a synthetic method of pure (E)- and (Z)-vinylic sulfones as will be described in this paper.

In order to prepare pure (E)-vinylic sulfones, we first tried to introduce a double bond toward alkyl p-tolyl sulfones by phenylselenation on α-position of the sulfones followed by oxidative elimination, and found that this reaction affords exclusively (E)-isomers2) in contrast to the case of the preparation of 1-cyano-1-alkenes.3) This seems to be due to the bulkiness of tosyl group, namely, cis-elimination of benzeneselenic acid might proceed preferentially via the conforma-

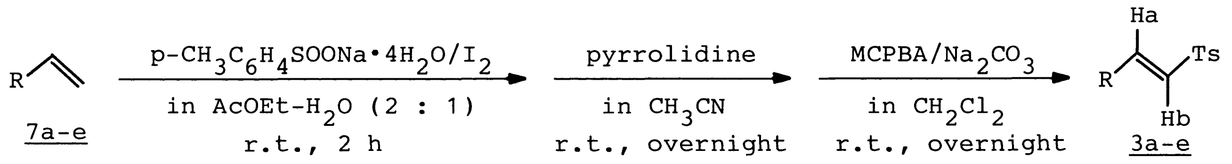


tion 1 in which the unfavorable steric interaction between alkyl and tosyl groups, represented in the conformation 2, does not exist. On the basis of such consideration, it was expected that Cope elimination of N-oxide of β-pyrrolidinylsulfone also affords only (E)-vinylic sulfone (3) via the conformation 5 which has similar steric circumstances to 1. This was actually demonstrated by the experiment of applying previously reported iodosulfonization of 1-alkene.$^{1)}$ Namely, 2-iodo-1-tosylalkane obtained by iodosulfonization of 1-alkene (7) was treated with excess pyrrolidine in acetonitrile to afford 2-pyrrolidinyl-1-tosylalkane. Oxidation of the crude product with m-chloroperbenzoic acid (MCPBA) in dichloromethane in the presence of Na_2CO_3 resulted in the formation of stereochemically pure (E)-vinylic sulfone (3) in high yield as shown in Table 1. This procedure is much easier than the previous one via α-phenylselenation$^{2)}$ and applicable in large scale too.

On the other hand, the preparation of (Z)-vinylic sulfones was achieved through iodosulfonization of 1-alkyne (8) to (E)-2-iodo-1-tosyl-1-alkene (9) under similar conditions for 1-alkene (7) and the subsequent deiodination with 5% Pd-C deactivated by the addition of a small amount of quinoline in methanol in the presence of sodium acetate under hydrogen atmosphere. (Z)-Vinylic sulfones (4a-e) corresponding to (E)-isomers (3a-e) were prepared in this manner in high yields as listed in Table 2.

Now, both (E)- and (Z)-vinylic sulfones have come available. Not only are these compounds useful as building blocks in organic synthesis,$^{4-7)}$ but also they made our initial project possible to examine the stereochemistry of the conversion of the vinylic sulfones to the corresponding allylic sulfones under basic conditions. The experimental results obtained using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a base are summarized in Table 3. (E)-Vinylic sulfones (3a-e) preferentially afforded (Z)-allylic sulfones (10a-e) and (Z)-vinylic sulfones (4a-e) gave (E)-10a-e exclusively. It was further found that when the reaction mixture in Entry 4 was refluxed for 1.5 h, E/Z ratio of 10d (98% yield) changed to 78/22.

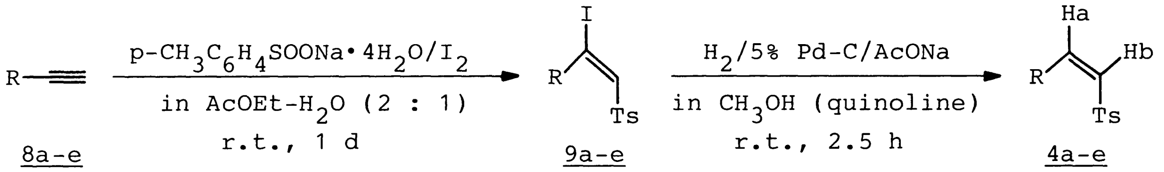
Table 1. Synthesis of (E)-Vinylic Sulfones$^{a)}$



Entry	R (7a-e)	Yield of 3a-e/%	Remarks (δ values of Ha and Hb; J_{Ha-Hb})$^{b)}$
1	$CH_3(CH_2)_2$ (7a)	quant$^{c)}$ (3a)	liquid (6.95, 6.30 ppm; 15.0 Hz)
2	$CH_3(CH_2)_3$ (7b)	86 (3b)	liquid (6.96, 6.29 ppm; 15.3 Hz)
3	$CH_3(CH_2)_5$ (7c)	73 (3c)	liquid (6.95, 6.29 ppm; 15.0 Hz)
4	$CH_3(CH_2)_8$ (7d)	83 (3d)	solid$^{d)}$ (6.95, 6.29 ppm; 15.0 Hz)
5	$PhCH_2CH_2$ (7e)	81 (3e)	liquid (6.95, 6.28 ppm; 15.0 Hz)

a) Following equivalents of reagents were used: p-$CH_3C_6H_4SOONa \cdot 4H_2O$ (1.5), I_2 (1.0), pyrrolidine (4.0), MCPBA (1.4), Na_2CO_3 (2.0). b) Recorded on JEOL JNM-GX 400 (400 MHz) FT-NMR spectrometer. c) 1.5 equiv. of 7a was used. Yield was estimated based on iodine. d) Mp 44 °C (from hexane).

Table 2. Synthesis of (Z)-Vinylic Sulfones[a]



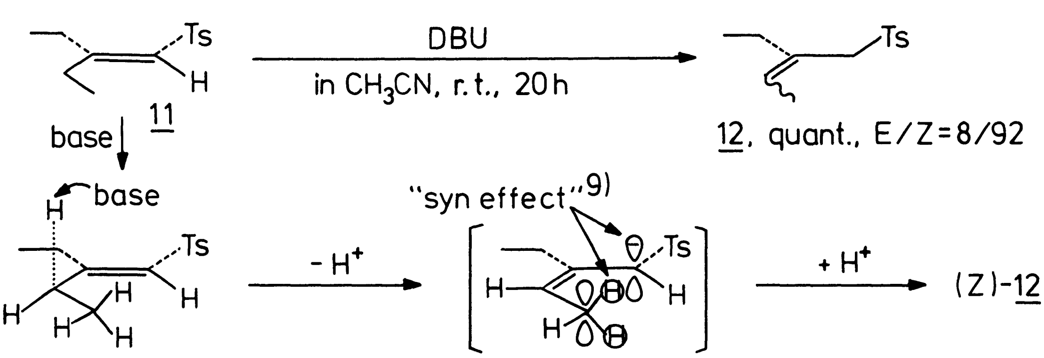
Entry	R (8a-e)	Yield of 9a-e[b]/%	Yield of 4a-e/%	Remarks (δ values of Ha and Hb; J_{Ha-Hb})[c]
1	$CH_3(CH_2)_2$ (8a)	88 (9a)	98 (4a)	liquid (6.16, 6.32 ppm; 11.0 Hz)
2	$CH_3(CH_2)_3$ (8b)	95 (9b)	98 (4b)	liquid (6.17, 6.32 ppm; 11.0 Hz)
3	$CH_3(CH_2)_5$ (8c)	92 (9c)	96 (4c)	liquid (6.17, 6.31 ppm; 11.0 Hz)
4	$CH_3(CH_2)_8$ (8d)	76 (9d)	96 (4d)	solid[d] (6.16, 6.32 ppm; 11.0 Hz)
5	$PhCH_2CH_2$ (8e)	75 (9e)	98 (4e)[e]	liquid (6.18, 6.31 ppm; 11.3 Hz)

a) Following equivalents of reagents were used: p-CH$_3$C$_6$H$_4$SOONa•4H$_2$O (1.5), I$_2$ (1.0), AcONa (2.0). b) 9a,b and 9d were liquid. 9c: Mp 51-52 °C (from i-PrOH); 9e: Mp 88-89 °C (from EtOH). c) Recorded on JEOL JNM-GX 400 (400 MHz) FT-NMR spectrometer. d) Mp 28-30 °C (not recrystallized). e) Mixed solvent [CH$_3$OH-CH$_3$CN (5 : 1)] was used.

These results suggest that (Z)-10d is the kinetically-controlled product from 3d and the more stable (E)-10d is the thermodynamically-controlled one.

Recently, Block and his co-workers observed independently the similar phenomena for the vinylogous Ramberg-Bäcklund reaction and they attributed the stereoselectivity of the reaction to a "syn effect".[8] It seems to be reasonable as an explanation for the kinetically-controlled products, however, it should be noted that the (E)-allylic sulfones are more stable than their (Z)-isomers as can be seen in the above results and in comparison of the results of the reactions carried out at 10 °C to those at 25 °C in Entries 1-5 in Table 3. Such observation was not possible in the Ramberg-Bäcklund reaction since the subsequent desulfonylation proceeded readily at low temperature.

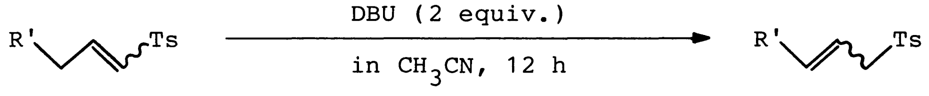
The above results suggest that the acidity of the protons at γ-position of vinylic sulfones varies considerably in each conformation. A remarkable result was obtained in the reaction of 2-ethyl-1-tosyl-1-butene (11) with DBU. It afforded exclusively (Z)-2-ethyl-1-tosyl-2-butene (12) as shown in the following scheme.



We would like to propose to call such acidity of a proton characteristic to each conformation "Conformational Acidity".

Related works are in progress in our laboratory.

Table 3. Conversion of (E)- and (Z)-Vinylic Sulfones to the Corresponding Allylic Sulfones under Basic Conditions



(E): 3a-e
(Z): 4a-e

10a-e

Entry	Substrate 3 or 4	R'	Reaction Temp/°C	Yield of 10/% (Recovery/%)[a)]	E/Z ratio[b)] of 10
1	3a	CH_3CH_2	10	89 (7)	24/76
			25	95 (5)	34/66
2	3b	$CH_3(CH_2)_2$	10	96 (4)	26/74
			25	96 (4)	35/65
3	3c	$CH_3(CH_2)_4$	10	93 (4)	24/76
			25	97 (3)	30/70
4	3d	$CH_3(CH_2)_7$	10	95 (5)	25/75
			25	97 (3)	32/68
5	3e	$PhCH_2$	10	98 (2)	44/56
			25	98 (1)	70/30
6	4a	CH_3CH_2	10	93 (7)	94/6
			25	96 (1)	93/7
7	4b	$CH_3(CH_2)_2$	25	96 (1)	93/7
8	4c	$CH_3(CH_2)_4$	25	96 (1)	94/6
9	4d	$CH_3(CH_2)_7$	25	97 (1)	95/5
10	4e	$PhCH_2$	25	94 (1)	90/10

a) 3 was recovered in Entries 1-5, and 4 in Entries 6-10. As the product 10 was not separable from 3 and 4, the recovery of 3 or 4 was estimated by 400 MHz ^{1}H-NMR spectra. b) Determined by 400 MHz ^{1}H-NMR spectra.

References
1) K. Inomata, T. Kobayashi, S. Sasaoka, H. Kinoshita, and H. Kotake, Chem. Lett., 1986, 289.
2) K. Inomata, S. Sasaoka, T. Kobayashi, Y. Tanaka, S. Igarashi, T. Ohtani, H. Kinoshita, and H. Kotake, Bull. Chem. Soc. Jpn., in press.
3) D. N. Brattesani and C. H. Heathcock, Tetrahedron Lett., 1974, 2279.
4) P. D. Magnus, Tetrahedron, 33, 2019 (1977).
5) T. Durst, "Comprehensive Organic Chemistry," ed by D. H. R. Barton and W. D. Ollis, Pergamon, Oxford (1979), Vol. 3, p. 197.
6) J. -L. Fabre, M. Julia, and J. -N. Verpeaux, Tetrahedron Lett., 1982, 2469.
7) J. Sumner, M. Julia, M. Launay, and J. -P. Stacino, Tetrahedron Lett., 1982, 3265.
8) E. Block, M. Aslam, V. Eswarakrishnan, K. Gebreyes, J. Hutchinson, R. Iyer, J. -A. Laffitte, and A. Wall, J. Am. Chem, Soc., 108, 4568 (1986) and references cited therein.
9) This effect should be considered in a transition state since (Z)-allylic sulfone (12) is a kinetically-controlled product.

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