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CONVENIENT METHODS FOR THE PREPARATION OF VINYLIC AND ALLYLIC SULFONES FROM ALKENES

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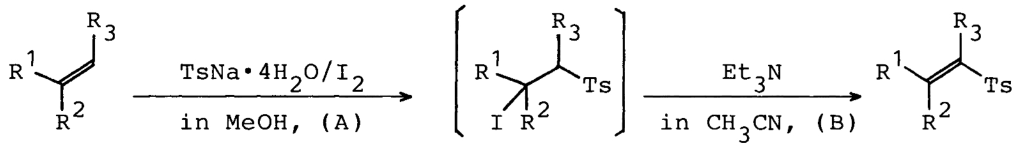
1 or 2-p-Toluenesulfonyl(=tosyl)-1-alkenes were regioselectively prepared from 1-alkenes via iodosulfonization or sulfonylmercuration, respectively. Conversion of 1-tosyl-1-alkenes to the corresponding allylic sulfones, 1-tosyl-2-alkenes, was achieved by the treatment of their acetonitrile solution with DBU in high yield.

In an earlier paper,1) we reported the regio- and stereocontrolled synthesis of allylic sulfones from allylic acetates and sodium p-toluenesulfinate in the presence of [Pd(PPh_3)$_4$] as the catalyst in THF-MeOH. This convenient method for the preparation of allylic sulfones was successfully employed for the synthesis of a naturally occurring (±)-(E)-8-dodecen-11-olide, recifeiolide.2)

In connection with the studies on the reaction of allylic sulfones,2-5) we herein report a facile method for the preparation of vinylic sulfones from alkenes and the conversion of the vinylic sulfones to the corresponding allylic sulfones.

Recently Kao Liu and his co-workers reported a convenient synthesis of various β-iodo sulfones,6) which involves additions of alkane- and arenesulfonyl iodides to alkenes under the catalytic action of copper(II) chloride in aprotic solvents. Though they and others7) established from the various evidences that tosyl iodide adds homolytically to alkenes, we thought it possible to prepare β-iodo sulfones in an ionic fashion from iodine and sulfinate just like iodolactonization. Therefore, we tried the iodosulfonization and the subsequent elimination of hydrogen iodide with a base to yield the corresponding vinylic sulfones. When iodine (254 mg, 1.0 mmol) was added to a mixed solution of styrene (<u>1a</u>, 104 mg, 1 mmol) and sodium p-toluenesulfinate tetrahydrate (375 mg, 1.5 mmol) in methanol (2 ml) at room temperature, a lot of yellowish solid8) precipitated immediately. The solvent was replaced by ethyl acetate after stirring for 15 min, and the solution was successively washed with water, aqueous $NaHCO_3$ containing a small amount of $NaHSO_3$, and brine, and dried over Na_2SO_4. The residue obtained by evaporation of the solvent was treated with Et_3N (202 mg, 2 mmol) in dry CH_3CN at room temperature for 15 min. After working up in the usual way, 1-tosyl-2-phenylethene (<u>3a</u>) was separated with a preparative TLC (SiO_2, hexane/AcOEt = 5/2) as solid product in 89% yield (229 mg). Such iodosulfonization and subsequent dehydroiodination reaction was found to proceed for other alkenes (<u>1b-g</u>) giving the corresponding vinylic sulfones (<u>3b-g</u>) as summarized in Table 1.

Table 1. Preparation of Vinylic Sulfones from Alkenes via Iodosulfonization



1a-g 2a-g 3a-g

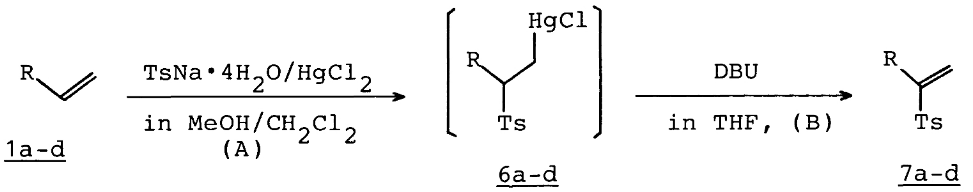
Olefins 1a-g	R^1 R^2	R^3	Molar Ratio of 1/TsNa•4H_2O/I_2	Conditions (A), (B)	Yield/% 3a-g a)
1a	C_6H_5 H	H	1/1.5/1	(A) r.t., 15 min (B) r.t., 15 min	89 b)
1b	$CH_3(CH_2)_2$ H	H	1.5/1.5/1	(A) r.t., 1 d (B) r.t., 15 min	94 c)
1c	$CH_3(CH_2)_3$ H	H	1.5/1.5/1	(A) r.t., 1 d (B) r.t., 15 min	90 d)
1d	$CH_3(CH_2)_7$ H	H	1/1.5/1	(A) e) r.t., 1 d (B) r.t., 15 min	77 f)
1e	CH_3 CH_3	H	ca.10/1.5/1	(A) -70 °C/r.t., 3 h (B) r.t., 15 min	quant. g)
1f	CH_3 CH_3	CH_3	1.5/1.5/1	(A) r.t., 16 h (B) r.t., 17 h	80 h)
1g	$-(CH_2)_4-$ H		1/1.5/1	(A) r.t., 3 d (B) i) r.t., 15 min	76 j)

a) All compounds gave satisfactory spectral data. b) Mp 120-121 °C (from EtOH, lit.6) 120-121 °C). c) E/Z = 78/22. d) E/Z = 78/22. e) MeOH/CH_2Cl_2 (4/1) was used as solvent. f) E/Z = 83/17. g) Mp 62-63 °C (from cyclohexane). h) Mp 65 °C (from hexane, lit.6) 66-67 °C). CH_2=C(CH_3)CH(CH_3)Ts was obtained as a by-product in 6% yield. i) DBU was used instead of Et_3N. j) Mp 81-82 °C (from EtOH, lit.6) 81-82 °C).

We have checked the possibility of the initial formation of tosyl iodide as an intermediate in the above iodosulfonization by observation of the behavior of tosyl iodide itself under the similar conditions. We could not exclude the possibility because the present reaction was also retarded in the dark9) as in the case of the reaction of tosyl iodide with alkenes. The use of excess sodium p-toluenesulfinate was effective to improve the yields of the addition products even for the reaction with tosyl iodide in methanol.10) Further detailed investigation concerning the reaction mechanism is under way. However, the present method has obviously an advantage that it does not require the preparation of unstable tosyl iodide and permits the direct iodosulfonization of alkenes with iodine and sodium p-toluenesulfinate.

The results in Table 1 shows that the iodosulfonization proceeds regioselectively. This is considered as follows: If the reaction proceeds in an ionic fashion, p-toluenesulfinate ion attacks a less hindered carbon of the iodonium intermediate (4), and if in an radical fashion, more stable radical intermediate (5) is preferentially formed as shown in Scheme 1.

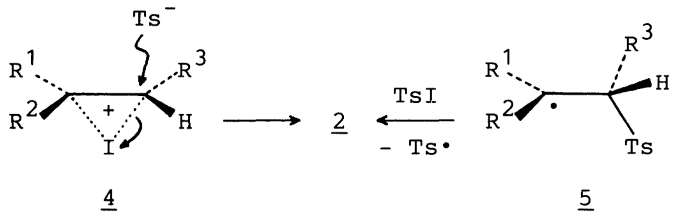
Table 2. Preparation of Vinylic Sulfones from Alkenes via Sulfonylmercuration



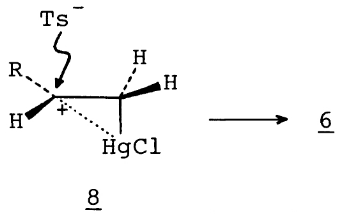
Olefins 1a-d	R	Molar Ratio of 1/TsNa•4H$_2$O/HgCl$_2$	Conditions (A), (B)	Yield/% 7a-d[a)]
1a	C_6H_5	1/1/1	(A) r.t., 1 d (B) r.t., 10 min	61
1b	$CH_3(CH_2)_2$	1.5/1/1	(A) 0 °C, 3 d (B) r.t., 8 h	67
1c	$CH_3(CH_2)_3$	1/1.5/1.2	(A) 0 °C, 3 d (B) r.t., 6 h	72
1d	$CH_3(CH_2)_7$	1/2/2	(A) r.t., 6 h (B) r.t., 12 h	77

a) All compounds gave satisfactory spectral data.

In contrast to the iodosulfonization, we found that sulfonyl group is introduced on the C-2 position in sulfonylation of alkenes, when mercuric chloride is used instead of iodine. The treatment of the addition product of sulfonylmercuration with a base afforded exclusively 2-tosyl-1-alkenes. This fact seems to suggest that Hg (II) atom of the intermediate (8) does not exist on the central position of olefinic bond, being different from the ionic intermediate (4) of the iodosulfonization mentioned above, but lies on the less hindered carbon. Therefore, the tosylate ion attacks the C-2 position as shown in Scheme 2. The following procedure was representative for the sulfonylmercuration. To the solution of 1-hexene (1c, 84 mg, 1 mmol) in methanol (1.5 ml) and dichloromethane (0.7 ml) were added $HgCl_2$ (326 mg, 1.2 mmol) and sodium p-toluenesulfinate tetrahydrate (375 mg, 1.5 mmol) at 0 °C. After stirring for 3 d at 0 °C, the reaction mixture was diluted with ethyl acetate (ca. 15 ml) and the insoluble substances were filtered off through a Celite bed. The residue obtained by evaporation of the solvent was treated with DBU (0.25 ml, 1.7 mmol) in dry THF (4 ml) at room temperature for 6 h. After working up in the usual manner, 2-tosyl-1-hexene was isolated with a preparative TLC (SiO_2, hexane/AcOEt = 5/1) as a colorless oil in 72% yield (172 mg). Results for other 1-alkenes were summarized



Scheme 1.



Scheme 2.

in Table 2.

O'Conner and Lyness have reported that the equilibrium between 1-methanesulfonyl-1-hexene (9) and 1-methanesulfonyl-2-hexene (10) under basic conditions (t-BuOK in t-BuOH at room temperature) almost completely shifts to 10.[11] We therefore tried the conversion of 3b-d to the corresponding allylic sulfones (11b-d) with DBU as a base in acetonitrile as shown in the following scheme. In each case, proton rearranged products (11b-d) were obtained in excellent yields.

In conclution, the present reactions provide a convenient method for the preparation of allylic sulfones from alkenes via vinylic sulfones.

$$RCH_2CH{=}CHTs \xrightarrow[\text{in } CH_3CN\text{, r.t., overnight}]{\text{DBU (2 equiv.)}} RCH{=}CHCH_2Ts$$

3b, R = CH_3CH_2 — 11b, 92%, E/Z = 84/16

3c, R = $CH_3(CH_2)_2$ — 11c, 91%, E/Z = 52/48

3d, R = $CH_3(CH_2)_6$ — 11d, quant., E/Z = 65/35

Further work is in progress to elucidate the scope and limitation of the present synthetic method in our laboratory.

References

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8) This compound was $C_6H_5CHICH_2Ts$. Mp 139-140 °C (from benzene/chloroform=2/1, lit.[6] 138-139 °C).
9) The yield of 3a was 75% in the reaction carried out in the dark (other conditions were same as those in Table 1).
10) The reaction of tosyl iodide and styrene (1a) with or without additives in methanol was examined under similar conditions as ones in Table 1. The yield of 3a varied with the additives as follows: Additives (equiv.), yield (%); none, 40; NaI (1), 57; $TaNa \cdot 4H_2O$ (0.5), 67; NaI (1) + $TsNa \cdot 4H_2O$ (0.5), 95. TsI was more readily soluble in methanol in the presence of NaI.
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