Reactions of Arenesulfonyl Chlorides with *cis*- or *trans*-β-Methylstyrene Catalyzed by Ruthenium(II) Complex

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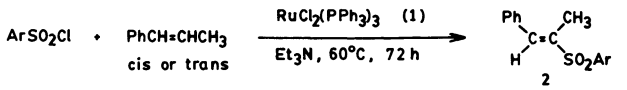
(Received June 16, 1983)

Synopsis. The reactions of arenesulfonyl chlorides with *cis*- or *trans*-β-methylstyrene catalyzed by dichlorotris(triphenylphosphine)ruthenium(II) in the presence of triethylamine proceeded smoothly to give only (*E*)-2-arylsulfonyl-1-phenylpropene. The recovered *cis*-β-methylstyrene was isomerized to trans form, while *trans*-β-methylstyrene did not isomerize to the cis one.

Recently, much attention has been paid to the radical reactions formed from halides treated with transition metal complexes.[1] We have reported the reactions of arenesulfonyl chlorides with vinylarenes catalyzed by dichlorotris(triphenylphosphine)ruthenium(II) (**1**) in the presence of triethylamine to give α,β-unsaturated sulfones.[2] We report here the reactions of arenesulfonyl chlorides with *cis*- or *trans*-β-methylstyrene catalyzed by ruthenium(II) complex.

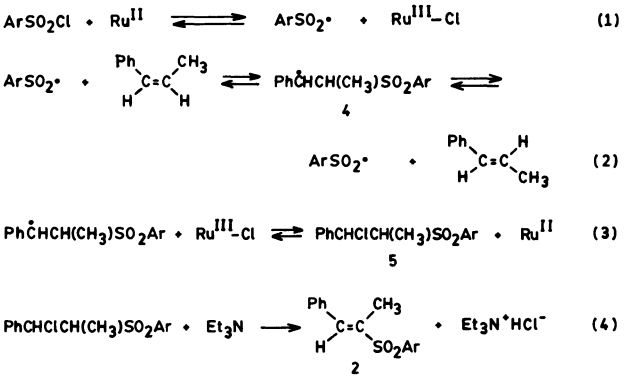
The reaction of *p*-toluenesulfonyl chloride with *trans*-β-methylstyrene was carried out in benzene, using ruthenium(II) complex **1** as catalyst in the presence of a molar equivalent of triethylamine at 60 °C for 72 h in a degassed sealed tube. The reaction mixture was chromatographed on Florisil column using benzene as an eluent to give (*E*)-1-phenyl-2-(*p*-tolylsulfonyl)propene (**2a**) as colorless crystals, mp 122.5—123.0 °C (from ethanol). The stereochemistry of **2a** was confirmed by its spectral data (see Experimental section). Its stereoisomer, (*Z*)-1-phenyl-2-(*p*-tolylsulfonyl)propene (**3a**), mp 54—55 °C, prepared by oxidation of 1-phenyl-1-phenylseleno-2-(*p*-tolylsulfonyl)propane exhibited different spectral properties.

The reaction of *p*-toluenesulfonyl chloride with *cis*-β-methylstyrene was carried out under similar conditions to give also **2a**; none of its (*Z*)-isomer **3a** was detected. Similarly, reactions of several arenesulfonyl chlorides with *cis*- and *trans*-β-methylstyrene catalyzed by **1** were studied and only (*E*)-2-arylsulfonyl-1-phenylpropene (**2**) were obtained in all the cases. The results are summarized in Table 1.



No isomerization of (*Z*)-1-phenyl-2-(*p*-tolylsulfonyl)-propene (**3a**) to its (*E*)-isomer **2a** was observed when **3a** was treated with ruthenium(II) catalyst **1** in benzene at 60 °C. This excluded the possibility that **3a** is first formed in the reaction of *p*-toluenesulfonyl chloride with *cis*- or *trans*-β-methylstyrene and then isomerized to **2a** during the reaction period. The formation of **2** may be explained by the base-catalyzed elimination of hydrogen chloride from the adduct 2-arylsulfonyl-1-chloro-1-phenylpropane (**5**) shown in Scheme 1 as one plausible mechanism. Accordingly, even though the adduct **5** formed is a mixture of threo and erythro isomers, the formation of **2** as a sole product may be accounted for by assuming that the elimination proceeded by E2 mechanism, the formation of *Z*-isomer **3** is very slow, and also the Eqs. 1—3 are equilibrium ones.

The stereochemistry of the β-methylstyrene which was recovered was examined by HPLC. No isomerization of *trans*-β-methylstyrene to *cis*-isomer was ob-



Scheme 1.

TABLE 1. REACTIONS OF ARENESULFONYL CHLORIDES WITH *cis*- OR *trans*-β-METHYLSTYRENE CATALYZED BY **1**

Sulfonyl chloride	β-Methylstyrene	Conversion of β-methylstyrene %	Product	Yield[a] %	Cis/trans ratio of recovered β-methylstyrene
p-$CH_3C_6H_4SO_2Cl$	trans	39	**2a**	67	0/100
p-$CH_3OC_6H_4SO_2Cl$	trans	43	**2b**	82	0/100
$C_6H_5SO_2Cl$	trans	35	**2c**	55	0/100
p-$ClC_6H_4SO_2Cl$	trans	40	**2d**	85	0/100
p-$CH_3C_6H_4SO_2Cl$	cis	42	**2a**	74	9/91
p-$CH_3OC_6H_4SO_2Cl$	cis	46	**2b**	70	4/96
$C_6H_5SO_2Cl$	cis	26	**2c**	73	42/58
p-$ClC_6H_4SO_2Cl$	cis	32	**2d**	69	37/63

a) The yields are based on the β-methylstyrene (cis or trans) consumed.

served, while a large part of *cis*-β-methylstyrene was found to be converted to trans form (see Table 1). The isomerization of *cis*-β-methylstyrene was not observed when a mixture of *cis*-β-methylstyrene, ruthenium(II) catalyst **1**, and triethylamine in benzene was heated at 60 °C for 72 h. This means that *cis*-β-methylstyrene does not isomerize to trans in the absence of arenesulfonyl chloride. The fact that *cis*-β-methylstyrene isomerized to trans only when a solution of *cis*-β-methylstyrene, ruthenium(II) catalyst, and arenesulfonyl chloride in benzene was heated in the presence or absence of triethylamine means that Eq. 2 in Scheme 1 is reversible and that thermodynamically stable *trans*-β-methylstyrene is preferably formed from the radical **4**.

Experimental

Measurement. Melting points and boiling points are uncorrected. The infrared absorption spectra were determined on a Hitachi Model EPI-G2 spectrophotometer using samples as KBr disks. The proton magnetic resonance spectra were recorded at 60 MHz using a Hitachi R-20B spectrometer with Me_4Si as an internal standard in $CDCl_3$. Mass spectra were determined with a JEOL JMS-07 mass spectrometer at an ionizing voltage of 30—75 eV. Elemental analyses were operated with a Perkin-Elmer 240 elemental analyzer. HPLC was carried out on a Waters ALC-204 HPLC using a silica-gel column using benzene as an eluent.

Materials. Dichlorotris(triphenylphosphine)ruthenium(II) (**1**) was prepared by the methods described in the literature.[3] *p*-Toluenesulfonyl chloride and *p*-chlorobenzenesulfonyl chloride of Tokyo Kasei Chemicals were recrystallized prior to use. Benzenesulfonyl chloride of Wako Chemicals, *cis*-β-methylstyrene of ICN Pharmaceuticals, and *trans*-β-methylstyrene of Tokyo Kasei Chemicals were purified by distillation under nitrogen prior to use. *p*-Methoxybenzenesulfonyl chloride was prepared by the methods described in the literature.[4]

General Procedures in the Reaction of Arenesulfonyl Chloride with cis- *or* trans-*β-Methylstyrene Catalyzed by 1.* A solution containing 2.0 mmol of arenesulfonyl chloride, 2.0 mmol of *cis*- or *trans*-β-methylstyrene, 2.0 mmol of triethylamine, and 0.16 mmol of **1** in 3.0 cm^3 of benzene was heated at 60 °C in a degassed sealed tube for 72 h. The remaining β-methylstyrene (cis and trans) was quantitatively analyzed by HPLC using an internal standard. The reaction mixture was chromatographed on Florisil using benzene as an eluent to give (*E*)-arylsulfonyl-1-phenylpropene **2** which were characterized by IR, ^1H NMR, and mass spectra, and elemental analyses.

*(E)-1-Phenyl-2-(p-tolylsulfonyl)propene (**2a**)*: Mp 122.5—123.0 °C. IR (KBr): 1150 and 1310 cm^{-1}. ^1H NMR ($CDCl_3$): δ=2.10 (3H, d, *J*=1.8 Hz), 2.44 (3H, s), 7.34 (2H, d, *J*=8.4 Hz), 7.38 (5H, s), 7.80 (1H, q, *J*=1.8 Hz), and 7.82 (2H, d, *J*=8.4 Hz). Mass: *m/z* 272 (M^+). Found: C, 70.26; H, 6.01%. Calcd for $C_{16}H_{16}O_2S$: C, 70.56, H, 5.92%.

*2-(p-Methoxyphenylsulfonyl)-1-phenylpropene (**2b**)*: Mp 82—83 °C. IR (KBr): 1147 and 1300 cm^{-1}. ^1H NMR ($CDCl_3$): δ=2.10 (3H, d, *J*=1.8 Hz), 3.87 (3H, s), 7.02 (2H, d, *J*=8.4 Hz), 7.39 (5H, s), 7.81 (1H, q, *J*=1.8 Hz), and 7.89 (2H, d, *J*=8.4 Hz). Mass: *m/z* 288 (M^+). Found: C, 66.70; H, 5.58%. Calcd for $C_{16}H_{16}O_3S$: C, 66.64; H, 5.59%.

*1-Phenyl-2-(phenylsulfonyl)propene (**2c**)*: Mp 88.5—89.0 °C. IR (KBr): 1152 and 1305 cm^{-1}. ^1H NMR ($CDCl_3$): δ= 2.10 (3H, d, *J*=1.8 Hz), 7.42 (5H, s), 7.86 (1H, q, *J*= 1.8 Hz), and 7.5—8.1 (5H, m). Mass: *m/z* 258 (M^+). Found: C, 69.80; H, 5.48%. Calcd for $C_{15}H_{14}O_2S$: C, 69.74; H, 5.46%.

*2-(p-Chlorophenylsulfonyl)-1-phenylpropene (**2d**)*: Mp 104—105 °C. IR (KBr): 1158 and 1310 cm^{-1}. ^1H NMR ($CDCl_3$): δ=2.13 (3H, d, *J*=1.8 Hz), 7.50 (5H, s), 7.62 (2H, d, *J*=8.4 Hz), 7.95 (1H, q, *J*=1.8 Hz), and 8.01 (2H, d, *J*=8.4 Hz). Mass: *m/z* 294 and 292 (M^+). Found: C, 61.51; H, 4.51%. Calcd for $C_{15}H_{13}ClO_2S$: C, 61.53; H, 4.48%.

*Preparation of (Z)-1-Phenyl-2-(p-tolylsulfonyl)propene (**3a**).* A solution containing 3.2 g (10.3 mmol) of *Se*-phenyl *p*-toueneselenosulfonate and 1.46 g (12.3 mmol) of *trans*-β-methylstyrene in 11 cm^3 of benzene was heated at 80 °C in a degassed sealed tube for 20 h. Removal of the solvent left a light yellow solid, which when recrystallized from ethanol afforded 2.4 g (54%) of a colorless crystalline solid, whose structure was assigned as 1-phenylseleno-1-phenyl-2-(*p*-tolylsulfonyl)propane on the basis of its physical and spectral properties: Mp 118—119 °C. IR (KBr): 1190, 1295, and 1305 cm^{-1}. Found: C, 61.56; H, 5.19%. Calcd for $C_{22}H_{22}O_2SSe$: C, 61.53; H, 5.16%. To a solution containing of 1-phenylseleno-1-phenyl-2-(*p*-tolylsulfonyl)propane 1.0 g (2.3 mmol) in 10 cm^3 of THF, 2.0 cm^3 of 30% hydrogen peroxide was added slowly at room temperature and the mixture was stirred for an additional hour. The organic layer was extracted with ether, and the extract was dried over with anhydrous magnesium sulfate. After evaporation of the solvent, the residual oil was subjected to preparative thick-layer chromatography. The component isolated from the plate contained 0.35 g (55%) of a white solid, mp 54—55 °C (from ethanol), whose structure was assigned as (*Z*)-1-phenyl-2-(*p*-tolylsulfonyl)propene (**3a**) on the basis of its physical and spectroscopic data: Mp 54—55 °C. IR (KBr): 1150 and 1315 cm^{-1}. ^1H NMR ($CDCl_3$): δ=2.16 (3H, d, *J*=1.2 Hz), 2.33 (3H, s), 7.03 (1H, q, *J*= 1.2 Hz), 7.14 (2H, d, *J*=8.4 Hz), 7.27 (5H, s), and 7.53 (2H, d, *J*=8.4 Hz). Mass: *m/z* 272 (M^+). Found: C 70.62; H, 6.00%. Calcd for $C_{16}H_{16}O_2S$: C, 70.56; H, 5.92%.

*Attempt at the Isomerization of **3a** to **2a**.* A solution containing 102 mg (0.38 mmol) of **3a** and 84 mg (0.03 mmol) of **1** in 1.5 cm^3 of benzene was heated at 60 °C in a degassed sealed tube for 72 h. The reaction mixture was subjected to preparative thick-layer chromatography. The only one component isolated from the plate (98 mg) consisted of 100% of recovered **3a** and no **2a** was detected by its mp, IR, and ^1H NMR spectra.

Attempt at the Isomerization of cis- *or* trans-*β-Methylstyrene in the Absence of Arenesulfonyl Chloride.* A solution containing 236 mg (2.0 mmol) of *cis*- or *trans*-β-methylstyrene and 153 mg (0.16 mmol) of **1** in 3.0 cm^3 of benzene in the presence or absence of 202 mg (2.0 mmol) of triethylamine was heated at 60 °C in a degassed sealed tube for 72 h. After removal of the solvent, the residue was subjected to the elution chromatography on a short column of silica gel, using hexane as the eluent to remove the catalyst. The component concentrated by evaporation of the solvent was subjected to the HPLC. In every case, neither *cis*- to *trans*- nor *trans*- to *cis*-isomerization of β-methylstyrene was observed under these conditions.

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