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REACTIONS OF p-TOLUENESULFONYL CHLORIDE WITH STYRENES CATALYZED BY DICHLOROTRIS(TRIPHENYLPHOSPHINE)RUTHENIUM(II)

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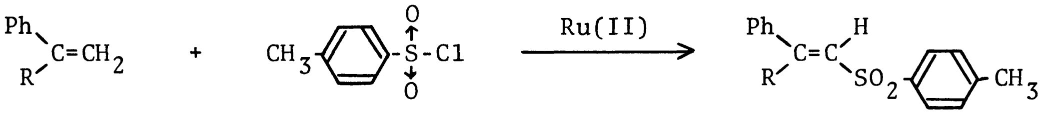
In the presence of dichlorotris(triphenylphosphine)ruthenium(II) p-toluenesulfonyl chloride was found to react with styrenes under mild reaction conditions to give alkenyl sulfones in good yields. The reaction was highly regio- and stereoselective and formed only β-hydrogen-substituted (E)-isomers.

While organosulfur compounds have played important roles in organic syntheses, little attention has been paid to their utilization in organo-transition metal chemistry. Studies on the insertion of sulfur dioxide into transition metal-alkyl bond$^{1)}$ and reverse process, the extrusion of sulfur dioxide from arenesulfonate- and arenesulfinate-transition metal complexes have been reported.$^{2)}$ More recently, Tamaru, Kagotani, and Yoshida reported the reaction of 1,3-dienes and sodium alkanesulfinates in acetic acid in the presence of palladium(II) chloride produces di-μ-chloro-bis(1-syn-alkylsulfonylmethyl-π-allyl)dipalladium(II) complexes, which on treatment with dimethylglyoxime in methanol are degradated selectively to γ,δ-unsaturated sulfone.$^{3)}$

We report herein our finding that in the presence of dichlorotris(triphenylphosphine)ruthenium(II), p-toluenesulfonyl chloride reacted smoothly with styrenes to give α,β-unsaturated sulfones in good yields under mild reaction conditions without desulfonylation according to the following scheme. The good yields of the products indicate that the ruthenium(II) catalyzed reaction was accompanied by but little telomerization.



R: H, Me, Ph

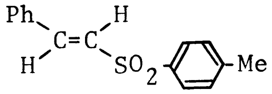
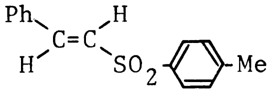
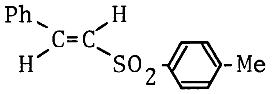
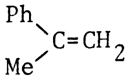
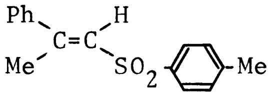
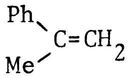
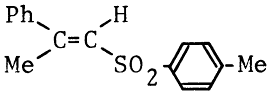
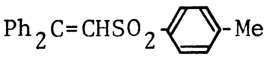
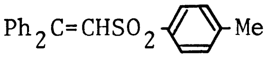
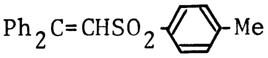
In a typical procedure, a solution containing 381 mg(2.0 mmol) of p-toluenesulfonyl chloride, 229 mg(2.2 mmol) of styrene, 19 mg(0.02 mmol) of dichlorotris(triphenylphosphine)ruthenium(II) and 371 mg(2.0 mmol) of tri-n-butylamine in 3.0 ml of benzene in degassed sealed tube was heated at 60°C for 72 h. TLC analysis of the resulting mixture disclosed that the p-toluenesulfonyl chloride had been completely consumed and one major product and a trace amount of minor product were formed. The crude reaction mixture was subjected elution chromatography on Florisil using benzene as the eluent. The minor product was identified as S-(p-tolyl) p-toluenethiosulfonate by comparison with its mp(74°C, lit., 75°C), IR, and NMR spectra of the authentic sample. The major fraction (445 mg) solidified on standing, mp 124°C (from ethanol), and was assigned the structure of (E)-β-(p-tolylsulfonyl)styrene on the basis of the following data: IR(KBr) 1310 and 1143 cm^{-1}; NMR($CDCl_3$) δ 2.40(3H, s), 6.85(1H, d, J=15.0 Hz), 7.30(2H, d, J=8.4 Hz), 7.38(5H, s), 7.66(1H, d, J=15.0 Hz), and 7.84(2H, d, J=8.4 Hz); Mass(30 eV) m/e 258(M^+), 194, 193, 139, 119, 103, 102, 92 91(base), and 77; Anal. Calcd for $C_{15}H_{14}O_2S$: C, 69.74; H, 5.46. Found: C, 69.67; H, 5.46.

Similarly, p-toluenesulfonyl chloride was treated with α-methylstyrene and 1,1-diphenylethylene in the presence of ruthenium(II) catalyst for 72 h to give α,β-unsaturated sulfones. When the reaction was carried out in the absence of ruthenium(II) catalyst no reaction was observed and all the starting materials were recovered. Addition of amines such as triethylamine or tri-n-butylamine in the reaction media improved the yield of the product from 7 to 80 and 86% respectively in the styrene case. Other bases such as pyridine, 2,6-lutidine, and piperidine were also increased the product yield. Addition of base in the reaction media seems to assist the recyclization of the ruthenium(II) catalyst. The results are summarized in Table 1.

The observed reactions were highly regio- and stereoselective. Namely, only β-hydrogen was substituted of the styrenes and only (E)-isomers were formed. The low yield of 1,1-diphenylethylene case could be accounted for the steric hindrance in the coordinated state with transition metal-phosphine complex and the olefin.

Other transition metal catalyst such as chlorotris(triphenylphosphine)rhodium(I), tetrakis(triphenylphosphine)palladium(0), palladium chloride, and 1:2 mixture of palladium acetate and triphenylphosphine were also effected the reaction of p-toluenesulfonyl chloride with styrenes, but conversion was invariably low at temperatures

Table 1. Reactions of p-toluenesulfonyl chloride with styrenes in the presence of dichlorotris(triphenylphosphine)ruthenium(II)[a]

Olefin	Ru(II) (mmol)	Amine (mmol)	Product[b] (yield, %)[c]	Conversion
$PhCH{=}CH_2$	0	—— (0)	——— (0)	0
$PhCH{=}CH_2$	0	Et_3N (2.0)	——— (0)	0
$PhCH{=}CH_2$	0.02	—— (0)	 (7)	10
$PhCH{=}CH_2$	0.02	Et_3N (2.0)	 (80)	100
$PhCH{=}CH_2$	0.02	Bu_3N (2.0)	 (86)	100
	0.02	Et_3N (2.0)	 (86)	79
	0.02	Bu_3N (2.0)	 (88)	88
$Ph_2C{=}CH_2$	0.06	—— (0)	 (trace)	22
$Ph_2C{=}CH_2$	0.02	Et_3N (2.0)	 (37)	78
$Ph_2C{=}CH_2$	0.02	Bu_3N (2.0)	 (36)	59

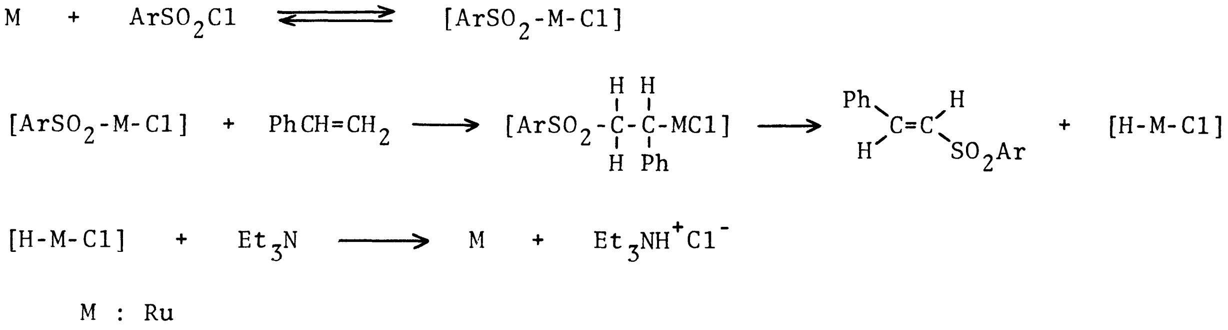
a) Reactions were carried out on homogeneous benzene solution at 60°C for 72 h in degassed sealed tube using 2.2 mmol of olefin and 2.0 mmol of p-toluenesulfonyl chloride. A trace amount of S-(p-tolyl) p-toluenethiosulfonate was formed in all the cases when the ruthenium(II) catalyst was presented in the reaction media.

b) NMR, IR, and mass spectra and elemental analyses were in good agreement with the assigned structures.

c) Yields were determined by isolation (based on the p-toluenesulfonyl chloride consumption).

60-100°C in various solvents. While aliphatic terminal olefins such as methyl acrylate reacted with p-toluenesulfonyl chloride in the presence of ruthenium(II) catalyst to give corresponding vinyl sulfones, non terminal olefins such as cyclohexene did not give the expected vinyl sulfones under the similar reaction conditions.

Present results are likely explained by reaction mechanism involving an oxidative-adduct of p-toluenesulfonyl chloride to Ru(II), which is similar to the one proposed by Mori[4)] and Heck[5)] for the palladium-catalyzed (vinylic hydrogen substitution) reactions with aryl halides.



$$M + ArSO_2Cl \rightleftharpoons [ArSO_2\text{-}M\text{-}Cl]$$

$$[ArSO_2\text{-}M\text{-}Cl] + PhCH{=}CH_2 \longrightarrow [ArSO_2\text{-}\overset{H}{\underset{H}{C}}\text{-}\overset{H}{\underset{Ph}{C}}\text{-}MCl] \longrightarrow \begin{matrix} Ph & & H \\ & C{=}C & \\ H & & SO_2Ar \end{matrix} + [H\text{-}M\text{-}Cl]$$

$$[H\text{-}M\text{-}Cl] + Et_3N \longrightarrow M + Et_3NH^+Cl^-$$

$$M : Ru$$

Comprehensive studies on the scope and limitation of the reactions are in progress.

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