

1,3-REARRANGEMENT OF ALLYLIC p-TOLYL SULFONES CATALYZED BY $[\text{Pd}(\text{PPh}_3)_4]$
AND ITS APPLICATION TO THE SYNTHESIS OF α,β -UNSATURATED KETONES

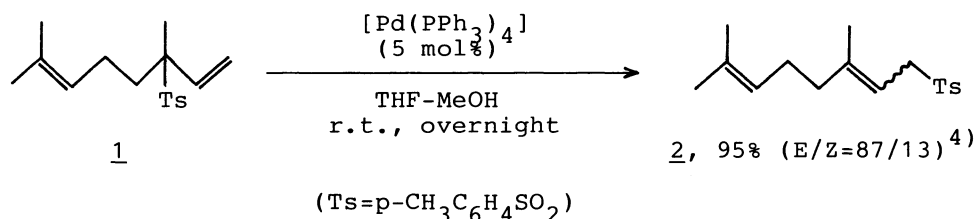
Katsuhiko INOMATA,^{*} Yasue MURATA, Hisatoyo KATO, Yuhko TSUKAHARA,
Hideki KINOSHITA, and Hiroshi KOTAKE

Department of Chemistry, Faculty of Science, Kanazawa University, Kanazawa 920

The treatment of allylic p-tolyl sulfones with a catalytic amount of $[\text{Pd}(\text{PPh}_3)_4]$ gave the 1,3-rearrangement products in high yields. A convenient method for the preparation of α,β -unsaturated ketones using $[\text{Pd}(\text{PPh}_3)_4]$ as a catalyst from the 1,3-rearrangement products, 2-tosylhomoallyl alcohols, is also described.

In the previous paper,¹⁾ it was reported that the reaction of allylic acetates with sodium p-toluenesulfinate in the presence of $[\text{Pd}(\text{PPh}_3)_4]$ as the catalyst in THF-MeOH gave the regio- and stereocontrolled allylic p-tolyl sulfones in good yields. 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⁾

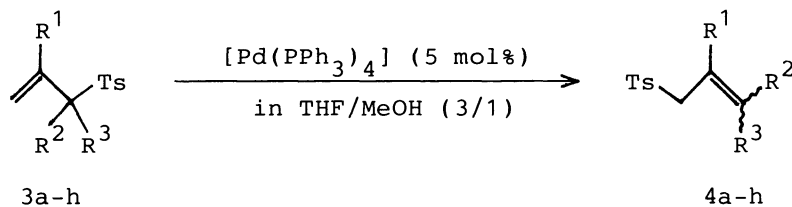
The recent publication by Lin and Whitham³⁾ describing 1,3-rearrangement of allylic sulfones under thermal conditions; e.g., under reflux in CCl_4 containing $(\text{PhCO}_2)_2$ (5 mol %), prompted us to report our observations regarding to Pd(0)-catalyzed 1,3-rearrangement of allylic sulfones. A part of results has been described briefly in the previous paper.¹⁾ Thus, linalyl p-tolyl sulfone (1), when treated with a catalytic amount of $[\text{Pd}(\text{PPh}_3)_4]$ in THF and methanol (2/1, v/v), was converted into the mixture of geranyl (E-isomer of 2) and neryl (Z-isomer of 2) p-tolyl sulfones as shown below. This finding encouraged us to explore whether such 1,3-rearrangement of allylic sulfones takes place in general.



When the allylic p-tolyl sulfone derivatives (3a-h) prepared by the alkylation of allyl or methallyl p-tolyl sulfones were treated with 5 mol% of $[\text{Pd(PPh}_3)_4]$ in THF/methanol (3/1), the 1,3-rearrangement of the p-toluenesulfonyl (tosyl) group was found to take place easily in all the cases giving E-isomers predominantly as listed in Table 1. Such 1,3-rearrangement of secondary or tertiary sulfones to primary sulfones was also observed in the case of 2-tosyl-homoallyl alcohols (6a-c) which were prepared by the reaction of lithium salt of 5 and aldehydes. The results are shown in Table 2. It is noteworthy that the reaction afforded exclusively E-isomers of 7.

The rearrangement products (7a-c) were applied to the synthesis of α,β -unsaturated ketones. The alkylation of 7 on the carbon atom attached to tosyl

Table 1. Palladium-Catalyzed 1,3-Rearrangement of Allylic p-Tolyl Sulfones 3



Entry	<u>3a-h</u>	R ¹	R ²	R ³	Conditions	Yield/% <u>4a-h</u>	Ratio ^{a)} E/Z
1	<u>3a</u>	H	C ₆ H ₅ (CH ₂) ₂	H	reflux, 35 min	86 (<u>4a</u>)	79/21
2	<u>3b</u>	H	C ₆ H ₅ CH ₂	H	reflux, 50 min	86 (<u>4b</u>)	92/8
3	<u>3c</u>	H	CH ₃ (CH ₂) ₄	H	reflux, 1 h 45 min	96 (<u>4c</u>)	81/19
4	<u>3d</u>	CH ₃	C ₆ H ₅ (CH ₂) ₂	H	reflux, 3.5 h	87 (<u>4d</u>)	64/36
5	<u>3e</u>	CH ₃	CH ₃ (CH ₂) ₄	H	reflux, 3 h 10 min	85 (<u>4e</u>)	71/29
6	<u>3f</u>	H	C ₆ H ₅ (CH ₂) ₂	CH ₃	reflux, 1.5 h	78 (<u>4f</u>)	74/26
7	<u>3g</u>	H	C ₆ H ₅ CH ₂	CH ₃	r.t., 1.5 d	86 (<u>4g</u>)	82/18
8	<u>3h</u>	H	CH ₃ (CH ₂) ₄	CH ₃	reflux, 2.5 h	quant (<u>4h</u>)	84/16

a) Determined by 400 MHz ¹H-NMR spectra.⁵⁾

Table 2. Palladium-Catalyzed 1,3-Rearrangement of 2-Tosylhomomallyl Alcohols 6

$ \begin{array}{ccccc} \text{Ts-CH=CH-CH}_2\text{R} & \xrightarrow[\text{2) RCHO in THF}]{\text{1) BuLi}} & \text{Ts-CH=CH-CH(OH)-CH}_2\text{R} & \xrightarrow[\text{in THF/MeOH (3/1)}]{\text{[Pd(PPh}_3)_4] (5 \text{ mol}\%), \text{ reflux, 1 h}} & \text{Ts-CH=CH-CH(OH)-CH}_2\text{R} \\ \text{5} & & \text{6a-c} & & \text{7a-c} \end{array} $				
Entry	R	Yield/%		Stereochemistry of <u>7</u> ^{b)} Ratio of E/Z
		<u>6a-c</u> ^{a)}	<u>7a-c</u>	
1	C ₆ H ₅	86 (<u>6a</u>)	87 (<u>7a</u>)	96/4
2	CH ₃ (CH ₂) ₇	82 (<u>6b</u>)	90 (<u>7b</u>)	97/3
3	(CH ₃) ₂ CH	75 (<u>6c</u>)	97 (<u>7c</u>)	95/5

a) Yield of the mixture of diastereoisomers. In the case of 6a, they were separable (mp 67-68 °C and 88-89 °C) and their ratio was ca. 1/1.

b) Determined by 400 MHz ¹H-NMR spectra.⁵⁾

group was achieved via dianion produced by treatment with 2 equiv. of butyl lithium. The alkylated products (8a-c) were then treated with 5 mol% of [Pd(PPh₃)₄] in the presence of triethylamine to give the corresponding α,β-unsaturated ketones (9a-c) in fairly good yields (Table 3).

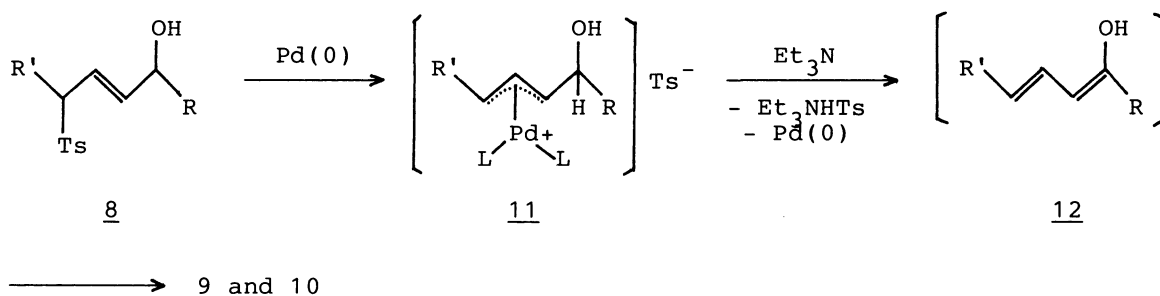
Table 3. The Synthesis of α,β-Unsaturated Ketones 9

$ \begin{array}{ccccc} \text{7a-c (E)} & \xrightarrow[\text{2) R'I, -78 °C} \rightarrow \text{-30 °C in THF}]{\text{1) 2BuLi, THF/HMPA, -78 °C, 1 h}} & \text{R'-CH=CH-CH(OH)-CH}_2\text{R} & \xrightarrow[\text{in C}_2\text{H}_4\text{Cl}_2/\text{MeOH (3:1)}]{\text{[Pd(PPh}_3)_4] (5 \text{ mol}\%), \text{ Et}_3\text{N, reflux}} & \text{R'-CH=CH-CH(OH)-CH}_2\text{R} \\ & & \text{8a-c} & & \\ & \xrightarrow[\text{r.t., overnight in MeOH/CHCl}_3]{\text{p-TsOH}} & \text{R'-CH=CH-C(=O)-CH}_2\text{R} & + & \text{R'-CH=CH-C(=O)-CH}_2\text{R} \\ & & \text{9a-c} & & \text{10a-c} \end{array} $					
Entry	R	R'	Yield/% ^{a)}		
			<u>8a-c</u> ^{b)}	<u>9a-c</u>	<u>10a-c</u>
1	C ₆ H ₅	CH ₃ (CH ₂) ₇	76 (<u>8a</u>)	59 (<u>9a</u>)	-
2	CH ₃ (CH ₂) ₇	CH ₃ (CH ₂) ₁₇	57 (<u>8b</u>)	65 (<u>9b</u>)	7 (<u>10b</u>)
3	(CH ₃) ₂ CH	CH ₃ (CH ₂) ₁₇	65 (<u>8c</u>)	71 (<u>9c</u>)	11 (<u>10c</u>)

a) The ratio of 9/10 was determined by 400 MHz ¹H-NMR spectra.

b) Yield of the mixture of diastereoisomers. For instance, their ratio of 8a was 54/46.

The formation of β,γ -unsaturated ketones (10b,c) (entries 2 and 3) was seemed to support the following mechanism.⁶⁾



The allylic sulfone (8) reacts with palladium (0) catalyst affording π -allyl complex (11), which has been proposed in the 1,3-rearrangement of the allylic sulfones,¹⁾ followed by elimination of triethylammonium p-toluenesulfinate and Pd (0) to give dienol intermediate (12) which tautomerizes to 9 and 10.

The experimental procedure for conversion of 8 to α,β -unsaturated ketone (9) is as follows: To a mixture of 8b (30 mg, 0.051 mmol) and triethylamine (18 mg, 3.49 equiv.) in dry methanol (1.5 ml) was added a solution of [Pd(PPh₃)₄] (3 mg, 5 mol%) in dry 1,2-dichloroethane (4.5 ml) under nitrogen. After refluxing for 7.5 h, the solvent was evaporated. The residue was dissolved in methanol containing p-toluenesulfonic acid (10 mg, 1.0 equiv.) and chloroform and the solution was allowed to stand overnight at room temperature. After replacement of the solvent by ethyl acetate, the solution was subsequently washed with 10% NaHCO₃ solution containing a small amount of KCN and with a NaCl saturated solution, and dried over MgSO₄. Evaporation of the solvent followed by preparative TLC (SiO₂, hexane/AcOEt=30/1, developed twice) afforded a mixture of 9b and 10b as an oil (16 mg, 72% yield) in the ratio 9/1.

References

- 1) K. Inomata, T. Yamamoto, and H. Kotake, *Chem. Lett.*, **1981**, 1357.
- 2) A. Ahmed, N. Taniguchi, H. Fukuda, H. Kinoshita, K. Inomata, and H. Kotake, *Bull. Chem. Soc. Jpn.*, **57**, 781 (1984).
- 3) P. Lin and G. H. Whitham, *J. Chem. Soc., Chem. Commun.*, **1983**, 1102.
- 4) The ratio was determined by GLPC (Shimadzu GC-6A, SE-30, 270 °C, N₂ 50 ml/min).
- 5) These isomers are commonly separable with a preparative TLC (SiO₂), but the ratios were estimated by 400 Mz ¹H-NMR spectra of the mixture of the isomers.
- 6) M. Suzuki, Y. Oda, and R. Noyori, *J. Am. Chem. Soc.*, **101**, 1623 (1979).

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