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REGIO- AND STEREOCONTROLLED SYNTHESIS OF ALLYLIC p-TOLYL SULFONES CATALYZED BY PALLADIUM (0) COMPLEX

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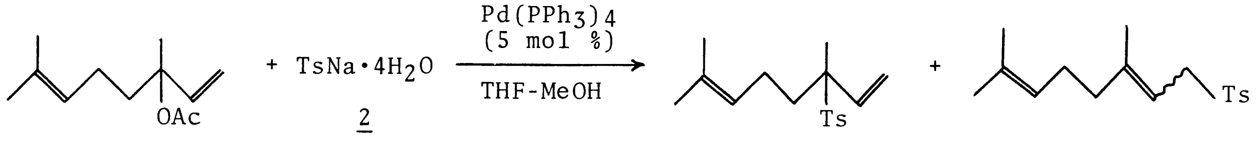
The reaction of allyl esters with sodium p-tolylsulfinate in tetrahydrofuran and methanol catalyzed by $Pd(PPh_3)_4$ gave the regio- and stereocontrolled allylic p-tolyl sulfones in good yields at room or lower temperature.

The useful synthetic procedures using allylic sulfones as synthons have been recently developed,[1-3] however, only a few general methods for the preparation of the allylic sulfones have been found in literatures[4-6] except the classical method by the reaction of allyl halides with alkali arenesulfinates.

M. Julia and co-workers have reported[6] that the reaction of dienes with arenesulfinic acids or sodium arenesulfinates in acetic acid in the presence of palladium catalysts gave high yields of allylic sulfones containing large proportions of the more substituted isomer and that the reaction of linalyl or geranyl acetate with alkali arenesulfinates catalyzed by $Pd(PPh_3)_4$ gave the mixture of linalyl (10%), geranyl (60%), and neryl (20%) arenesulfones in THF at 60°C.

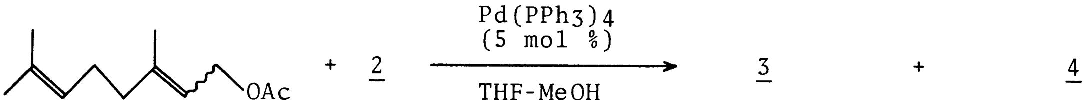
In connection with our continued interest to extend the synthetic utility of sulfones[7a-e] we have tried a similar reaction of linalyl acetate (1) with sodium p-tolylsulfinate tetrahydrate (2) catalyzed by $Pd(PPh_3)_4$ in THF and methanol (to dissolve the sulfinate) at relatively low temperature and in contrast with the result reported by M. Julia and co-workers we have found that linalyl p-tolyl sulfone (3) was exclusively obtained when the reaction was carried out at 0°C and was worked up with the addition of aqueous potassium cyanide to deactivate the palladium (0) catalyst at 0°C. This reaction proceeded more rapidly at room temperature (ca. 25°C) and afforded 3 in 62% yield accompanying the formation of 4 (23%, E/Z=70/30) after one min. When the reaction mixture was allowed to stand overnight at room temperature, 3 was not detectable on TLC (silica gel, hexane/ethyl acetate, 8/1, v/v) but only 4 was isolated in 84% yield (E/Z=87/13) as shown in the following scheme.



1 2 (Ts=p-$CH_3C_6H_4SO_2$) 3 4

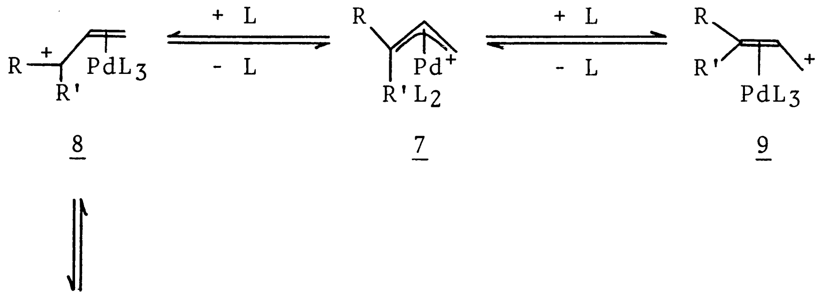
	3	4
0°C, 3.5 h	78%	9% (E/Z=81/19)
r.t., 1 min	62%	23% (E/Z=70/30)
r.t., overnight	-	84% (E/Z=87/13)

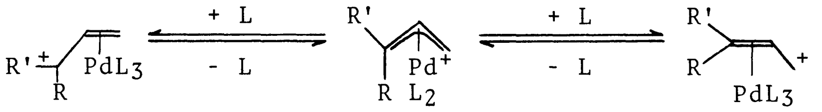
These results appear to suggest that 3 is the kinetically-controlled product and the more stable 4 is the thermodynamically-controlled one. The results of the similar reaction of geranyl (5) and neryl (6) acetate with 2 have made this point clearer, that is, while the reaction was more sluggish than the case of 1, 3 was initially formed predominantly, but only 4 was obtained on standing overnight as shown in the following scheme.



		3	4
5 (E)	r.t., 25 min	48%	28% (E/Z=97/3)
	r.t., overnight	-	90% (E/Z=86/14)
6 (Z)	r.t., 20 min	57%	8% (E/Z=79/21)
	r.t., overnight	-	87% (E/Z=82/18)

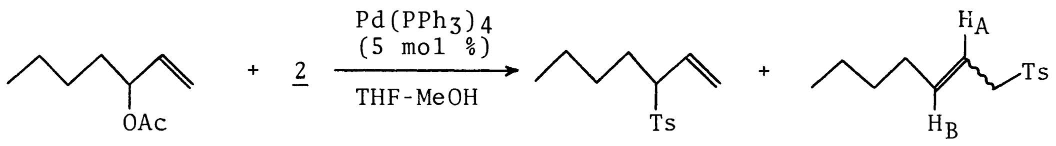
Initially formed π-allyl complex 7 (or 7'), which is more smoothly formed from a tertiary ester 1 than a primary ester 5 or 6, may be in equilibrium with 8, 8' and 9, 9'. Since a tertiary carbonium ion intermediate 8 (or 8') seems to be more stable than the others, the kinetically-controlled product 3 might be obtained at low temperature in the case of 1 or at initial step of the reaction of 5 or 6. From the fact that the treatment of 3 with a catalytic amount of Pd(PPh_3)$_4$ gave 4, 3 might be reversibly converted to π-allyl complex 7 (or 7') and ultimately the thermodynamically stable 4 (especially (E)-form) might be obtained through 9 (if R>R') on standing overnight at room temperature.





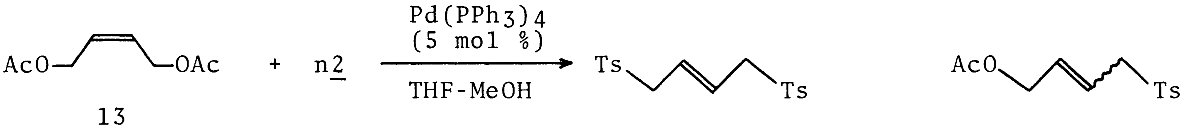
8' 7' 9'

Additional support of this consideration was found in the reaction of 1-hepten-3-yl acetate (10) with 2 under similar condition as shown below. Three products, which seemed to correspond to 11 and 12 (E and Z), were observed by GLPC at initial step and finally these were converted to (E)-form of 12 (established by NMR, J_{AB}=16.1 Hz) on standing overnight.



10 r.t., overnight 11, - 12 (E), 98%

On the other hand, it was found that (Z)-2-butenylene diacetate (13) afforded 1,4-bis(p-tolylsulfonyl)-(E)-2-butene (14)[8] in either case using one equivalent or two equivalents of 2. We could not observe the formation of a monosulfonylated product such as 15, which suggested that the second sulfonylation step was faster than the first one. As the above examples, this reaction predominantly gave (E)-allylic sulfones, which seems to be reasonable from the discussion described above.

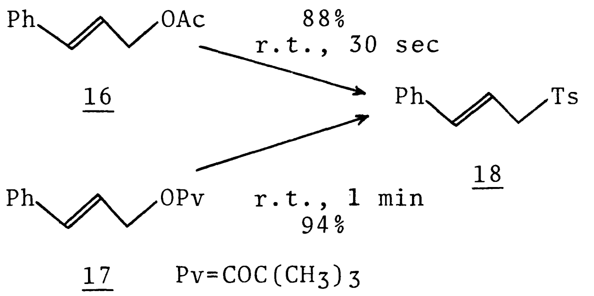


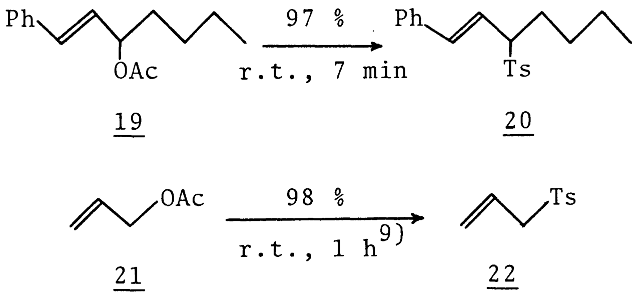
13 14 15

n=1, r.t., 2 min 47%

n=2, r.t., 2 min 70%

The usual allylic sulfones were also readily prepared by this reaction from the corresponding allyl acetates in excellent yields described below.[8,9)





From the above results, it is clear that the reaction of allyl acetates with sodium p-tolylsulfinate catalyzed by $Pd(PPh_3)_4$ provides a convenient regio- and stereocontrolled synthetic method of allylic sulfones. The related work is now in progress.

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References

1) P. D. Magnus, Tetrahedron, 33, 2019 (1977).

2) B. M. Trost, N. R. Schmuff, and M. J. Miller, J. Am. Chem. Soc., 102, 5979 (1980).

3) K. Sato, S. Inoue, A. Onishi, N. Uchida, and N. Minowa, J. Chem. Soc., Chem. Commun., 1981, 761.

4) M. Julia and D. Arnold, Bull. Soc. Chim. Fr., 746, 743 (1973).

5) A. Fischli and H. Mayer, Helv. Chim. Acta, 58, 1492 (1975).

6) M. Julia, M. Nel, and L. Saussine, J. Organomet. Chem., 181, C 17 (1979).

7) a) H. Kotake, K. Inomata, Y. Murata, H. Kinoshita, and M. Katsuragawa, Chem. Lett., 1976, 1073; b) H. Kotake, K. Inomata, and M. Sumita, Chem. Lett., 1978, 717; c) K. Inomata, H. Kinoshita, H. Takemoto, Y. Murata, and H. Kotake, Bull. Chem. Soc. Jpn. 51, 3341 (1978); d) K. Inomata, Y. Nakayama, M. Tsutsumi, and H. Kotake, Heterocycles, 12, 1467 (1979) and references cited therein; e) H. Kotake, K. Inomata, H. Kinoshita, Y. Sakamoto, and Y. Kaneto, Bull. Chem. Soc. Jpn., 53, 3027 (1980).

8) All new compounds (12, 14, and 20) have been fully characterized by spectral means and elemental analyses. 14: mp 200.0-201.5°C (1,4-bis(p-tolylsulfonyl)-(Z)-2-butene derived from (Z)-2-buten-2,3-diol melted at 157.0-158.5°C). 20: mp 90-92°C.

9) 5 mol % $Pd(PPh_3)_4$ was used as catalyst except 21, in the case of which it was 1 mol %.

10) A typical experimental procedure for the preparation of allylic sulfone is described as follows: to a solution of sodium p-tolylsulfinate tetrahydrate (2, 275 mg, 1.1 mmol) in methanol (0.8 ml) was successively added a solution of cinnamyl acetate (16, 176 mg, 1.0 mmol) in THF (1.5 ml) and a solution of $Pd(PPh_3)_4$ (58 mg, 5.0×10^{-2} mmol) in THF (1.5 ml) at room temperature under nitrogen. The color of reaction mixture was changed from brown to yellow and a lot of precipitate appeared within 30 sec. After addition of aqueous potassium cyanide (13 mg, 0.2 mmol), the solvent was evaporated. The residue was treated with water and undissolved crystalline compound was recrystallized from ethanol to give 18. In the cases of 1, 5, 6, and 10, the oily products (4: a mixture of E and Z and the ratio was estimated by GLPC. 12: confirmed by 100 MHz NMR spectrum) were separated by preparative TLC.

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