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PALLADIUM(II)-ASSISTED CONVERSION OF A 2-ALKENYL SULFONE INTO A 3-ACETOXY(OR CHLORO)-1-ALKENYL SULFONE

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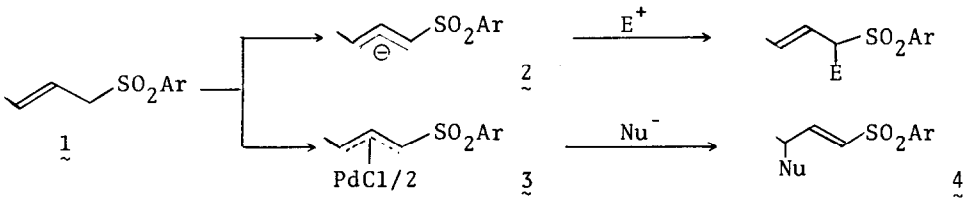
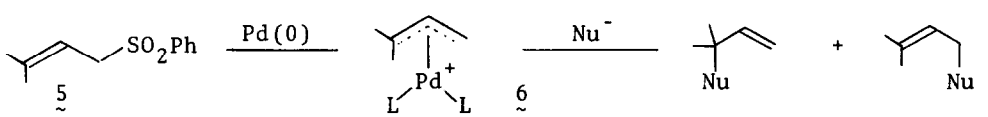
Abstract: 2-alkenyl p-tolyl sulfone was converted into the corresponding 3-acetoxy-1-alkenyl p-tolyl sulfone via a π-allyl palladium complex which underwent regiospecific attack of a nucleophile, acetate ion, and the reaction conditions for predominant formation of 3-chloro-1-alkenyl p-tolyl sulfone are also described.

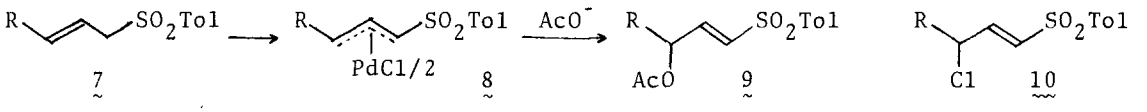
To date, it has been well established that an electrophile (E^+) can be regiospecifically introduced at the 1-position of a 2-alkenyl sulfone (1) by means of generation of the corresponding allyl anion (2) and the subsequent reaction with the electrophile.[1] However, scant attention has been payed to introduction of a nucleophile (Nu^-) into 1 *via* an allyl cation system, which is expected to produce a useful 3-functionalized 1-alkenyl sulfone (4) by regiospecific attack of the nucleophile. As a model for this system, we had chosen a di-μ-chlorobis(1-sulfonyl-π-allyl)dipalladium (3), and our investigation had been undertaken on preparation of 3 and its reaction with a nucleophile.



Recently, Trost et al. reported on the reaction of 2-alkenyl phenyl sulfone (5) with Pd(0), where the sulfonyl group behaved as a leaving group, resulting in formation of a π-allyl palladium complex (6).[2] This prompts us to disclose



our findings that 2-alkenyl p-tolyl sulfone (7) reacts with $PdCl_2$ in the presence of $CuCl_2$ and AcONa to give a sulfonyl-substituted π-allyl palladium complex (8) and that 3-acetoxy-1-alkenyl p-tolyl sulfone (9) is produced by regiospecific attack of acetate ion on 8.



7 8 9 10

a: R = Ph b: R = H c: R = CH_3 d: R = n-C_9H_{19}

[Tol ≡ p-tolyl]

Di-μ-chlorobis[1-phenyl-3-(p-tolyl)-π-allyl]dipalladium (8a)[3] could be prepared in 74% yield from 3-phenyl-2-propenyl p-tolyl sulfone (7a) by the reaction with $PdCl_2$ (1 equiv) in the presence of $CuCl_2$ (2.7 equiv), AcONa (13 equiv), and NaCl (13 equiv) in AcOH at 60 °C for 70.5 h and at 80-85 °C for 25 h.[4,5] When 8a was heated with AcONa (24 equiv) in AcOH at 80-88 °C for 42 h, 3-acetoxy-3-phenyl-1-propenyl p-tolyl sulfone (9a)[6,7] was afforded and we could not observe formation of its regioisomer (1-acetoxy-3-phenyl-2-propenyl p-tolyl sulfone) by an NMR analysis.

From these results, it was suggested that 7a could be converted to 9a without isolation of intermediary 8a by prolonged heating along with $PdCl_2$, $CuCl_2$, and AcONa in AcOH. In fact, 9a was obtained in 60% yield by stirring a suspension involving 7a (1 equiv), $PdCl_2$ (1 equiv), $CuCl_2$ (6.2 equiv), AcONa (13 equiv), and NaCl (13 equiv) in AcOH at 60 °C for 96 h and at 80 °C for 88 h. In a similar manner, 2-propenyl p-tolyl sulfone (7b), 2-butenyl p-tolyl sulfone (7c), and 2-dodecenyl p-tolyl sulfone (7d) were transformed into the corresponding 3-acetoxy-1-alkenyl p-tolyl sulfone (9)[8] as summarized in Table 1.

Furthermore, we examined the possibility that $PdCl_2$ could opperate as a catalyst in the above reaction, because a large excess of $CuCl_2$ is expected to oxidize not only the hydridopalladium species[3] involved as an intermediate during formation of 8, but also the palladium metal produced by the reaction of 8 with AcONa. As being apparent from a persual of Table 1, a catalytic amount of $PdCl_2$ was effective to the conversion of 7 to 9 and a smooth reaction took place even when 0.03 equiv of $PdCl_2$ was employed, except the case of 7b. Surprisingly, 7b gave 3-chloro-1-propenyl p-tolyl sulfone (10b) as a major product when the amount of $PdCl_2$ was reduced to 0.03 equiv, whereas 9b was mainly formed in the reaction using 1.0 or 0.1 equiv of $PdCl_2$.[9]

For production of 9 in the present reaction, there are two conceivable paths, *i.e.* (i) nucleophilic attack of acetate ion on 8 and (ii) initial formation of 10 followed by substitution with acetate ion. However, the latter appears improbable because 10b and 10c were recovered unchanged when subjected to either the reaction with AcONa in AcOH or the present reaction system ($PdCl_2$-$CuCl_2$-AcONa-NaCl in AcOH).

Finally, it should be noted that introduction of chlorine atom instead of acetoxyl group into 7 to afford 10 could be achieved by performing the above reaction in the absence of AcONa. For example, treatment of 7c with 1.0 or 0.03

Table 1. Direct conversion of 2-Alkenyl p-Tolyl Sulfone (7) to 3-Acetoxy- (or Chloro)-1-alkenyl p-Tolyl Sulfone (9 or 10)[a]

R	$PdCl_2$ (equiv)[b]	$CuCl_2$ (equiv)[b]	Temperature [Time]	Yield (%) 9	Yield (%) 10
Ph	1.0	6.2	60 °C [96 h] → 80 °C [88 h]	60	---[c]
	0.1	6.9	80 °C [144 h]	53 (58)[d]	---[c]
	0.03	6.9	80 °C [144 h]	41 (47)[d]	---[c]
H	1.0	3.4	60 °C [75 h]	70	---[c]
	0.1	2.8	60 °C [57 h]	72	---[c]
	0.03	5.9	60 °C [18 h]	5 (6)[d]	76 (93)[d]
	0.03	5.9	60 °C [96 h]	7	84
CH_3	1.0	2.7	60 °C [39 h] → 80 °C [98 h]	75	---[c]
	0.1	2.7	80 °C [52 h]	80	---[c]
	0.03	2.7	80 °C [48 h]	79	---[c]
	0.01	2.7	80 °C [78 h]	80 (89)[d]	---[c]
	1.0[e]	5.4	80 °C [49 h]	9	74
	0.03[e]	2.7	70-80 °C [156 h]	14	68
$n\text{-}C_9H_{19}$	1.0	2.7	60 °C [140 h]	80	---[c]
	0.03	3.0	80 °C [60 h]	86	---[c]

[a] A suspension containing $PdCl_2$, $CuCl_2$, AcONa (13 equiv), and NaCl (13 equiv) in AcOH was stirred at 90 °C for 2 h, and, after addition of 7, the resulting mixture was heated. [b] to 7. [c] Judging from TLC and NMR analyses, very small amount of the corresponding 10 was produced, if any. [d] based on the unrecovered 7. [e] in the absence of AcONa.

equiv of $PdCl_2$ in the presence of $CuCl_2$ and NaCl in AcOH gave 10c in 75% or 68% yield, respectively, as shown in Table 1.

Thus, we have found a convenient method for regiospecifically making 3-acetoxy-1-alkenyl p-tolyl sulfone (9) and 3-chloro-1-alkenyl p-tolyl sulfone (10), which seem to be useful intermediates for organic syntheses.

References and Notes:

1) For example, D. Savoia, C. Trombini, and A. Umani-Ronchi, *J. Chem. Soc. Perkin trans. 1*, 1977, 123.
2) B. M. Trost, N. R. Schmuff, and M. J. Miller, *J. Am. Chem. Soc.*, 102, 5979 (1980).
3) A yellow solid: mp 200-204 °C (dec) (from DMSO-AcOH-H_2O); IR (KBr) 1325,

1304, 1289, 1141, 1139, 1077, 773, 683, 667, 566 cm^{-1}. Anal. Calcd for $C_{32}H_{30}O_4Cl_2Pd_2S_2$: C, 46.51; H, 3.66%. Found: C, 46.25; H, 3.77%.
Although 8a is partly soluble in DMSO, easy decomposition of 8a occurs in the absence of AcOH to give 3-hydroxy-3-phenyl-1-propenyl p-tolyl sulfone. This makes it difficult to take its NMR spectrum.

4) These reaction conditions are analogous to those decribed by Trost et al. in preparation of di-μ-chlorobis(1,2-tetramethylene-π-allyl)dipalladium: B. M. Trost, P. E. Streze, L. Wever, T. J. Fullerton, and T. J. Dietsche, *J. Am. Chem. Soc.*, 100, 3407 (1978).

5) After addition of water and benzene, the complex (8a) floating in the benzene layer was collected by filtration. From the benzene layer, 7a and 9a were also obtained in 12% and 3% yields, respectively.

6) Satisfactory spectral data and elemental analyses were obtained for all new compounds reported herein.

7) Solvolysis (HCl-MeOH; room temperature) gave stable 3-hydroxy-3-phenyl-1-propenyl p-tolyl sulfone.

8) The structural difference between 9 and its regioisomer, 1-acetoxy-2-alkenyl p-tolyl sulfone, was easily recognized by the NMR splitting pattern of 9 when R is H, CH_3, or n-C_9H_{19}.
NMR ($CDCl_3$) of 9b: δ 2.06 (3H, s), 2.42 (3H, s), 4.74 (2H, dd, J = 1.7 and 3.8 Hz), 6.53 (1H, td, J = 1.7 and 15 Hz), 6.91 (1H, td, J = 3.8 and 15 Hz), 7.31 (2H, d, J = 8 Hz), 7.73 (2H, d, J = 8 Hz).
NMR ($CDCl_3$) of 9c: δ 1.36 (3H, d, J = 7 Hz), 2.04 (3H, s), 2.42 (3H, s), 5.32-5.64 (1H, m), 6.48 (1H, dd, J = 1.8 and 15 Hz), 6.86 (1H, dd, J = 4.2 and 15 Hz), 7.32 (2H, d, J = 8 Hz), 7.74 (2H, d, J = 8 Hz).
NMR ($CDCl_3$) of 9d: δ 0.75-2.00 (19H, m), 2.05 (3H, s), 2.43 (3H, s), 5.30-5.56 (1H, m), 6.44 (1H, dd, J = 1.6 and 15 Hz), 6.83 (1H, dd, J = 4.8 and 15 Hz), 7.31 (2H, d, J = 8 Hz), 7.73 (2H, d, J = 8 Hz).

9) At the present time, we cannot give any explanation to these intriguing phenomena and more detailed study on the effect of the $PdCl_2$ concentration is in progress.

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