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A CONVENIENT METHOD FOR THE SYNTHESIS OF HOMOALLYL ALCOHOL USING A NEW DESULFONYLATION METHOD

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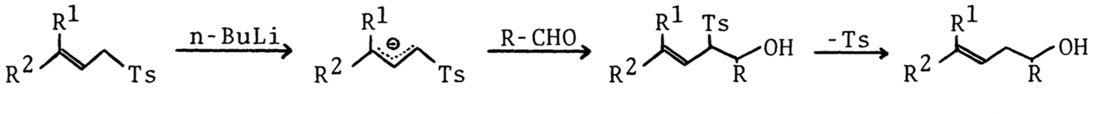
2-Tosyl homoallyl alcohol obtained by the reaction of allylic p-tolyl sulfone with aldehyde was found to be easily desulfonylated to homoallyl alcohol by the use of $Pd(PPh_3)_4$ as a catalyst and hydride ion as a nucleophile, without any side reactions.

Allylic sulfones have been proven to be very useful intermediates for carbon-carbon bond formation via the sulfur-stabilized carbanions and effectively used in synthetic chemistry$^{1)}$.

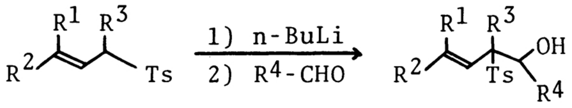
In connection with our continued interest to extend the synthetic utility of sulfones$^{2)}$, we now investigated the reaction of allylic p-tolyl sulfones$^{3)}$, which were easily obtained from allyl esters and sodium p-tolylsulfinate in the presence of $Pd(PPh_3)_4$, with a variety of aldehydes and found that treatment of the lithium salt of allylic p-tolyl sulfone (1) with aldehydes afforded exclusively the regioselective product, 2-tosyl homoallyl alcohols (2) in good yields as shown in Table 1.



(1) (2) (3)

The reaction was carried out as follows: to a solution of cinnamyl p-tolyl sulfone(272 mg, 1 mmol) in dry THF(5 ml) was added a hexane solution of n-BuLi(1.1 eq.) over 5 min at -78°C under N_2. After stirring for 1 h at -78°C a solution of 1-nonanal(156 mg, 1.1 mmol) in dry THF(3 ml) was added to it. The temperature was gradually raised up to -25°C over a period of 5 h. Then, the reaction mixture was worked up and a crude product was purified by preparative TLC(hexane:AcOEt=5:1 V/V) to give the desired product(2b) in 90 % yield.

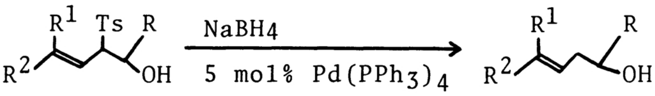
Table 1. The Reaction of Allyl p-Tolyl Sulfones with Aldehydes



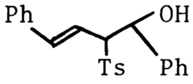
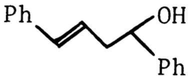
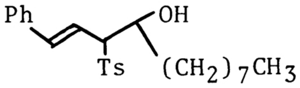
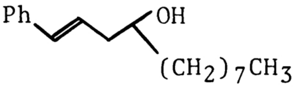
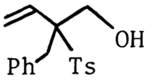
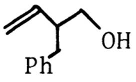
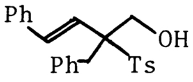
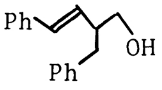
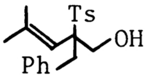
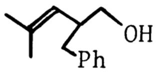
(1) (2)

R^1	R^2	R^3	R^4	Temp(°C)	Time(hr)	Yield(2a-e)[6](%)
H	Ph	H	Ph	-78--40	5-6	84 (2a)
H	Ph	H	$CH_3(CH_2)_7$	-78--25	5	90 (2b)
H	H	$PhCH_2$	H	-78-0	3	82 (2c)
H	Ph	$PhCH_2$	H	-78-0	3	86 (2d)
CH_3	CH_3	$PhCH_2$	H	-78--20	4	85 (2e)

Table 2. Preparation of Homoallyl Alcohols



(2) (3)

Run	Tosyl alcohol		$NaBH_4$	Reaction condition[a)]		Product	Yield(%)
	(2a-e)		(eq.)	Temp(°C)	Time(hr)	(3a-e)[7)]	
1		(2a)	7.3	-35-0	6		75
2		(2b)	7.3	r.t.	0.5		81
3		(2c)	7.3	0	1		91
4		(2d)	5.5	0	2		91
5		(2e)	14.6	20	5		72

a) The mixed solution of THF-i-PrOH(2:1 v/v) was used as solvent except for run 5, in which THF-EtOH-i-PrOH(5:2:2 v/v) was used.

Next, we tried to convert the resulting tosyl alcohols(2a-e) to the corresponding homoallyl alcohols(3) using a reagent such as Al(Hg)$^{4)}$, Na(Hg)$^{5)}$or Li-$EtNH_2$$^{8)}$. Unfortunately, in every case these desulfonylation procedures were accompanied with migration of double bond or retroaldol reaction.

Recently, Trost et al. reported$^{9)}$that treatment of the allyl sulfone with palladium(0) complex in the presence of nucleophile led to a smooth alkylation. Apparently the sulfonyl group serves as leaving group in this nucleophilic displacement. This fact suggests that this reaction may be used as a desulfonylation reaction if hydride ion is used as a nucleophile. Based on this assumption, we investigated the conditions and finally found a new effective desulfonylation of allyl sulfones without any migration of double bond$^{10)}$or retroaldol reaction by the use of $NaBH_4$ as a hydride donor.

A typical experimental procedure for the detosylation of tosyl alcohol is as follows: to a mixed solution of 2-benzyl-4-phenyl-2-tosyl-3-buten-1-ol(152 mg, 0.388 mmol)(2d) and $NaBH_4$(21 mg, 5.5 eq.) in THF(3 ml) and isopropyl alcohol(2 ml) was added dropwise a solution of $Pd(PPh_3)_4$(21 mg, 5 mol%) in THF(1 ml) at 0°C under N_2. After stirring was continued for 2 h at 0°C, the reaction mixture was quenched with KCN followed by extraction with ether. The ether extract was dried over Na_2SO_4 and evaporated to dryness in vacuo. The resulting residue was subjected to preparative TLC(silica gel, hexane-ethyl acetate=5:1) to give β-benzyl-δ-phenylhomoallyl alcohol(2-benzyl-4-phenyl-3-buten-1-ol) in 91 % yield as a colorless oil. Various types of homoallyl alcohol were prepared by this method in good yields as shown in Table 2.

References

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6) Compounds (2a-e) have been fully characterized by spectral means and elemental analyses.

2a: Mp 138-145°C; IR (KBr) 3490, 1590, 1275, 1125, 968 cm^{-1}; NMR ($CDCl_3$) δ 2.36 (s, 3H), 3.41-4.55 (m, 2H), 5.16-6.53 (m, 3H), 6.75-7.73 (m, 14H); Found: C, 72.80; H, 5.92%. Calcd for $C_{23}H_{22}O_3S$: C, 72.99; H, 5.88%.

2b: Mp 97-99.5°C; IR (KBr) 3560, 1590, 1290, 1140, 970 cm^{-1}; NMR ($CDCl_3$) δ 0.75-1.63 (m, 17H), 2.38 (s, 3H), 3.03 (d, J=3 Hz, 1H), 3.42-3.60 (m, 1H), 4.27-4.62 (bm, 1H), 5.88-6.52 (m, 2H), 7.08-7.23 (m, 7H), 7.61 (d, J=8 Hz, 2H); Found: C, 72.52; H, 8.37%. Calcd for $C_{25}H_{34}O_3S$: C, 72.42; H, 8.27%.

2c: Mp 112-114°C; IR (KBr) 3540, 1590, 1410, 1275, 1140, 930 cm^{-1}; NMR ($CDCl_3$) δ 2.40 (s, 3H), 2.74-3.92 (m, 5H), 4.83 (d, J=17.2 Hz, 1H), 5.29 (d, J=10.8 Hz, 1H), 5.72 (q, J=10.8 and 17.2 Hz, 1H), 6.96-7.23 (m, 7H), 7.59 (d, J=8 Hz, 2H); Found: C, 68.27; H, 6.29%. Calcd for $C_{18}H_{20}O_3S$: C, 68.32; H, 6.37%.

2d; Mp 158-159°C; IR (KBr) 3530, 1585, 1280, 1130, 1010, 926 cm^{-1}; NMR ($CDCl_3$) δ 2.33 (s, 3H), 3.09-4.10 (m, 5H), 5.92 (s, 2H), 6.93-7.15 (m, 12H), 7.54 (d, J=8 Hz, 2H); Found: C, 73.75; H, 6.13%. Calcd for $C_{24}H_{24}O_3S$: C, 73.44; H, 6.16%.

2e: Mp 128-130°C; IR (KBr) 3540, 1590, 1270, 1120, 1025, 810 cm^{-1}; NMR ($CDCl_3$) δ 1.40 (s, 3H), 1.63 (s, 3H), 2.39 (s, 3H), 3.09-4.06 (m, 5H), 4.71 (bs, 1H), 7.00-7.26 (m, 7H), 7.60 (d, J=8 Hz, 2H); Found: C, 69.44; H, 6.92%. Calcd for $C_{20}H_{24}O_3S$: C, 69.75; H, 7.02%.

7) Compounds (3a-e) have been also characterized by spectral means and elemental analyses. 3a and 3b were crystalline compounds (Mp 86-88° and 50-51.5°C).

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