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

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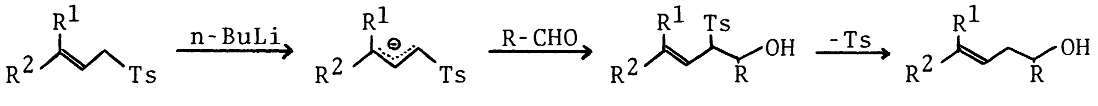
2-Tosyl homoallyl alcohol obtained by the reaction of allylic p-tolyl sulfone with aldehyde was found to be easily desulfonylated to homoallyl alcohol by the use of $Pd(PPh_3)_4$ as a catalyst and hydride ion as a nucleophile, without any side reactions.

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 chemistry1).

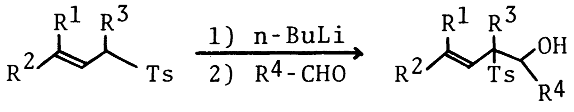
In connection with our continued interest to extend the synthetic utility of sulfones2), we now investigated the reaction of allylic p-tolyl sulfones3), which were easily obtained from allyl esters and sodium p-tolylsulfinate in the presence of $Pd(PPh_3)_4$, with a variety of aldehydes and found that 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.

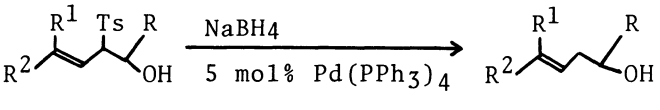
Table 1. The Reaction of Allyl p-Tolyl Sulfones with Aldehydes



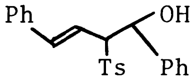
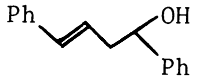
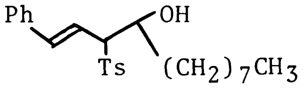
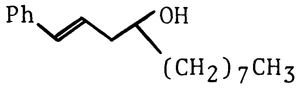
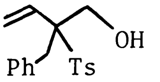
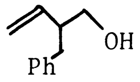
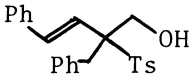
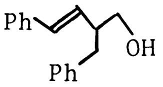
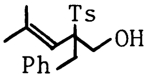
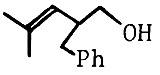
(1) (2)

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. reported9)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 bond10)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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