

Transition Metal-catalysed Elimination of Unactivated Sulfones

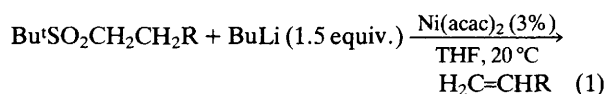
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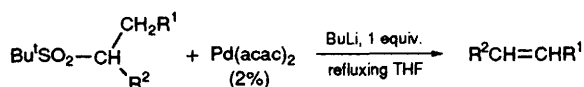
Lithiated *tert*-butyl alkyl sulfones undergo an easy elimination in the presence of catalytic amounts of bisacetylacetonatopalladium, thus leading to desulfonylated alkenes.

The sulfonyl auxiliary group is useful in organic synthesis¹; it is often removed by hydrogenolysis.² Base-promoted elimination is usually an inefficient reaction requiring drastic conditions^{3a} unless the new double bond is conjugated with some unsaturated group already present in the molecule.^{3b} A more general reaction is clearly desirable.

During the investigation^{4b} of the nickel-catalysed homocoupling^{4a} of sulfonyl carbanions, it turned out that an excess of the base used to convert the sulfone into its carbanion led to elimination of the sulfinate ion and formation of the alkene in good yield [eqn. (1); Hacac = acetylacetonate; THF = tetrahydrofuran].



With *tert*-butyl dodecyl sulfone, a 65% yield of dodecene (dodec-1-ene/dodec-2-ene = 92/8; *E/Z* = 70/30) was formed after 15 minutes; however after 20 hours, the olefin had isomerized (yield 80%; dodec-1-ene/dodec-2-ene = 4/96; *E/Z* = 64/36). Authentic alk-1-enes were also shown to isomerize under these conditions.



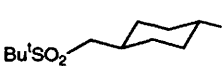




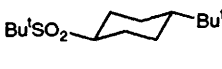
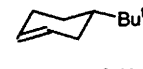
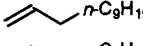
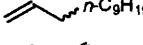
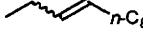
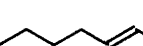
A stoichiometric elimination was observed when stabilised nickel sulfone complexes were treated with Lewis acids.⁵ It is not yet clear whether it bears any relation to the elimination reaction of aliphatic bromides carried out with a stoichiometric amount of nickel(0).⁶

Lithiated secondary alkyl sulfone also underwent elimination (50%) when treated with a catalytic amount of bisacetylacetonatopalladium, but the reaction was not regioselective and competitive formation of a symmetric dimeric olefin (20–30%) could not be avoided. Therefore, this nickel-promoted elimination appeared rather useless in synthesis, and other transition metal salts were tried under similar conditions.

Iron(III) and to a lesser extent cobalt(II) acetylacetonate complexes also proved effective in promoting elimination of lithiated *tert*-butyl alkyl sulfones, showing that this process is not limited to nickel.⁷ Nevertheless the two major drawbacks outlined in nickel activation, *i.e.* isomerization of the alkenes and competitive formation of the symmetrical dimeric olefin, still made the reaction of little practical use.

Palladium, which had already proved able to promote efficient elimination of allylic sulfones to produce polyenes⁸ was then studied. Indeed, with Pd(acac)₂ elimination took place without isomerization of the alkene, and formation of the coupling product was restricted to a minor side reaction. A systematic investigation of the palladium-induced elimination of lithiated *tert*-butyl dodecyl sulfone showed that the reaction had to be performed in refluxing THF, that the highest yields were obtained with 0.02 mol. equiv. of Pd(acac)₂, that

Table 1 Elimination of various lithiated *tert*-butyl sulfones upon treatment with 2% Pd(acac)₂ in boiling THF

Sulfone	Elimination, Overall yield (%)	Isomer distribution	Recovered sulfone (%)	Dimeric olefin (%)
$\text{Bu}^t\text{SO}_2\text{CH}_2\text{CH}_2\text{-}n\text{-C}_{10}\text{H}_{21}$	70	dodec-1-ene 98%	10	10
Bu^tSO_2 	42	 88%  12%	40	10
$\text{Bu}^t\text{SO}_2-\text{CH}(\text{n-C}_6\text{H}_{13})_2$	50	$n\text{-C}_5\text{H}_{11}-\text{CH}=\text{CH}-\text{n-C}_6\text{H}_{13}$ <i>E/Z</i> 84/16	34	4
Bu^tSO_2 	43		48 ^d	
Bu^tSO_2 	48		46 ^d	
$\text{Bu}^t\text{SO}_2-\text{CH}(\text{Me})(\text{n-C}_{10}\text{H}_{21})$	63	 30%  64%  6%	17	7
$\text{Bu}^t\text{SO}_2-\text{CH}(\text{Bu}^t)(\text{CH}_2\text{Ph})$	64	 91% <i>E/Z</i> 91/9 Other isomers 9%	33	

^a Mixture of *cis*- and *trans*-isomers. ^b Pure *cis*-isomer obtained from oxidation of the corresponding sulfide.⁹ ^c Pure *trans*-isomer. ^d Recovered as pure *trans*-isomer.

palladium chloride was less effective than Pd(acac)₂, and that the use of an exact stoichiometric amount of base (1.0 equiv.) to deprotonate the sulfone provided the best results. Phenyl alkyl sulfones proved unreactive.

Using these conditions,† several lithiated *tert*-butyl primary or secondary alkyl sulfones were treated with Pd(acac)₂. Results are given in Table 1. Primary alkyl sulfones led to the terminal alkene; even the easily isomerized methylenecycloalkane was obtained with good selectivity. Not unexpectedly, elimination of unsymmetric secondary sulfones was not regioselective. Since isomerization of alkenes is restricted to a few percent, the isomer ratio obtained actually corresponds to the selectivity of the elimination process. Formation of the more substituted double bond was preferred in the elimination of 1-methylundecyl sulfone.

Work is in progress to gain mechanistic information, such as

to determine whether an intermediate vinyl sulfone is involved or an initial reduction of Pd^{II} to Pd⁰ is required.

Received, 1st June 1993; Com. 3/031031

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† *Representative experimental procedure*: a solution of *n*-butyllithium in hexane (1.6 mol l⁻¹; 1.25 ml, 2 mmol) was added dropwise at 0°C under argon to a clear yellow solution of *tert*-butyl *n*-dodecyl sulfone (580 mg, 2 mmol) and Pd(acac)₂ (12.4 mg, 0.04 mmol) in THF (5 ml), and the mixture was stirred under reflux for 18 hours. The colour of the solution turned to black while a grey precipitate separated out. After work-up and extraction with dichloromethane, the yields were determined by GLC using appropriate standards, and analytically pure samples were obtained by preparative GLC.