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3-Bromo-2-(tert-butylsulfonyl)-1-propene. A multi-coupling reagent
Part 1.

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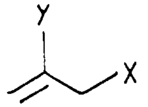
Summary -

3-Bromo-2-(tert-butylsulfonyl)-1-propene 4 is easily available in two steps from allyl-tert-butylthioether 5 (70% overall yield). It reacts with a great variety of carbanions to give functionnalized α,β-unsaturated sulfones of type 7 in high yields. A second nucleophile (lithium cuprates) can then be added to compounds 7 to furnish functionnalized sulfones of type 3 ($Y=SO_2$-tert-butyl).



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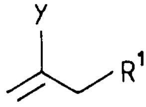

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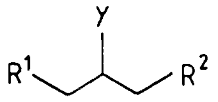

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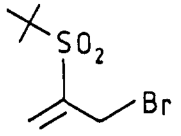

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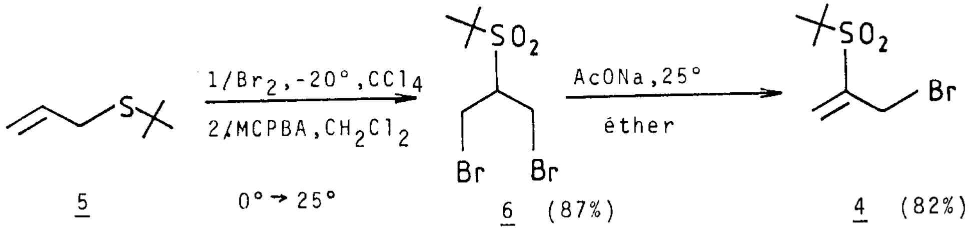
Functionnalized allylic reagents of type 1 (Y=COOR[1,2], NO_2[3], $-P(OR)_2$[2,4], SR[5], -SOR and SO_2R[6], $-SiMe_3$[7]) are useful reagents in organic syntheses. They can act either as electrophiles (if X is a leaving group), or as nucleophiles (if X is a metal). The products of type 2 thus obtained can again form a new carbon-carbon bond (leading to 3) in an electrophilic or nucleophilic way depending on the nature of the functionnal group Y. Thus reagents of type 1 are potentiel multi-coupling reagents[8].

We report here the synthesis of 3-bromo-2-(tert-butylsulfonyl)-propene 4 and its reactivity towards nucleophiles[9]. The sulfone 4 can be obtained in ≈ 70% overall yield from allyl-tert-butylthioether 5 (see scheme 1). A carbon tetrachloride solution of 1 eq. of bromine is added[10] at -20° to a stirred carbon tetrachloride solution of 5. The reaction mixture is allowed to reach 25°, stirred for 5 min and is added to a methylene chloride solution of 2.4 eq. of m-chloroperbenzoic acid (MCPBA) at -10° and stirred 4 hr at 25°. After work-up a white solid (m.p. 137°) of 1,3-dibromo-2-(tert-butylsulfonyl)-propane 6 is isolated in 87% yield. Addition of 1.5 eq. of dry sodium acetate

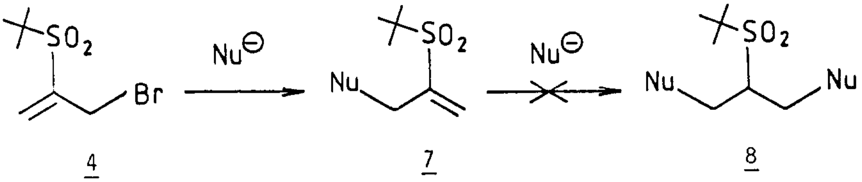
Scheme 1



to a well stirred etheral solution of 6 leads after 2.5 hr to the sulfone 4 in 90% yield (purity $\approx$ 90%). A flash-chromatography using methylene chloride as eluent increases the purity to $\geqslant$95% (82% yield ; m.p. 43°).

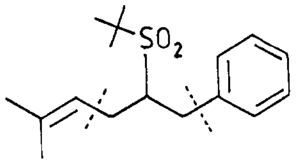
As expected, due to the allylic bromine atom, vinyl sulfone 4 shows an enhanced electrophilicity as compared to a simple α,β-unsaturated sulfone : in fact, if proper conditions are chosen (low temperature, inverse addition[3]), mono-addition leading to sulfone 7 can be carried out without subsequent readdition of the nucleophile (no 8 formed) ; see scheme 2.

Scheme 2

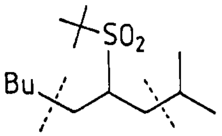


Thus, reagent 4 reacts with a great variety of nucleophiles (see table), ranging from soft ones like lithium thiophenolate or lithium ketone enolates, to harder ones (which require the inverse addition procedure, i.e. addition of the nucleophile to a THF solution of 4), such as indolylmagnesium bromide[11], an ester enolate or alkynyl, aryl, vinyl as well as prim., sec. and tert. Grignard derivatives. All these additions are performed at -90°. The temperature is allowed to rise until the reaction has proceeded (usually between -70° and -50°).

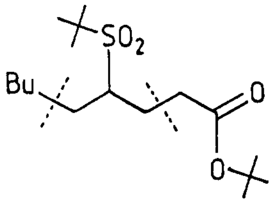
We have found that α,β-unsaturated sulfones of type 7 react readily with 2 eq. of lithium cuprates[12] (at -40° to -30°, 1 hr) in ether. The saturated functionnalized sulfones 9a-c are formed in good yields. Thus demonstrating the multi-coupling[8] ability of reagent 4.



9a : from 7j (see table) and $Ph_2CuLi.MeSMe$ (72%); m.p. 49°

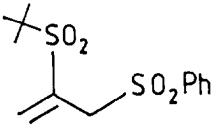


9b : from 7i (see table) and Bu_2CuLi (92%) ; m.p. 34°



9c : from 7e (see table) and Bu_2CuLi (89%) ; m.p. 68°

On the other hand, the vinyl sulfone 7a can be easily oxidized with MCPBA (in methylene chloride, 5°, 1 hr, 94%) to 2-(tert-butylsulfonyl)-3-(phenylsulfonyl)-propene 10.



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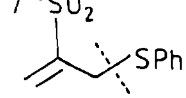
The reactivity of this interesting disulfone is currently investigated in our laboratory. Applications of the compounds of type 7 and other reactivities of the reagent 4 will be reported shortly.

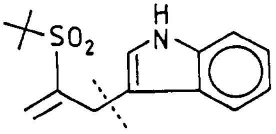
Acknowledgments -
We thank the C.N.R.S. for financial support (ERA 825).

Table -

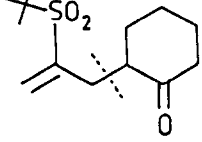
Products 7a-7h obtained by the reaction of lithium or magnesium derivatives with reagent 4 at temperatures between -60° and -90°. The yields given are those of flash chromatographically purified materials. All spectroscopic data (I.R., ^1H-NMR and ^{13}C-NMR) are compatible with the structures shown. The melting points of solid products and the ^{13}C-NMR shifts (δ (ppm), $CDCl_3$) of the olefinic carbon atoms together with the precursors employed are listed below the *formulae*. Newly formed bonds according to scheme 2 are indicated by dotted lines.



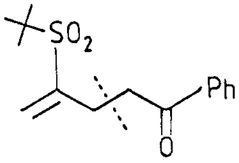
7a : 84% ; m.p. 89° ; from PhSLi



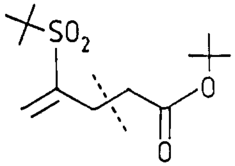
7b : 60% ; m.p. 180° ; from indolylmagnesium bromide in toluene[11]



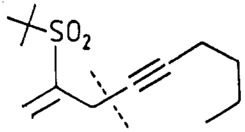
7c : 94% ; m.p. 86° ; from the lithium enolate of cyclohexanone



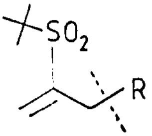
7d : 84% ; m.p. 110° ; from the lithium enolate of acetophenone



7e : 86% ; m.p. 43° ; from the lithium enolate of tert-butyl acetate



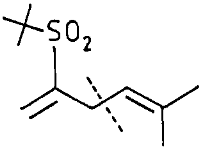
7f : 80% ; δ = 143.8, 130.2 ; from C_6H_9Li



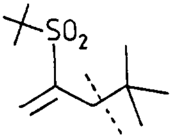
7g : R=Ph ; 89% ; m.p. 72° ; from PhMgBr

7h : R=Bu ; 85% ; δ =147.9 128.0; from BuMgBr

7i : R=iPr ; 90% ; δ =146.4, 129.2 ; from iPrMgCl



7j : 93% ; δ =146.9,135.8, 128.7,118.9; from i.butenylmagnesium bromide



7h : 94% ; m.p.91° from tert-butylmagnesium chloride

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