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ORGANIC SYNTHESES WITH SULFONES n°XXXVI : CONVERSION OF SULFONES INTO ALDEHYDES AND KETONES.

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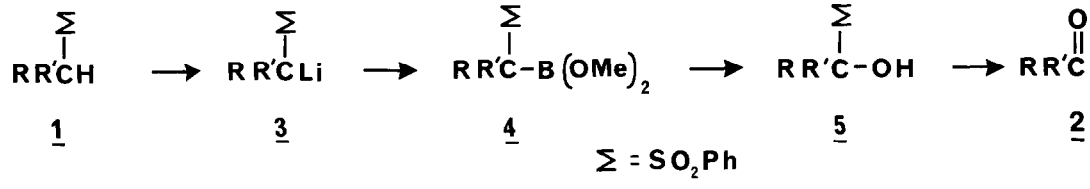
ABSTRACT : *Alkyl and allyl sulfones can be converted into boronic esters, oxidation of which leads to aldehydes or ketones.*

The sulfone group which is a very useful auxiliary group in organic synthesis [1] must, at some stage, be removed from the target molecule. This can be carried out by hydrogenolysis, elimination or substitution by organometallic reagents. Its conversion into an oxygen function is of course very desirable as pointed out by Magnus. [1]

Very recently, an elegant conversion of sulfones 1 into carbonyl compounds 2 has been reported, using $(Me_3SiO)_2$ [2]. Previous results had been less general [3-7].

This letters reports another solution to this problem. Carbanions can be efficiently converted into alcohols by oxidation of the related alkyl resp. aryl boronic esters [8,9]. With α-sulfonyl carbanions advantage would then be taken from the ready elimination of benzenesulfinic acid in the product 5.



In this respect trimethoxyborane and fluorodimethoxyborane did not satisfactorily convert the lithiated sulfones 3 into the desired 4 boronic esters. Chlorodimethoxyborane in THF however efficiently effected the conversion, perhaps because lithium chloride separates out.

The usual oxidation procedure with alkaline hydrogen peroxide gave only 30-40% yields of carbonyl compounds, considerable starting sulfone 1 being reformed. The α-sulfonyl boronic esters are however stable in acidic protic solution. The protodeboronation might take place in the hydroxy borate derivative.

Smooth oxidation of 4 to 2 could however be efficiently carried out with m-chloroperbenzoic acid in dichloromethane at low temperature when m-chlorobenzoic acid crystallizes out.

The table shows the results in a variety of cases : aldehydes and ketones, both saturated and α, β unsaturated are obtained in 70-90% yield. With unsaturated substrates the peracid gave side reactions, its sodium salt however proved satisfactory (procedure B).

Σ = $PhSO_2$	Sulfone 1	Procedure	Product	Yield	
				g.l.c.	isolated
1	n-Hex-CH_2- Σ	A	n-Hex-CHO	94	90
2	n-Hex-CHMe- Σ	A	n-Hex-CO-CH_3	94	90
3	Ph-CH_2- Σ	A	Ph-CHO	92	88
4	geranyl-Σ(E/Z 100/0)	B	geranial E/Z 95/5		72
5	neryl - Σ (Z/E 95/5)	B	neral Z/E 90/10		70
6	cinnamyl -Σ	B	cinnamaldehyde	72	68

Experimental procedure :

A - n-Heptanal from n-heptylphenylsulfone : n-butyllithium (1.5M in hexane, Aldrich ; 2.2 mmol) is added to a solution of n-heptylphenylsulfone (480mg ; 2mmol) in THF (4ml) under argon at -78°C. After raising the temperature to 20°C, a solution of chlorodimethoxyborane [10] (27mg, 2.5mmol) in hexane (3ml) is added. After 0.25h at -20°C and 1h at room temperature the solvent is evaporated in vacuo. The residue is extracted with methylene chloride (5ml) under argon and the extract added to a solution of m-chloro perbenzoic acid (86% ; Aldrich : 500mg, 2.5mmol) in methylene chloride (15ml) at -20°C. After 1h, aqueous sodium carbonate and ether are added and the organic phase is separated, washed with brine, dried over magnesium sulfate and evaporated. The carbonyl compound is analysed by g.l.c. . Heptanal (205mg, 80%) is isolated by "flash chromatography" (Kieselgel Merck ; pentane).

B - Geranial from geranyl phenyl sulfone : As above for the two first steps. Then the crude boronic ester is taken up in methylene chloride-hexane (20-80) and added to a suspension of sodium m-chloroperbenzoate, prepared from peracid (500mg ; 2,5mmol) and sodium hydride (90mg ; 3mmole) in methylene chloride (10ml) at -60°C during 0.5h. After 1h stirring at -60°C and 16h at room temperature the mixture is worked up as above.

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