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CLEAVAGE OF SELENOACETALS BY CLAY-SUPPORTED METAL NITRATES

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Abstract : Bis(methylseleno)acetals and bis(phenylseleno)acetals are cleaved into aldehydes or ketones, under very mild conditions, by K10 clay-supported ferric or cupric nitrate.

Selenoacetals have proven their worth for protection or umpolung of the carbonyl group[1-4]. Regeneration of this function can be a crucial step[4,5].

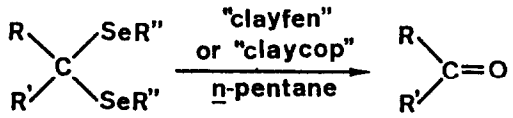
In a previous paper[6], we reported the efficient cleavage of thiocetals by clay-supported ferric nitrate ("clayfen") and clay-supported cupric nitrate ("claycop"), two nitrosonium ion (NO^+) sources[7]. Hence, it was tempting to apply an analogous procedure to selenoacetals. Indeed, it complements and maybe improve upon earlier procedures[4,5] in providing better yields (Table) for bis(phenylseleno)acetals than for bis(methylseleno)acetals.

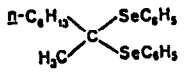
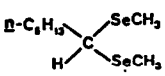
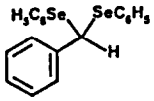
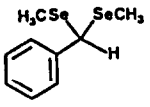
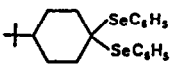
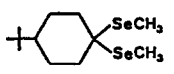
Experimental

To a solution of selenoacetal (1 mmol) in n-pentane (25 ml), "clayfen" (1.5 g[8], method A), or "claycop" (1.5 g[8], method B), prepared as previously described[7], are added. The mixture is stirred at room temperature and evolution of nitrogen oxides occurs. Stirring is maintained until disappearance of these coloured oxides. The clay is filtered off, and washed three times with solvent, in 10 ml portions. Products are separated from diselenides (resulting of the oxidation of the seleno moiety) by column chromatography on silica, using a mixture of ether and n-pentane (1/9) as eluent. The carbonyl compounds are identified by comparison (tlc, capillary gc, ir) with authentic samples.

This new carbonyl regeneration procedure commends itself by its efficiency and rapidity under mild conditions, requiring only low-cost reagents, and by its exceedingly easy work-up.

Table : Cleavage of selenoacetals[9] by "clayfen" or "claycop".



Selenoacetals	Method	Reaction time (min)	Isolated yield (%)
	A	120	90
	B	(very slow)	-
	A	90	73
	B	90	65
	A	10	73
	B	10	78
	A	10	63
	B	10	62
	A	30	97
	B	30	86
	A	45	61
	B	120	60

Acknowledgments :

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References and notes :

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8. A lesser quantity gives lesser yields and a larger quantity does not improve the procedure.
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