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NAFION-H®, A SOLID PERFLUOROALKANERESINSULFONIC ACID CATALYZED CONVERSION OF ACETALS TO THIOACETALS [1]

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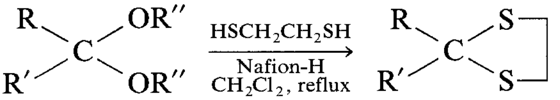
Nafion-H has been found to be an excellent acid catalyst for the direct conversion of acetals to thioacetals with 1,2-ethanedithiol in methylene chloride solution.

Keywords: Solid superacids, Nafion-H, acetals, thioacetals

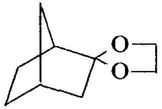
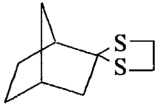
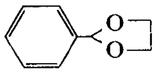
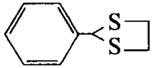
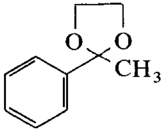
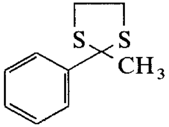
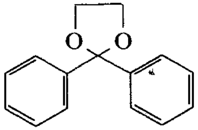
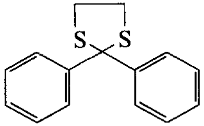
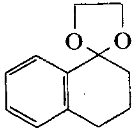
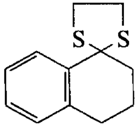
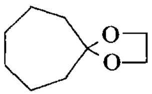
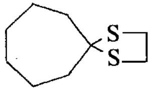
Thioacetals serve as useful protecting group for carbonyl compounds as they are stable to hydrolytic cleavage under acidic conditions [2]. Furthermore, thioacetals of aldehydes are also useful synthons as carbonyl anion equivalents [3]. A variety of synthetic methods exists for the thioacetalization of carbonyl compounds using Brönsted and Lewis acid catalysis [2]. However, few methods exist for the direct conversion of acetals to thioacetals [4]. Some selective methods have been developed for the selective conversion of aldehyde acetals to the corresponding thioacetals in the presence of ketones. For example, silica gel treated thionyl chloride [5], bis(diisobutyl aluminium) 1,2-ethanedithiolate [6] and magnesium bromide [7] have all been used as catalysts.

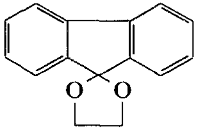
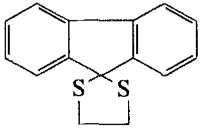
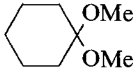
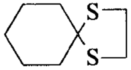
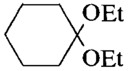
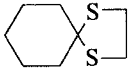
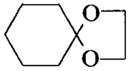
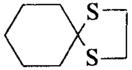
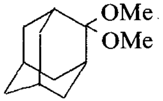
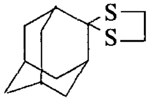
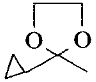
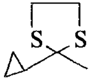
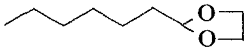
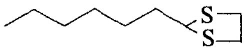
Over the years we have used Nafion-H, a superacidic perfluoroalkaneresinsulfonic acid as an acid catalyst for a wide variety of synthetic transformations [8] including preparation of thioacetals from carbonyl compounds [9]. Now we wish to report direct thioacetalization of acetals of both aldehydes and ketones with 1,2-ethanedithiol very efficiently under Nafion-H catalysis.



The results of the reaction with 1,2-ethanedithiol is presented in table 1. The isolated yields of thioacetals are excellent and the reaction works with a variety of acetals in acyclic, cyclic and polycyclic frameworks. Even the acetal of cyclopropyl methyl ketone gives the corresponding thioacetal in 90% isolated yield. No evidence was obtained for any concomitant cleavage of the acid labile cyclopropyl grouping. Nafion-H is truly used as a catalyst in these reactions. The work-up

Table 1
Nafion-H catalyzed direct conversion of acetals to thioacetals with 1,2-ethanedithiol

Acetal/Ketal	Reaction conditions		Product ^{a} (%)	Yield	m.p. (°C) or bp (°C)/Torr		
	Temp (°C)	Time (h)			found	reported	ref.
	reflux	6		92	124/5mm	–	[12a]
	reflux	3		88	135/5mm	109.5/0.7mm	[12b]
 CH_3	reflux	12	 CH_3	84	130/3mm	162–163.5/11 mm	[12c]
	reflux	60		80	105	104–105	[12d]
	25°	12		78	50	48	[12e]
	reflux	8		86	50	52–4	[12f]

	reflux	10		75	126	125	[12c]
	25°	6		88	108/5 mm	107/5 mm	[12c]
	25°	3		85			
	reflux	48		86			
	25°	16		98	54	55–55.5	[12g]
	reflux	6		90	110/4 mm		
	reflux	12		86	105/3 mm	–	[12g]
	25°	12		92	110/3 mm	115–18/4 mm	[12b]

[a] Products were characterized by ^{1}H and ^{13} NMR spectroscopy and mass spectrometry.

of the reaction involves simple filtration of the catalyst followed by evaporation of the solvent and ether extraction of the residue. The used catalyst can be reused by a simple regeneration procedure.

In conclusion, the presently developed method for the direct thioacetalization of acetals using 1,2-ethanedithiol under Nafion-H catalysis provides excellent yields, easy work-up and isolation of products and ready regeneration of catalyst.

TYPICAL PROCEDURE

A mixture of acetal [10] (10 mmol), 1,2-ethanedithiol, (11 mmol) and Nafion-H [11] (100 mg) in dry methylene chloride is either stirred or heated under reflux for the appropriate time specified in table 1.

The progress of the reaction is monitored by GC. After the reaction, the mixture was filtered, filtrate evaporated and the residue is extracted with diethyl ether (2 × 50 ml). The ether extract was dried over anhydrous magnesium sulfate and evaporated. The remaining residue is either recrystallized or purified by bulb to bulb distillation. All the thioacetals were characterized by ^{1}H, ^{13}C NMR and GC-MS analysis.

REGENERATION OF THE CATALYST

The filtered catalyst was washed several times with acetone and deionized water, followed by drying at 105 ° C for 10 h. The catalytic activity of regenerated catalyst was as good as that of fresh catalyst.

Acknowledgement

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