Catalysis by Solid Superacids; 8[1]. Improved Nafion-H[2] Perfluorinated Resinsulfonic Acid-Catalyzed Preparation of Dimethyl Acetals and Ethylenedithioacetals, and Hydrolysis of Dimethyl Acetals

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Claisen[3] first reported a convenient method for the conversion of aldehydes and ketones into their dimethyl acetals by the acid-catalyzed reaction with trimethyl orthoformate. Since then, many methods have become available utilizing a variety of catalysts[4]. Recently, a previous procedure[6] has been improved[5] by preabsorbing trimethyl orthoformate on the montmorillonite clay K-10 and this reagent was found to be effective in acetal formation. Many of the above methods employ harsh reagents and/or inconvenient procedures.

In continuation of our interest in the use of Nafion-H, a solid perfluorinated resinsulfonic acid catalyst, in rearrangement reactions[7], as well as in electrophilic aromatic alkylation[8], aroylation[9], nitration[10,11], and isomerizations[1] we now wish to report the use of Nafion-H catalyst in an improved and convenient synthesis of dimethyl acetals and ethylenedithioacetals.

When ketones or aldehydes (**1**) are treated with trimethyl orthoformate in the presence of Nafion-H, the corresponding dimethyl acetals (**2**) are formed in excellent yields (Table 1). The reactions do not require any preabsorption on the catalyst, as is the case with other solid acids[5]. We have also studied the Nafion-H-catalyzed cleavage of dimethyl acetals. In the absence of water, the acetals decompose sluggishly to yield the corresponding aldehyde or ketone. In the Nafion-H-catalyzed hydrolysis, formation of the corresponding carbonyl compounds is instantaneous and these are obtained in excellent yields (Table 1).

Similarly, ethylenedithioacetals (**3**, 1,3-dithiolanes) are obtained in nearly quantitative yields by Nafion-H catalysis. In this case, heating under reflux a solution of the corresponding carbonyl compound (**1**), 1,2-ethanedithiol, and Nafion-H in benzene with azeotropic removal of water from the reaction mixtures enables the isolation of pure products by simple filtration followed by crystallization of distillation (Table 2).

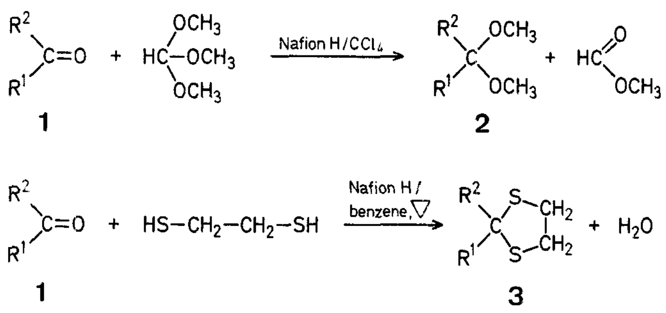


Table 1. Nafion-H-Catalyzed Preparation of Dimethyl Acetals (**2**) and their Hydrolysis

R^1	R^2	Yield[a] [%] of **2**	m.p. or b.p./torr [°C] found	m.p. or b.p./torr [°C] reported	Yield [%] of **1** upon Hydrolysis[b]
$-(CH_2)_5-$		98	67°/27	65°/25[12]	95
CH_3	$n-C_5H_{11}$	83	65–66°/8.5	—[d]	94
CH_3	C_6H_5	93 (100)[c]	61–62°/1.9	85–87°/15[13]	100
C_6H_5	C_6H_5	91 (100)[c]	106°	106–107°[14]	100
H	C_6H_5	87 (100)[c]	80°/7.4	73°/10[15]	95
H	$n-C_3H_7$	86	65°/16	109–112/740[16]	89

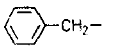
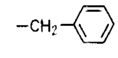
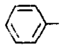
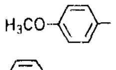
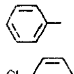
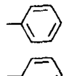
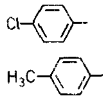
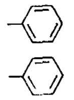
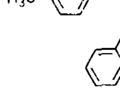
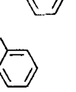
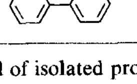
[a] Yield of isolated product, characterized by physical and spectral data.

[b] Spectral data were identical with those of authentic compounds.

[c] Reported yields for acetalization using trimethyl orthoformate/montmorillonite K-10[5].

[d] New compound, gave correct microanalysis.

Table 2. Nafion-H-Catalyzed Preparation of Ethylene Dithioacetals (**3**)

R^1	R^2	Yield[a] [%] of **3**	m.p.[b] or b.p./torr [°C] found	m.p.[b] or b.p./torr [°C] reported
$-(CH_2)_5-$		91	53–55°/1.5	107°/15[17]
$-(CH_2)_6-$		100[c]	54	52–54°[18]
CH_3	$-COOC_2H_5$	79	98°/1.5	—[d]
		100[c]	85.8°	87–88°[19]
	CH_3	96	94–95°/0.55	131°/3[17]
	CH_3	92	124°/0.3	—[d]
		100[c]	103.3°	106°[20]
		80	56°	44°[21]
		85	52.7°	—[d]
		96	125.1°	125°[17]

[a] Yield of isolated product characterized by physical and spectral data.

[b] Melting points were obtained on a Mettler FP 1 melting point apparatus and are uncorrected.

[c] Product characterized by G.L.C.; purity >98%. G.L.C. analysis was carried out using a Varian Associates Model 3700 gas chromatograph equipped with a 150′ OV-101 glass capillary column.

[d] New compound, gave correct microanalysis.

0039-7881/81/0432-0282 $ 03.00

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The ease of work-up and easy regeneration[7] of the catalyst makes the present method very convenient for the protection of carbonyl groups and their regeneration from the corresponding dimethyl acetals.

Nafion-H-Catalyzed Preparation of Dimethyl Acetals (2); General Procedure:

A solution of the aldehyde or ketone (**1**; 15 mmol) in carbon tetrachloride (20 ml) is stirred with Nafion-H (500 mg) in a dry atmosphere and trimethyl orthoformate (5.84 g, 55 mmol) is added. The reaction is monitored by ^{1}H-N.M.R. and I.R. spectroscopy. On completion of the reaction, the mixture is filtered and the residue washed with carbon tetrachloride (2 × 10 ml). The combined filtrate is fractionally distilled and the pure acetal isolated.

Hydrolysis of Benzophenone Dimethyl Acetal; Typical Procedure:

Benzophenone dimethyl acetal (2 g) is dissolved in aqueous acetone (1/20, 40 ml). Nafion-H (100 mg) is added and the reaction mixture stirred for 30 min. Filtration of the catalyst and evaporation of the solvent gives *benzophenone; yield: 1.6 g (100%); m.p. 48 °C.*

Nafion-H-Catalyzed Preparation of Ethylenedithioacetals; General Procedure:

To a stirred solution of the carbonyl compound (**1**; 20 mmol) and 1,2-ethanedithiol (2.26 g, 24 mmol) in benzene, Nafion-H (1 g) is added. The mixture is heated under reflux using a Dean-Stark trap for water separation. The course of the reaction is followed by T.L.C. on silica gel (benzene as eluent) and I.R. spectroscopy. Upon completion of the reaction (5–12 h), the mixture is filtered while hot and the residue washed with hot benzene (2 × 10 ml). The solvent is evaporated and the product isolated by crystallization or distillation.

Support of our work by the National Institutes of Health is gratefully acknowledged.

Received: February 6, 1978
(Revised form: September 4, 1980)

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[1] Part 8. For Part 7, see G. A. Olah, J. Kaspi, *Nouv. J. Chim.* **2**, 585 (1978).

[2] Nafion is a registered trademark of the Dupont Company whom we thank for the Potassium Salt of Nafion-501.

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