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N-Benzyl Pyridinium Salts as New Useful Catalysts for Transformation of Epoxides to Cyclic Acetals, Orthoesters, and Orthocarbonates

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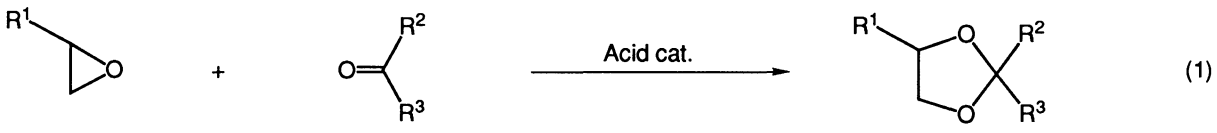
In the presence of catalytic amount of N-(4-methoxybenzyl)-2-cyanopyridinium hexafluoroantimonate, the reaction of a few epoxides with aldehydes, ketones, lactones, and carbonates efficiently afforded corresponding cyclic acetals, orthoesters, and orthocarbonates under mild conditions.

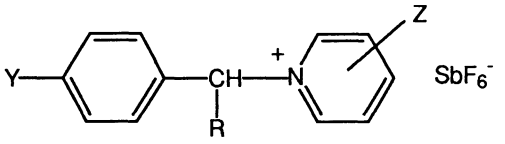
Acetal derivatives are important intermediates or end products in synthetic organic chemistry. The preparation of cyclic acetals from epoxides and carbonyl compounds can be advantageously carried out under mild conditions without formation of water or its equivalent (Eq. 1).[1] However, there is always observed polymerization of epoxide used and/or acetal produced, as side reaction, even when excess carbonyl compound is employed. Although complete suppression of it may be essentially impossible, one can find selective catalyst and/or reaction conditions enable to change the polymerization-acetalization ratio. Such catalysts as BF_3, anhydrous $CuSO_4$, activated acid Bentonite, and $(C_2H_5)_4N^+Br^-$, which are sometimes difficult to handle due to their hygroscopicity, are reported so far.[1,2]

Recently we have developed a new class of acid catalysts, N-benzyl pyridinium hexafluoroantimonates (**1**),[3] which are characterized by easy synthesis, easy handling due to good stability toward air and moisture (e.g. they can be recrystallized from methanol and stored for a long time).



(1)

R^1; alkyl, aryl R^2 or R^3; alkyl, aryl, O-alkyl



1

	1a	1b	1c	1d	1e	1f
Y	MeO	H	H	MeO	H	H
R	H	Me	H	H	Me	H
Z	2-CN	2-CN	2-CN	4-CN	4-CN	4-CN

In this paper is described efficient acetalization of various carbonyl compounds with epoxides in the presence of N-(4-methoxybenzyl)-2-cyanopyridinium hexafluoroantimonate (**1a**) as a new type of acid catalyst.

Catalytic activity of several pyridinium salts (**1a-1f**, 1 mol%) was examined in the reaction of styrene oxide (StO) with acetone (15 equiv.) to 2,2-dimethyl-4-phenyl-1,3-dioxolane. With **1a** and **1b** were achieved 93 and 92% yields of the dioxolane, respectively, within 10 min at room temperature. The yields and reaction times, obtained at 35 °C for other catalysts, were as follows; **1c**: 12%/3 d; **1d**: 86%/12 h; **1e**: trace/3 d; **1f**: 0%/7d. **1d** could not catalyze the reaction of propylene oxide (PO) with acetone (20 equiv.) at 35 °C.

Table 1. Synthesis of Acetal Derivatives from Epoxides and Carbonyl Compounds[a)]

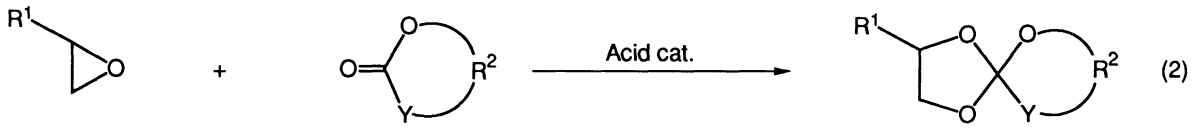
Entry	Epoxide	Carbonyl compound	Ratio of C=O/Epoxide	Temp ℃	Time min	Yield[b)] %	Bp/°C (Torr)
1	StO	PhCHO	20	rt	10	100	-
2	PO		20	rt	30	100	-
3	EPH		20	rt	120	100	-
4	EPH		2	40[c)]	20	80, 77[d)]	-
5	EPH	$n\text{-}C_5H_{11}CHO$	5	rt	70	87[d)]	100 (8.5)
6	StO	CH_3COCH_3	15	rt	10	93	-
7	PO		20	rt	30	88[d)]	98 (760)
8	EPH		20	40	20	90[d)]	73 (40)
9	EPH		2	40[c)]	20	72	-
10	EPH	$O{=}C(CH_2)_5$	20	rt	ON[e)]	78[d)]	93(6)
11[f)]	EPH	$PhCOCH_3$	2	rt	180	61, 59[d)]	-

a) The mixture of an epoxide and a carbonyl compound was stirred in the presence of **1a** (1 mol%) without solvent. After addition of hexane or ether, the mixture was washed with alkaline water. The product was purified by distillation or chromatography. b) Yield based on the epoxide was estimated by 1H NMR. c) CH_2Cl_2 refluxing temperature. d) Isolated yield. e) ON; overnight. f) With 3 mol% **1a**.

In the reaction of epichlorohydrin (EPH) with acetophenone (2 equiv.), **1a** was more effective catalyst than **1b** and yielded 53% of the corresponding 1,3-dioxolane while **1b** afforded 31% of the dioxolane for 12 h at 35 °C. Therefore, the most active catalyst **1a** was selected and used for the reaction of epoxides and carbonyl compounds.

As shown in Table 1, with 1 mol% of **1a**, StO, PO, and EPH were quantitatively converted to the corresponding 1,3-dioxolanes by the reaction with excess benzaldehyde at room temperature. Hexanal also reacted with EPH (5 equiv.) to afford the corresponding acetal in 87% yield. Cis - trans ratio was almost unity in all cases (by NMR) (entries 1-4). Using two equivalents of benzaldehyde, the yield of the acetal somewhat decreased to 80%, owing to an increase of the competitive polymerization of EPH (entry 4). In the case of acetone, these three epoxides were also converted to the corresponding 1,3-dioxolanes in high yields under the mild conditions (entries 6-9). Acetophenone sluggishly reacted with EPH to give the respective acetal in a good yield (entry 11).[4] Poly(EPH) was separated as by-product in a few cases.

Further, the catalyst (**1a**) was applied to the synthesis of spiroorthoester (SOE) and spiroorthocarbonate (SOC) (Eq. 2), which are very important compounds undergoing polymerization without volume shrinkage5) and are quite difficult to be prepared in good yields.[6] As shown in Table 2, PO or EPH reacted with γ-butyrolactone (BL), δ-valerolactone (VL), or ethylene carbonate (EC) to afford satisfactory yields of the corresponding spirocyclic compounds.



(2)

R^1; CH_3, CH_2Cl R^2; $-(CH_2)_n-$ (n=2,3) Y; CH_2, O

The yields of the acetals and related compounds, achieved in this paper, were higher than those reported so far, even under the mild reaction conditions. Owing to various advantages, this catalyst is expected to function as a potent catalyst for varieties of acid-catalyzed reactions.

Table 2. Synthesis of Spiroorthoesters and Spiroorthocarbonates by the Reactions of Epoxides with Lactones and Cyclic Carbonates[a)]

Entry	Epoxide	Carbonly compound	Ratio of C=O/Epoxide	Temp ℃	Time h	Yield[b)] %	Bp/°C (torr)
1	PO	BL	20	60	2	45	67(11)
2	EPH	VL	5	rt	5.5	72	61(1)
3	PO	EC	10	rt	4	24	67(1)
4	PO	PE	5	rt	12	trace	-

a) The mixture of an epoxide and a lactone or carbonate was stirred in the presence of **1a** (1 mol%) without solvent. After addition of benzene, the mixture was washed with alkaline water (more than 1 equivalent of NaOH was added to decompose unreacted lactone or carbonate). The product was purified by distillation.
b) Isolated yields.

References

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4) Only an example of the reaction of aryl alkyl ketone with ethylene oxide is reported so far. α,α-Dichloroacetophenone reacts with ethylene oxide at 170 °C for 1 h in the presence of tetramethylammonium bromide to give only 21% of the corresponding acetal.[2)]

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