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POLYMER-SUPPORTED AMMONIUM FLUORIDE: A USEFUL REAGENT FOR SI-O BOND CLEAVAGE

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<u>Abstract</u>: Polymer-supported ammonium fluoride $(\underline{1})$ is a convenient reagent for Si-O bond cleavage. Resin $\underline{1}$ is inexpensive, easy to prepare from commercial amine-containing anion exchange resins and aqueous hydrofluoric acid, easy to store. The product is easily separated from the reaction mixture by filtration. The used resins can be regenerated and reused without losing its reactivity.

Fluoride ion is extensively used as cleaving reagent for Si-O bond in deprotection of alkylsilyl-protected alcohols.⁽¹⁾ However, alkali fluoride and tetraalkylammonium flouride are hygroscopic. The removal of their water of hydration presents considerable difficulties. Therefore new sources of fluoride ion have been developed. A few of strongly basic anion exchange resins, such as Dowex MSA-1, Amberlyst A-26 and A-27^(2,3) in fluoride form seems to be promising, especially suitable for nonaqueous solvent system. Tetrabutylammonium flouride (TBAF) is one of the

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sources of naked F⁻ and is commonly used when aprotic and mild condition are needed.^[4] However, the necessary aqueous workup makes the preparation of water-soluble compounds difficult. Recently Solladié-Cavallo and Khiar have reported that methylammonium fluoride (MAF) is a convenient reagent for cleavage of Si-O bond which allows the isolation of the desired alcohol without workup.^[5]

Herein we wish to report another type of useful reagent, e.g., polymer-supported ammonium fluoride (1), which is used as the source of naked F^- for cleavage of Si-O bond.

Fluoride-ion-containing resin <u>1</u>a or <u>1</u>b is prepared by reaction of commercially available basic anion exchange resin (D390 or D370) with 1N aqueous hydrofluoric acid in a polyethylene flask with magnetic stirrer. In the case of strongly basic anion exchange resin i.e., D296 (OH⁻ form), as support, resin <u>1</u>c is prepared in a polyethylene column packed with D296 through which 1N aqueous hydrofluoric acid is passed. On drying under reduced pressure, the anhydrous resins <u>1</u>a-c are used in cleavage of Si-O bond as shown in Equ. 1.

Resin <u>1</u>: (P)—CH₂NR₂ · HF (P)—CH₂N[·]R₃ · F⁻ <u>1</u>a R=H (from D390) <u>1</u>c R=CH₃ (from D296) <u>1</u>b R=CH₃ (from D370) (P) = Crosslinked polystyrene backbone

AMMONIUM FLUORIDE FOR Si-O BOND CLEAVAGE

In cleaving reaction methanol is a better solvent which allows the reaction at room temperature in shorter time. When aprotic condition is needed, the cleavage in tetrahydrofuran (THF) also gives good yield on refluxing. After completion of reaction, the used resin is filtered and washed with used solvent. On evaporating the solvent and volatile by-product i.e., trimethylsilyl fluoride, the pure deprotected alcohol is obtained in high yield. The results are summarized in Table. It is shown that the F^- ion supported on the basic anion resin appears to have higher reactivity than that of TBAF and MAF.⁽⁵⁾ Since the former allows the reaction under mild condition at a shorter reaction time.

It is observed that in deprotection of trimethylsilyl-protected alcohols fluoride ion supported on different basic anion resins seems to have the same reactivity. However, in comparison with strongly basic anion exchange resin D296, the weakly basic anion exchange resins (D390, D370) seem to be preferred, owing to their direct reaction with aqueous hydrofluoric acid used resins can be regenerated by stirring with IN aqueous hydrofluoride at room temperature for 24 h, and reused in dry state for cleaving Si-O bond. There is no loss of cleaving activity observed.

In conclusion, a novel type of cleaving reagent for Si-O bond supported on the commercially available basic anion exchange resins is practical because of low cost and ease of preparation and store.

R'OSiMe ₃ (<u>2</u>)	Resin <u>1</u>	Solvent	Temp.	Time (h)	ROH (isola	% ated)
Me(CH ₂),OSiMe ₃	b	МеОН	12	2	89	
(<u>2</u> a)	С	MeOH	20	2	98	
PhCH ₂ OSiMe ₃	a	MeOH	20	2.5	94	
(<u>2</u> b)	b	MeOH	15	1	73	
	с	MeOH	20	2	91	
O OSiMe ₃	a	MeOH	20	2	83	88°
$(MeO)_2 P-CHPh$	b	MeOH	20	2	90	84ª
(<u>2</u> c)	с	MeOH	20	1.5	88	89°
O OSiMe ₃	a	MeOH	20	2	89	
$(MeO)_2 P-CH-CH=CH_2$	b	MeOH	20	1.5	100	93°
(<u>2</u> d)	b	THF	reflux	2	100	
	с	MeOH	8	2	96	
CICH2 CH OSiMa	a	MeOH	r.t.	2	78 ^ъ	
CICH ₂ CH-OSIMe ₃	b	MeOH	r.t.	2	87°	
(<u>2</u> e)	с	MeOH	r.t.	2	72°	

Table Si-O bond cleavage using fluoride resin 1

a Regenerated resin 1 was used.

b Calculated from GC.

Experimental

Preparation of resin 1a, 1b

In a 250 ml polyethylene flask with Teflon covered stirring magnetic bar, 50 g of D390[®] or D370[®] (available from the Chemical Plant of Nankai University) is added to 90 ml of 1N aqueous hydrofluoric acid, allowing the mixture to stand overnight. Aqueous layer is decanted, the resin is washed with distilled water until neutral, filtered and dried under reduced pressure at 50°C for 12h and resin <u>la</u> or <u>lb</u> is obtained. The capacity of HF on resin <u>la</u> and <u>lb</u> by potentiometric titration is 4.53 and 3.12 mequiv/g, respectively.

Preparation of resin 1c

A 150 ml of D296[®] resin (Cl⁻ form, available from the Chemical Plant of Nankai University; its exchange capacity being 3.6 meq./g) is packed in a polyethylene column, and converted into OH⁻ form with 1N aqueous NaOH until no chloride ion is detected (AgNO₃ test). On washing with water to neutral, 750 ml of 1N aqueous hydrofluoric acid is slowly passed through the column. The resin is washed with water to neutral and filtered, dried under reduced pressure at 50°C overnight.

General procedure of cleaving Si-O bond: 4.5 mmol of the silyl derivatives is added to 9 mmol of F⁻ on resin <u>1</u> soaked in 6 ml of solvent, the slurry is stirred at the desired temperature in 1-2 h. The reaction is followed by TLC. After completion, the used resin is filtered and washed with used solvent. The filtrate is evaporated under vacuum to remove the solvent and the volatile Me₃SiF; the product is thus obtained. The results are listed in Table. The percentages of deprotection in Table are determined by purification of crude products using distillation under vacuum or recrystallization except special indication. The compounds are proved to be identical with authentic ones by melting point or refractions.⁽⁶⁾

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[6] The physical data of cleaving product <u>3</u> : <u>3</u>a, n¹⁵1.4305
(n²⁰ 1.4290); <u>3</u>b, n¹⁸1.5400 (n²⁰ 1.5400); <u>3</u>c, m.p.101-102°C
(lit: m.p. 102°C, Abramov, V.S., Zh. Obshch. Khim., 1952, 22, 647. C.A. 47, 5351); <u>3</u>d, n¹⁶1.4590 (lit: n²⁰ 1.4575, Pudovik, A.N., Doklady Akad. Nauk, S.S.S.R., 1950, 73, 499. C.A., 45, 2856.)

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