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MELAMINE-HYDROGEN FLUORIDE SOLUTION. A HIGHLY EFFECTIVE AND CONVENIENT HYDROFLUORINATION REAGENT OF ALKENES

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A solution of 14% (w/w) melamine in 86% (w/w) hydrogen fluoride has been found to be stable, and more convenient and effective hydrofluorinating reagent for alkenes than those of other organic amine-hydrogen fluoride reagents.

Hydrofluorination of alkenes with anhydrous hydrogen fluoride is always accompanied by severe difficulties such as the troublesome handling of anhydrous hydrogen fluoride, the need of pressure equipment and the undesirable polymerization of alkenes. Many efforts have been made to overcome such difficulties.[1] In particular, Olah and his coworkers investigated solutions of amines in anhydrous hydrogen fluoride, and established a 30% (w/w) pyridine-70% (w/w) hydrogen fluoride solution (Olah's reagent) to be an effective and convenient agent for organic fluorination reactions.[2] We wish to report here that a melamine-hydrogen fluoride solution (14:86 in w/w %) surpasses other amine-hydrogen fluoride reagents including the Olah's reagent, with regard to its preparation, handling, hydrofluorinating activity for alkenes, post-treatment, and deterioration of hydrofluorinating activity.

Although Olah et al. mentioned complexes of hydrogen fluoride with amines other than pyridine,[2] no detailed description was reported. Consequently, we explored the applicability of amine-hydrogen fluoride complexes for hydrofluonation of alkenes, some of which are summarized in Table 1.

Solutions of amines in anhydrous hydrogen fluoride were prepared by the addition of hydrogen fluoride distilled from a commercial cylinder into amines by portions with care under stirring in a 100 mL-polyethylene bottle at -78 °C. In the case of the preparation of melamine-hydrogen fluoride solution, solid melamine was gradually dissolved in hydrogen fluoride without any vigorous exothermic reactions which were usually observed in the preparation of pyridine or other amine-HF solutions.[3] The resulting melamine-anhydrous HF solutions are remarkably stable at atmospheric pressure and up to 50 °C. Representative hydrofluorination procedure of alkenes is as follows. A solution of 15 mL of 14% (w/w) melamine in HF was placed in a 100 mL-polyethylene reaction vessel under stirring. Cyclohexene (5 mmol) in THF (3 mL)was then added dropwise into the solution. The mixture was stirred at 0 °C for 60 min. The reaction was then quenched with ice-water and the mixture was neutralized with sodium hydrogen carbonate. The yellow milky precipitate formed was separated by filtration, which was assigned as melamine-6HF complex. The filtrate was extracted with ether. The ether layer was washed with aqueous sodium chloride solution, and finally dried over anhydrous magnesium sulfate. Thus, cyclohexyl fluoride (4.9 mmol, 98%) with a 99.9% of isomeric purity was obtained readily by evaporation of the solvents.

Among the amine-HF solutions examined, a 14% melamine (by weight)-HF solution was found to give excellent results for hydrofluorination of alkenes, as shown in Table 1. All amine-HF solutions depressed the polymerization of alkenes.

Table 1. Hydrofluorination of alkenes with Amine-Hydrogen Fluoride Reagents

Alkene	Amine	Amount of amine, mmol (wt %)	Reac. condts.[a)]	Conv. of alkene(%)	Yield of RF (%)	Hydrofluorination selectivity (%)
Cyclohexene	Without amine	0.0 (0)	C	98	71	72
"	Triethylamine	16.8 (51)	A	12	12	100
"	Butylamine	16.8 (29)	A	37	37	100
"	Dibutylamine	16.8 (42)	A	33	33	100
"	Hexylamine	16.8 (36)	A	28	28	100
"	Piperidine	16.8 (32)	A	9	9	100
"	Aniline	16.8 (34)	A	50	50	100
"	N,N-Dimethylaniline	16.8 (41)	A	62	62	100
"	*m*-Phenylenediamine	8.4 (19)	A	11	11	100
"	Pyridine	16.8 (30)	A	28	28	100
"	"	16.8 (30)	B	80	80	100
"	"	16.8 (30)	BD	22	22	100
Cyclopentene	"	16.8 (30)	B	65	65[2)]	100
2,3-Dimethyl-1-butene	"	16.8 (30)	A	25	25	100
"	"	16.8 (30)	B	82	82	100
Cyclohexene	Melamine	4.0 (14)	A	88	88	100
"	"	4.0 (14)	B	98	98	100
"	"	4.0 (14)	BD	98	98	100
"	"	0.8 (3)	C	95	89	94
"	"	2.4 (9)	C	77	75	97
"	"	4.0 (14)	C	77	77	100
"	"	5.6 (19)	C	65	60	92
"	"	7.1 (23)	C	46	40	87
Cyclopentene	"	4.0 (14)	B	90	90	100
2,3-Dimethyl-1-butene	"	4.0 (14)	A	83	83	100
"	"	4.0 (14)	B	85	85	100

a) Reaction conditions. Anhydrous HF (150 mmol) and an alkene (5 mmol) in 3 mL of THF were used in each case. A: reaction temperature (T) = 0 °C, reaction time (t) = 10 min. B: T = 0 °C, t = 60 min. C: T = 0 °C, t = 5 min. D: Instead of anhydrous HF, HF containing 1% water by weight was used.

In general, HF solutions of amines once prepared are hygroscopic, and such solutions absorbed moisture usually exhibit remarkably low fluorinating activity, as shown in a pyridine-HF solution under the BD conditions, whereas in a melamine-HF solution any deterioration was not observed. Thus, the melamine-HF solution is expected to be stable for prolonged storage under ordinary conditions.

References
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2) G.A.Olah, M.Nojima, and I.Kerekes, Synthesis, 1973, 779; G.A.Olah, J.T.Welch, Y.D.Vankar, M.Nojima, I.Kerekes, and J.A.Olah, J.Org.Chem., 44, 3872 (1979).
3) Proper precautions should be taken during addition of anhydrous HF into amines other than melamine.

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