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A MELAMINE/HF-CARBON TETRACHLORIDE LIQUID-LIQUID TWO-PHASE MIXTURE. A HIGHLY VERSATILE HYDROFLUORINATING AGENT FOR ALKENES TO FACILITATE CONTINUOUS OPERATIONS

Norihiko YONEDA,* Seiji NAGATA, Tsuyoshi FUKUHARA, and Akira SUZUKI
Department of Applied Chemistry, Faculty of Engineering,
Hokkaido University, Sapporo 060

A melamine/hydrogen fluoride-pentane or carbon tetrachloride liquid-liquid two phase mixture has been found to be a highly convenient hydrofluorinating agent for alkenes and a suitable system for the repeated use.

It has been recently demonstrated that a melamine-hydrogen fluoride solution (14:86 in w/w %) surpasses other amine-hydrogen fluoride solutions including pyridine-hydrogen fluoride (30:70 in w/w %), known as the Olah's reagent,[1] with regard to its preparation, handling ease, hydrofluorination activity for alkenes, post-treatment and so on.[2] However, in order to obtain hydrofluorinated products, it is necessary to quench the hydrofluorinating agent by adding a large amount of water and neutralizing with inorganic bases such as sodium hydrogencarbonate, which result in the destruction of the agent. We wish to report here on a melamine-hydrogen fluoride solution containing a co-solvent such as pentane or carbon tetrachloride.

The preparation of amine-HF solutions and the reaction procedure were carried out in the same manner described in the previous paper.[2] After the completion of the reaction, the mixture separated into two layers, except in the case of THF or no solvent. The organic layer, which was found to be free from HF,[3] was then distilled and the products thus obtained were identified by direct comparison with the corresponding authentic samples. In the case of repeated use of the hydrofluorinating agent, the agent layer separated from the organic layer was subjected to the next run without any treatment. Representative experimental results using cyclohexene as a substrate are summarized in Table 1.

Anhydrous HF itself tended to cause the undesirable polymerization of alkenes except in the case where THF was used as the solvent. Both of the pyridine-HF and melamine-HF agents, on the other hand, gave fluorinated products with high selectivity. Particularly, the melamine-HF agent in pentane or polychlorinated methanes was found to give almost quantitative yields of fluorinated products from alkenes. In addition, it should be emphasized that the present procedure is superior to others in its ready separation of products and the repeated use of the hydrofluorinating agents. Some examples of such results are shown in Table 2.

Table 1. Reaction[a] of Cyclohexene with HF, HF-Pyridine,[b] or HF-Melamine[c]

Solvent	HF		HF-Pyridine		HF-Melamine	
	Yield[d] %	Selectivity[e] %	Yield[d] %	Selectivity[e] %	Yield[d] %	Selectivity[e] %
None	2	2	76	79	50	50
THF	88	89	29	100	89	100
Pentane	0	0	71	100	99	100
CCl_4	1	1	70	100	99	100
$CHCl_3$	16	16	47	100	99	100
CH_2Cl_2	9	9	55	100	99	100

a) Reaction conditions: cyclohexene 5 mmol; HF 150 mmol; reaction temperature 0 °C; reaction time 10 min; amount of solvent 3 ml. b) HF-30% pyridine(w/w). c) HF-19% melamine(w/w). d) Yield of fluorocyclohexane. e) Based on cyclohexene reacted.

Table 2. Repeated Use of Agents[c,d] in the Reaction of Cyclohexene[a]

Agent	Number of Repeated Expt.	Yield of Fluorocyclohexane / %		
		CCl_4[b]	Pentane[b]	$CHCl_3$[b]
HF-Melamine[c]	1	98	99	-[e]
	2	97	95	
	3	99	97	
	4	94		
HF-Pyridine[d]	1	70	71	47
	2	48	55	35
	3	39	40	24

a) Reaction conditions: see Table 1. b) Amount of a co-solvent in each run, 3 ml. c) HF-19% melamine(w/w). d) HF-30% pyridine(w/w). e) Operation for repeated use of the agent is difficult because of the emulsion in the reaction system.

In contrast to the rapid deterioration of hydrofluorinating activity in pyridine-HF organic solvent systems, the present melamine-HF solution can be used repeatedly without a remarkable decrease of the activity by using together with a co-solvent such as pentane or carbon tetrachloride. However, chloroform was not a good co-organic solvent for the present purpose. For laboratory work-up, carbon tetrachloride was recommended as the most convenient co-solvent since the lower organic layer was readily separated from the upper reagent layer for work-up. The upper hydrofluorinating agent layer was then used for the next run.

Accordingly, the present procedure using melamine/HF-carbon tetrachloride solution seems to be the best method for hydrofluorination of alkenes so far available.

References

1) G.A.Olah, J.T.Welch, Y.D.Vankar, M.Nojima, I.Kerekes, and J.A.Olah, J.Org.Chem., 44, 3872 (1979).

2) N.Yoneda, T.Abe, T.Fukuhara, and A.Suzuki, Chem.Lett., 1983, 1135.

3) No evolution of carbon dioxide was observed when sodium hydrogencarbonate was added to the organic layer.

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