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Silver Fluoride Supported on Calcium Fluoride. Improved Fluorination and Halofluorination Reactions

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Silver fluoride dispersed on the surface of calcium fluoride shows improved fluoride nucleophilicity for halogen exchange and addition to alkenes.

Organofluorine compounds continue to be important for a wide variety of purposes and efficient methods for their syntheses are constantly being sought. We recently reported the improved reactivity, for nucleophilic fluorine transfer reactions, of the alkali metal fluorides supported on calcium fluoride.[1,2] Although the reason for the increased reactivity was not clearly established, we proposed that the calcium fluoride behaved as an inert non-hydroxylated surface over which KF or CsF could be dispersed without the accompanying loss of fluoride ion nucleophilicity seen for alumina or silica supported fluorides.[3] In an effort to discover more about the effectiveness of calcium fluoride as a support we have now studied some fluorine transfer reactions with calcium fluoride supported silver fluoride.

Silver fluoride was supported on calcium fluoride by slowly evaporating a mixture of silver carbonate (25 g) dissolved in water (30 mL), 50% aqueous HF (8 g) and CaF_2 (100 g) to dryness at 50 °C in the dark. The final reagent was/allowed a white free-flowing granular powder which, unlike the 'sticky' nature of the commercial AgF salt, allowed it to be easily and rapidly handled during weighing procedures. This is an important consideration as the salt is highly hygroscopic and light sensitive.

The dry supported $AgF-CaF_2$ reagent showed increased reaction rate for heterogeneous fluorination of alkyl and benzyl halides, as summarized in Table 1. The effect of support is clearly shown by comparing the fluorination of 1-bromooctane (runs 1 and 2). α-Phenetyl and benzhydryl bromides gave good yields of the corresponding fluorides in 10 min at 13 °C, whereas at 75 °C they gave complex mixtures of products. Benzyl bromide was converted to the fluoride almost quantitatively in 10 min (run 8). In general, alkyl iodides gave better yields than bromides, which in turn gave better yields than chlorides.

Our results show that $AgF-CaF_2$ is considerably more active than KF- or $CsF-CaF_2$ (cf. run 8 and Refs. 1,2).

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Table 1. Fluorination of alkyl Halides with AgF-CaF_2[a)]

Run	Substrate	Temp/$^{\circ}$C	Time/min	GC Yield/%
1	1-Bromooctane	75	30	41
2	1-Bromooctane	75	30	11[b)]
3	1-Iodooctane	75	10	80
4	1-Bromoheptane	75	30	42
5	$PhCH_2CH_2Br$	75	30	35
6	Ph_2CHBr	13	10	72
7	$Ph(CH_3)CHBr$	13	10	69
8	$PhCH_2Br$	75	10	92
9	$PhCH_2Cl$	75	60	50

a) Halides were shaken in the dark with AgF-CaF_2 (2 mol equiv.) in CH_3CN containing tetradecane as an internal standard. b) AgF powder (dried at 70 $^{\circ}$C/13 Pa/3 h) used instead of AgF-CaF_2.

Silver fluoride has been used in the presence of a halogen or a suitable N-haloamide, for the *in situ* generation of halogen fluorides, XF (X=I, Br, and Cl), and their addition to alkenes.[4)] Table 2 shows the halofluorination of some alkenes using the AgF-CaF_2 reagent. Bromofluorination was most effective with 1,3-dibromo-5,5-dimethylhydantoin, giving high yields, and the effect of CaF_2 is seen by comparing runs 1 and 2. N-Bromosuccinimide (run 3) gave poor results as dibromide by-products were formed. Iodofluorination is almost equally effective using either iodine or N-iodosuccinimide, and the yields of ca. 60% are similar to the literature values.[4)] Higher yields are presumably difficult to obtain due to the instability of the 1,2-iodofluoride products.

We have been able to utilize the 'inert' surface of finely powdered calcium fluoride for activation of silver fluoride as a fluorinating agent, and simultaneously make the handling and use of dry AgF more straightforward.

Table 2. Halofluorination of Alkenes with AgF-CaF_2 and Halogenating Reagents[a)]

Run	Substrate	Halogen source	Temp $^{\circ}$C	Product	Yield/% Isolated	(GC)
1	Hex-1-ene	DBH	20	1-bromo-2-fluorohexane	76	(90)
2		DBH	20			(39)[b)]
3		NBS	20			(13)
4		I_2[c)]	30	1-iodo-2-fluorohexane	54	
5		NIS	20			(60)
6	Cyclohexene	DBH	20	1-bromo-2-fluorocyclohexane	75	(84)
7		I_2[c)]	30	1-iodo-2-fluorocyclohexane	52	
8	Styrene	DBH	20	2-bromo-1-fluoro-1-phenylethane	68	(75)
9		I_2[c)]	30	2-iodo-1-fluoro-1-phenylethane	63	

a) The alkenes and 1,3-dibromo-5,5-dimethylhydantoin (DBH), N-bromosuccinimide (NBS), N-iodosuccinimide (NIS) or iodine were shaken in the dark for 1 h with AgF-CaF_2 (2 mol equiv.) in CH_2Cl_2 containing tetradecane internal standard. b) AgF powder (dried at 60 $^{\circ}$C/13 Pa/18 h) used instead of AgF-CaF_2. c) In CH_3CN.

References

1) J. Ichihara, T. Matsuo, T. Hanafusa, and T. Ando, J. Chem. Soc., Chem. Commun., 1986, 793. 2) J. H. Clark, A. J. Hyde, and D. K. Smith, J. Chem. Soc., Chem. Commun., 1986, 791. 3) *e.g.* T. Ando, J. H. Clark, D. G. Cork, T. Hanafusa, J. Ichihara, and T. Kimura, Tetrahedron Lett., 28, 1421 (1987). 4) *e.g.* L. D. Hall and D. L. Jones, Can. J. Chem., 51, 2902 (1973).

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