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Short Communication

Metal atom reactions with fluorocarbons. II. Defluorination by calcium atoms[1,2]

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We have utilized calcium atoms for defluorination of unsaturated fluorocarbons* and have investigated some of the aspects of the initial C–F insertion by calcium.

When calcium was vaporized under vacuum and deposited on a liquid nitrogen cooled surface simultaneously with perfluoro-2-butene (PFB) vapor, a clear glassy matrix was formed. On warm-up, perfluoro-2-butyne was released and a rust-colored residue left behind. Pyrolysis of the residue at *ca.* 100° yielded a small amount of additional alkyne while polymeric material and calcium salts remained in the reactor. Saturation of the PFB vapor with water vapor prior to deposition caused no significant difference in the yield of perfluoro-2-butyne based on calcium vaporized (*cf.* Table 1). However, if a 90:10 mixture of PFB:methanol

TABLE 1

PRODUCT YIELDS[a] FROM CALCIUM ATOM REACTIONS

Substrate	Products		
	$CF_3C{\equiv}CCF_3$	C_6F_5H	C_6H_6
PFB	13		
PFB(H_2O)[b]	13		
PFB(CH_3OH)[c]	1.0		
C_6F_6		12	
C_6F_6(H_2O)[b]		88	
C_6F_6(C_6H_6)[d]		2.4	
C_6H_5F(H_2O)[b]			39

[a] Yields are based on calcium vaporized and corrected for the fact that only *ca.* 60 % of the calcium reaches the reaction zone.
[b] Vapor of substrate saturated with water vapor before deposition.
[c] Substrate: additive was 90:10.
[d] Substrate: additive was 70:30.

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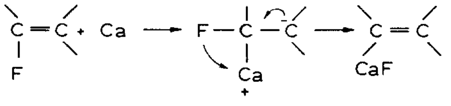
* Defluorination is not possible by normal dehalogenation methods.

was deposited, the alkyne yield was considerably lower. Experiments with perfluoropropene and perfluorocyclobutene yielded no volatile products but, instead, large amounts of polymer. It was anticipated that if perfluoropropene was defluorinated, the resulting allene or propyne could be trapped by vacuum distillation into cold methanol[3]. This experiment was not successful. Deposition of methanol *with* perfluoropropene only resulted in catalytic addition of methanol across the olefinic bond of the propene. The catalysis was probably caused by calcium methoxide formed.

Calcium atoms and perfluoropropane did not react. Benzotrifluoride did not react either. At this point only vinylic fluorine had been found to be susceptible to attack by calcium atoms.

We attempted the generation of tetrafluorobenzyne from perfluorobenzene and calcium atoms. Polymeric material resulted, and no dimeric or Diels–Alder products were found even when benzene was added as a trapping agent[4]. Initial insertion of calcium into the C–F bond did appear to have occurred, however, since the intermediate organocalcium fluoride could be trapped with water. Thus, if perfluorobenzene vapor saturated with water vapor was deposited a 88% yield of pentafluorobenzene resulted. No polymer was formed in this experiment. In a similar experiment, fluorobenzene was converted to benzene. Thus, we tentatively conclude that aryl carbon–fluorine bonds are also inserted by calcium atoms, and that the resulting organometal is relatively stable and lives long enough to be trapped by water*. If no scavaging protons are available, warming, in the case of the perfluoro-organo metal, causes calcium fluoride elimination. The resulting tetrafluorobenzyne polymerizes rather than yields Diels–Alder products due to the relatively low temperature of the matrix when the benzyne formation occurs.

Oxidative insertion of calcium atoms into C–F bonds must be the first step leading to defluorination. This insertion must be followed by a rapid calcium fluoride elimination in the case of PFB, since the intermediate R_fCaF could only be trapped with difficulty. Trapping was easy with AR_fCaF, however. The most interesting point to consider is why only vinylic or aryl C–F bonds are attacked. A π system is necessary. Perhaps some type of coordination by calcium with the π system lowers the activation energy for insertion. Alternatively, calcium may attack the double bond and then the resulting intermediate rearranges its fluorine atom.



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* We conclude that the reaction of calcium atoms with the small amount of water present in these experiments was not kinetically important for these reasons: (a) the presence of water made essentially no difference in the PFB experiments and (b) no significant hydrogen formation was ever observed.

Iron atoms or zinc atoms did not cause defluorination of PFB.

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