Synthesis of octafluoronaphtalene by perfluorodecalin defluorination

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Previously, Octafluoronaphtalene was obtained by passing Perfluorodecalin over Ni and Fe at 460 ^{o}C (1) by interaction of Octachloronaphtalene with anhydrous potassium fluoride in sulfolane at 235 ^{o}C in 50-60 % yield (2) and without solvent at 300-330 ^{o}C in 30% yield (3) by defluorination of Hexafluorobicyclo [4.4.0]dec-1(6)-ene over Zn in DMF at 80 ^{o}C (in 65% yield) [4]. It was supposed that the existence of at least one double bond is necessary for such defluorination.

Recently Octafluoronaphtalene synthesis from Perfluorodecalin in the presence of excess Al activated by $HgCl_2$ in THF at ambient temperature (in 40% yield) was described , but the reaction was realized only with metallocene catalysis [5].

It is shown that Perfluorodecalin containing no double bond can be easily defluorinated to perfluoronaphtalene by Al or Zn activated with M(II) salts (M=Pb, Sn, Cu, Hg). The yield and conversion are 73% and 55-60%, respectively. Low conversion can be explained by formation of metal fluoride layer on the surface by Al or Zn.

The reaction is accompanied by formation (up to 3%) of heptafluoronaphtalene (the structure is confirmed by spectrum ^{19}F NMR and mass-spectra) that indicate to a reaction scheme of reductive defluorination.

Experimental

In a four-necked flask fitted with a stirrer , dropping funnel, reflux condenser and a thermometer, a suspension of Al powder(9.45, 0.071 mol) and Pb $(OAc)_2$ (4g, 0.012 mol) was placed and mixed for 10 minutes. The mixture was heated to 110^{o}C, then the heating bath was removed and perfluorodecalin (46.2 g) was performed visually through formation of aluminum fluoride slurry. After finishing the process (approximately 5 hours), the mixture was refluxed for 3 hours and treated with hot octafluoronaphtalene (14.0g). Both fractions contained some water. The crude product was filtered off and recrystallized from light petroleum to afford 12g (73%yield, 60% conversion) of octafluronaphtalene. Boiling point 207-209 ^{o}C, melting point 84.5-86.0 ^{o}C. Calculated for $C_{10}F_8$, %:C, 44.12: F, 55.08. Found, %:C,44.92; F, 55.08.

^{19} F NMR (acetone -d_6 , external TFA): 78.0 (4F,S) and 69.0 (4F,S) chemical shifts.

Analogous results were obtained for Al/$HgCl_2$, Al/$SnCl_2$, and Zn/$Cu(OAc)_2$ in DMF and N,N,-dimethylacetamide

Conclusions

1. Octafluoronaphtalene is obtained from Perfluorodecalin in aprotic polar solvents with the use of M/M^{+2} system where M=Al, Zn, and M= Al, Zn, Me^{+2} =Pb^{+2}, Sn^{+2}, Cu^{+2}, Hg^{+2}
2. It is shown that along with the main reaction the reductive defluorination of Perfluorodecalin with Heptafluoronaphtalene formation is taken place.

References

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