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Preliminary communication

REACTION OF ALLYLTIN REAGENTS WITH PERFLUOROALKYL NITRILES

WILLIAM A. NUGENT* and BRUCE E. SMART

Central Research and Development Department, E.I. du Pont de Nemours and Company, Experimental Station, Wilmington, DE 19898 (U.S.A.)*

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Summary

N-Organostannyl ketimines produced via the title reaction generally undergo rearrangement to the corresponding fluoroalkyl enamines, I. However, reaction with triallyltin fluoride affords the doubly allylated amine derivatives II.

The reaction of allyltin reagents with aldehydes and ketones is well known [1] and has found increasing synthetic utility [2]. This chemistry apparently has not been extended to other unsaturated organic functionality. We now report that electron-deficient perfluoroalkyl nitriles readily react with a variety of allyltin reagents. With either perfluorobutyronitrile or perfluorooctanonitrile as the substrate, the reactivity of a series of allyltin reagents increased in the order $Ph_3Sn(allyl) < Me_3Sn(allyl) < (allyl)_4Sn < (allyl)_3SnF < (allyl)_3SnCl$. Practical reaction temperatures as well as the approximate stoichiometry for these reactions are indicated in Table 1. The stoichiometries were determined by monitoring the consumption of nitrile and tin reagent by GC at various Sn/nitrile ratios and are fairly independent of the relative proportion of reactants used. At temperatures higher than those indicated, increased nitrile consumption was observed due to the trimerization of nitrile to the triazine and further reaction of the tin adducts with additional nitrile.

In general, the ultimate products of these reactions were the corresponding perfluoroalkyl enamines. For instance, the reaction of allyltrimethyltin with perfluorooctanonitrile was carried out at 100°C and, after removal of the solvent, the product was distilled in vacuum to free it from a small amount of high-boiling side-product**. The distillate was shown by ^1H and ^{119}Sn NMR*** to

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[*] Contribution No. 3282.

[**] The non-volatile component is believed to be the product from the insertion of ketimine III into a second equivalent of nitrile. This material exhibited a singlet in the ^{119}Sn NMR at +31.1 ppm vs. Me_4Sn ($CF_2ClCFCl_2$) and showed IR absorbances at 1632 and 1678 cm^{-1}.

[***] Compounds Ib and Ic were observed as singlets in the ^{119}Sn NMR at +89.0 and +86.0 ppm from the internal standard tetramethyltin (solvent $CF_2ClCFCl_2$).

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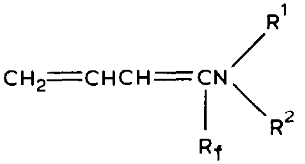
TABLE 1

REACTION OF ALLYLTIN COMPOUNDS WITH PERFLUOROOCTANONITRILE[a]

Tin compound	Temperature (°C)	Stoichiometry[b] (R_fCN/Sn)
$(allyl)_3SnCl$	0	3.2
$(allyl)_3SnF$	25	2.7[c]
$(allyl)_4Sn$	60	2.0
$(allyl)SnMe_3$	100	1.0
$(allyl)SnPh_3$	100	1.3[d]

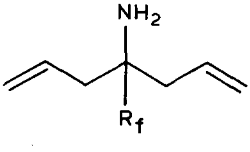
[a] All reactions involve 1.0 mmol tin reagent with varying amounts of nitrile in 5.0 ml $CF_2ClCFCl_2$ in sealed tubes for 16 h. [b] Ratio of nitrile consumed to Sn reagent consumed as determined by internal standard GC. [c] Based on nitrile consumption only, assuming complete reaction. [d] At 120°C $R_fCN/Sn = 2.7$ (see text).



($Ia, R^1, R^2 = H$;
$Ib, R^1 = H, R^2 = Me_3Sn$;
$Ic, R^1, R^2 = Me_3Sn$)

contain Ia (23%), Ib (70%), and Ic (7%).

Assignment of structure I is supported by a variety of spectroscopic evidence and in particular by the isolation and characterization of Ia ($R_f = C_7F_{15}$). Thus, fractional distillation (27—28°C, 0.5 torr) of the reaction product from tetraallyltin and perfluorooctanonitrile afforded Ia as a colorless liquid containing only a trace (~3%) of tetraallyltin. This material exhibited ν(NH) 3425, 3510 cm^{-1}* and ν(C=C) 1630, 1658 cm^{-1}; 360 MHz ^1H NMR: δ 3.42 (br s, 2H), 5.13 (d, *J* 10 Hz, 1H), 5.25 (d, *J* 17 Hz, 1H), 5.52 (d, *J* 11 Hz, 1H), 6.33 ppm (m, 1H). Nitrogen analysis confirmed the presence of 3.40% N (3.20% theory).



(II)

Triallyltin fluoride differed from the other allyltin reagents in this study in that it afforded significant yields of the doubly allylated product II. For example, 16 g of perfluorooctanonitrile in 200 ml $CF_2ClCFCl_2$ was stirred overnight with 10.4 g of finely powdered $(allyl)_3SnF$. The filtered product was adsorbed on Woelm alumina, washed with $CF_2ClCFCl_2$, and finally eluted with acetonitrile. Removal of solvent and distillation (52—53°C, 0.5 torr) afforded 3.85 grams (20%) of pure II. (360 MHz NMR: δ 1.38 (br s, 2H), 2.42 (m, 4H), 5.10 (d, *J* 18 Hz,

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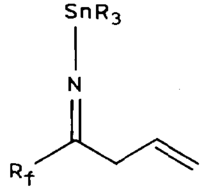
*In contrast, Ib showed only a single ν(N—H) at 3410 cm^{-1}.



(III)

2H), 5.12 (d, J 11 Hz, 2H), 5.87 (m, 2H), chemical ionization mass spec: $M + 1/e = 480$; Anal. Found: C, 35.25; H, 2.73; N, 2.82. $C_{14}H_{12}F_{15}N$ calcd.: C, 35.09; H, 2.53; N, 2.92%.

The initial product of these reactions is presumed to be the *N*-organostannyl ketimine III. The rearrangement of III to tautomeric Ib finds precedent in the analogous reaction of silyl ketimines reported by Chan and Rochow [3]. Indeed, the IR spectrum of a mixture of $(allyl)_3SnCl$ and $C_7F_{15}CN$ in 1,1,2-trichlorotrifluoroethane immediately upon mixing indicated the presence of an intermediate of structure III. Under these conditions, the C≡N stretching band of the nitrile at 2265 cm^{-1} was absent and in its place appeared a strong absorbance at 1678 cm^{-1}. It appears reasonable to assign this band to ν(C=N) of the ketimine by comparison with ν(C=N) 1613 cm^{-1} in $Ph_2C{=}NSnR_3$ [3] and the expected effect of fluorine substitution*. The 1678 cm^{-1} band disappeared over the course of 0.5 h with concommitant appearance of a band at 3425 cm^{-1} assigned as the NH stretching frequency of the corresponding enamine.

Formation of III might be presumed, by analogy to the reaction of allyltin species with aldehydes, to be a concerted process involving a pericyclic transition state [1,4]. We have found that $(prenyl)SnR_3$ compounds (prenyl = 3-methyl-2-butenyl; R = methyl, phenyl) do not add to perfluoroalkyl nitriles even at 200°C. This observation provides indirect evidence for an electrocyclic mechanism, since 3-substitution would not be expected to inhibit a simple Grignard-type addition.

References

1 A. Gambaro, D. Marton, V. Peruzzo, and G. Tagliavini, J. Organomet. Chem., 226 (1982) 149 and ref. therein.
2 See for example: T. Mukaiyama, T. Harada, and S. Shoda, Chem. Lett., (1980) 1507.
3 L.-H. Chan and E.G. Rochow, J. Organomet. Chem., 9 (1967) 231.
4 A. Gambaro, D. Marton, V. Peruzzo, and G. Tagliavini, J. Organomet. Chem., 210 (1981) 191.

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*In the analogous silicon series, fluorine substitution in $(CF_3)_2C{=}NSiMe_3$ shifted ν(C=N) to 1780 cm^{-1} from the normal 1640—1660 cm^{-1} [3].