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THE REACTION OF ORGANOLITHIUM REAGENTS WITH PERFLUOROVINYL DERIVATIVES OF TIN AND SILICON.

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It is known that phenyllithium undergoes nucleophilic addition to the olefinic double bond of triphenylvinylsilane to give, after hydrolysis, β-phenylethyltriphenylsilane.[2] The reaction of phenyllithium with triphenylvinyltin, on the other hand, is one of exchange, in which tetraphenyltin and vinyllithium are formed.[3]

We have investigated the action of organolithium reagents on perfluorovinyl derivatives of silicon and tin and have obtained very similar results, viz., an addition reaction with perfluorovinylsilanes and an exchange reaction with perfluorovinyltin compounds which gives the new perfluorovinyllithium reagent, $CF_2=CFLi$.

The reaction between triethylperfluorovinylsilane[4] and organolithium

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[2] L.F. Cason and H.G. Brooks, J. Amer. Chem. Soc. **74** 4582 (1952); J. Org. Chem. **19**, 1278 (1954).

[3] D. Seyferth and M.A. Weiner, Chem. and Ind. (London) 402 (1959).

[4] D. Seyferth, K.A. Brändle and G. Raab, Angew. Chem. **72**, 77(1960).

reagents in ether solution resembles that of lithium compounds with tetrafluoroethylene[5]: the adduct formed loses lithium fluoride, producing a new fluoroolefin. This reaction is a general one which usually results

$$Et_3SiCF{=}CF_2 \xrightarrow{RLi} Et_3SiCFLiCF_2R \xrightarrow{-LiF} Et_3SiCF{=}CFR$$

in good yields of silyl-substituted fluoroolefins. The action of phenyllithium, vinyllithium, allyllithium and n-butyllithium on triethylperfluorovinylsilane gave α,β-difluoro-β-triethylsilylstyrene (b.p. 91°/0.55 mm.; n_D^{25} 1.5113); 1,2-difluoro-1-triethylsilyl-1,3-butadiene (b.p. 43-4°/0.9 mm.; n_D^{25} 1.4562); 1,2-difluoro-1-triethylsilyl-1,4-pentadiene (b.p. 51°/1.6 mm.; n_D^{25} 1.4382); and 1,2-difluoro-1-triethylsilyl-1-hexene (b.p. 53°/0.4 mm.; n_D^{25} 1.4309). respectively.

A reaction between phenyllithium and triphenylperfluorovinyltin[4] carried out in diethyl ether at room temperature resulted in precipitation of tetraphenyltin in good yield, but no evidence could be obtained for the presence of perfluorovinyllithium in the dark brown, opaque solution. However, it was found that perfluorovinyllithium is stable in ether at low temperature. Thus addition of three equivalents of ethereal phenyllithium to 0.023 mole of phenyl-tris(perfluorovinyl)tin in ether at -35° to -40° resulted in instantaneous precipitation of tetraphenyltin (97% isolated yield) and formation of a dark solution. Addition of triethyltin chloride (0.0684 mole), dissolved in ether, was followed by slow warming to room temperature, filtration, treatment of the filtrate with potassium fluoride solution (to remove unreacted Et_3SnCl as the insoluble fluoride) and

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[5] S. Dixon, J. Org. Chem. 21, 400(1956).

fractional distillation. Triethylperfluorovinyltin[4] was obtained in 40% yield. A similar exchange reaction between n-butyllithium and n-butyl-tris(perfluorovinyl)tin could be effected in pentane. However, in this solvent exchange is not complete, and it was found best to use the lithium reagent and the tin compound in 2:1 molar ratio. When the perfluorovinyllithium preparation was carried out at -30° and triethyltin chloride used to characterize the lithium reagent formed, the work-up procedure described above gave triethylperfluorovinyltin in 46-50% yield. The stability of perfluorovinyllithium is greater in pentane than in ether. The reagent appeared to be stable in pentane at 0°, but short refluxing of its pentane solution destroyed it completely. The reactions of perfluorovinyllithium are under investigation.

An analogous difference in behavior of perfluorovinylsilicon and -tin compounds toward Grignard reagents in ether solution was noted. Similar behavior also was observed with more conventional nucleophiles. While

$$Et_3SiCF{=}CF_2 \quad + \quad C_6H_5MgBr \longrightarrow Et_3SiCF{=}CFC_6H_5 \quad + \quad MgBrF$$

$$(C_6H_5)_3SnCF{=}CF_2 \quad + \quad C_6H_5MgBr \longrightarrow (C_6H_5)_4Sn \quad + \quad CF_2{=}CFMgBr$$

alcoholic sodium ethoxide caused complete cleavage of the perfluorovinyl group in tri-n-butylperfluorovinyltin[4], giving tri-n-butyltin ethoxide (b.p. 115°/0.1 mm.), the reaction of this reagent with triethylperfluorovinylsilane gave the addition-elimination product, $Et_3SiCF{=}CFOEt$ (b.p. 47.5°/0.9 mm.; n_D^{25} 1.4252), in 28% yield, as well as triethylethoxysilane in 69% yield.

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