

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

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(Received 23 August 1960)

It is known that phenyllithium undergoes nucleophilic addition to the olefinic double bond of triphenylvinylsilane to give, after hydrolysis,  $\beta$ -phenylethyltriphenylsilane.<sup>2</sup> The reaction of phenyllithium with triphenylvinyltin, on the other hand, is one of exchange, in which tetraphenyltin and vinylolithium are formed.<sup>3</sup>

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 perfluorovinylolithium reagent,  $CF_2=CFLi$ .

The reaction between triethylperfluorovinylsilane<sup>4</sup> and organolithium

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<sup>2</sup> L.F. Cason and E.G. Brooks, J. Amer. Chem. Soc. **74** 4582 (1952); J. Org. Chem. **19**, 1278 (1954).

<sup>3</sup> D. Seyferth and M.A. Weiner, Chem. and Ind. (London) 402 (1959).

<sup>4</sup> D. Seyferth, K.A. Brändle and G. Raab, Angew. Chem. **72**, 77(1960).

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



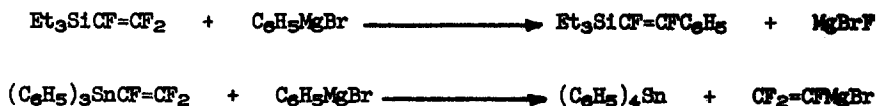
in good yields of silyl-substituted fluoroolefins. The action of phenyllithium, vinylolithium, allyllithium and n-butyllithium on triethylperfluorovinylsilane gave  $\alpha,\beta$ -difluoro- $\beta$ -triethylsilylstyrene (b.p. 91°/0.55 mm.;  $n_D^{25}$  1.5113); 1,2-difluoro-1-triethylsilyl-1,3-butadiene (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\* 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 perfluorovinylolithium in the dark brown, opaque solution. However, it was found that perfluorovinylolithium 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  $\text{Et}_3\text{SnCl}$  as the insoluble fluoride) and

<sup>5</sup> S. Dixon, J. Org. Chem. 21, 400(1956).

fractional distillation. Triethylperfluorovinyltin<sup>4</sup> 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 perfluorovinyl lithium 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 perfluorovinyl lithium 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 perfluorovinyl lithium 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



alcoholic sodium ethoxide caused complete cleavage of the perfluorovinyl group in tri-n-butylperfluorovinyltin<sup>4</sup>, giving tri-n-butyltin ethoxide (b.p. 115°/0.1 mm.), the reaction of this reagent with triethylperfluorovinylsilane gave the addition-elimination product, Et<sub>3</sub>SiCF=CFOEt (b.p. 47.5°/0.9 mm.;  $n_D^{25}$  1.4252), in 28% yield, as well as triethylethoxy-silane in 6% yield.

Acknowledgments. This work was supported by the U.S. Army Quartermaster Research and Engineering Command (Chemicals and Plastics Division, Chemical Products Branch) and by the U.S. Air Force under Contract No. AF 33(616)-7124, monitored by the Materials Laboratory, Wright Air Development Division, Wright-Patterson Air Force Base, Ohio.