

## NOTE

## NOVEL SYNTHESIS OF PERHALOSTYRENE COMPOUNDS

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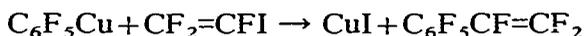
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The preparation and polymerization of styrene has been studied for many years. With the advent of perfluoroaromatic chemistry, interest in the synthesis and polymerization of the highly fluorinated styrene compounds has been shown by a number of investigators. Preparative methods for perfluorostyrene have been published<sup>1,2</sup>. These methods, unfortunately, are tedious and the yields are extremely low. We now would like to report an improved method for the synthesis of perfluorostyrene and some substituted perhalostyrenes.

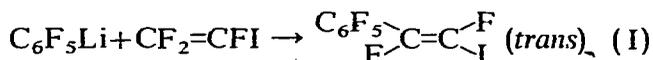
Pentafluorophenylcopper has recently been synthesized for the first time<sup>3-6</sup>. As an organometallic intermediate for the synthesis of other pentafluorophenyl compounds, it behaves in many respects as the pentafluorophenyllithium or pentafluorophenyl Grignard. However, unlike the latter organometallics, the copper reagent selectively displaces the higher halogens (Br and I)<sup>6</sup> in favor of fluorine from perfluoroaromatics or olefins. This contrast is exemplified by the preparation of perfluorostyrene.

Thus, the reaction between pentafluorophenylcopper and trifluorovinyl iodide yields perfluorostyrene in 55% yield:



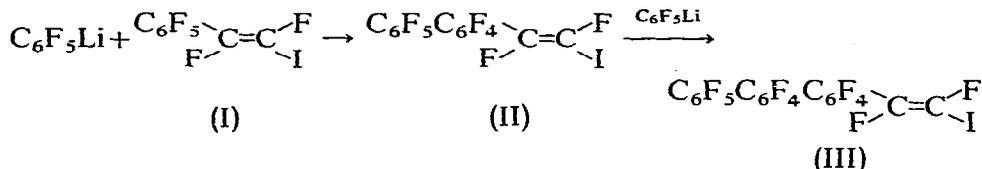
In addition, a small yield of iodopentafluorobenzene was indicated by VPC analysis. The presence of this compound indicates that copper-halogen interchange may take place, however, only to a minor extent.

Unlike the pentafluorophenylcopper reagent, pentafluorophenyllithium reacts with trifluorovinyl iodide in a different manner. The principal products of the reaction indicate that the pentafluorophenyllithium initially adds to the olefin followed by elimination of lithium fluoride to yield the pentafluorophenyliodoolefin (I).



Under the reaction conditions, this product then competes with trifluorovinyl iodide for the unconsumed pentafluorophenyllithium. One might expect *a priori* that the second molecule of pentafluorophenyllithium would also add to the olefin followed by elimination of lithium fluoride to form a disubstituted olefin. Results of this nature have been observed by Dixon<sup>7</sup> in his studies on the reaction of phenyllithi-

um and tetrafluoroethylene. In our case, however, the second molecule of pentafluorophenyllithium nucleophilically attacks the *para* fluorine to yield as the major product, the vinyl substituted biphenyl compound II. The reaction proceeds further to yield the triphenylvinyl compound III and minor (not isolated but indicated by VPC analysis) products which may be the polyphenylated vinyl derivatives.



#### EXPERIMENTAL

All organometallic preparations were carried out under an atmosphere of dry, oxygen-free nitrogen. Tetrahydrofuran was freshly distilled from sodium. VPC analysis were carried out on F&M Model 700 Gas Chromatograph using a 6' x 0.25" column, 20% Apiezon L on 60-80 mesh Chromasorb W. The mass spectral analysis were performed on a CEC-21-110B mass spectrometer. The  $^{19}\text{F}$  NMR spectra were recorded on a Varian A 56-60 spectrometer and the chemical shifts are reported in ppm from internal trichlorofluoromethane.

#### Preparation of pentafluorophenylcopper

n-Butyllithium (0.042 mole) was added to a THF solution (80 ml) of pentafluorobenzene (7.06 g, 0.042 mole) at  $-70^\circ$ . After 0.5 h at  $-70^\circ$ , cuprous iodide (7.98 g, 0.042 mole) was added to the reaction mixture and allowed to stir for an additional 12 h.

#### Reaction of pentafluorophenylcopper with trifluorovinyl iodide

Freshly distilled trifluorovinyl iodide (8.7 g, 0.042 mole) was added to the above described THF solution of pentafluorophenylcopper (0.042 mole). The reaction flask, equipped with a methanol-ice condenser, was heated gradually from 25-55°. After 5 h at 55°, the reaction mixture was cooled and analyzed by VPC. Analysis indicated the presence of two products  $\text{C}_6\text{F}_5\text{CF}=\text{CF}_2$  (55% yield) and  $\text{C}_6\text{F}_5\text{I}$  in a 20/1 area ratio, respectively. The solution was decanted from the precipitate, hydrolyzed with water (5 ml), filtered, dried ( $\text{CaCl}_2$ ) and distilled. The fraction b.p. 124-125°,  $n_D^{21} = 1.3984$  was further analyzed by VPC and indicated a purity of 98%. The perfluorostyrene had a characteristic C=C absorption in the infrared at 5.65  $\mu$ . Its  $^{19}\text{F}$  NMR spectrum (neat) showed multiplets at +97, +113, +138, +150, +162 and +171 ppm which were assigned the  $\text{F}_1$ - $\text{F}_6$ , respectively. The experimentally derived coupling constants were:  $J_{1,2} = 63$ ,  $J_{1,6} = 36$ ,  $J_{1,3} = 2.5$ ,  $J_{1,4} = 1$ ,  $J_{2,6} = 117$ ,  $J_{2,3} = 10.5$ ,  $J_{2,4} = 1.5$ ,  $J_{4,6} = 3.5$ ,  $J_{4,5} = 20$  Hz. The mass spectrum indicates the parent ion at  $m/e =$

