

NOTE

NOVEL SYNTHESIS OF PERHALOSTYRENE COMPOUNDS

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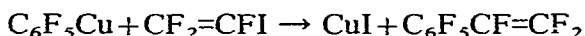
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(Received July 3rd, 1968; in revised form August 13th, 1968)

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^{1,2}. 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.

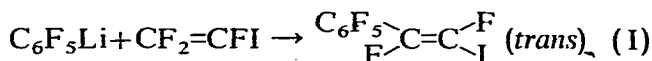
Pentafluorophenylcopper has recently been synthesized for the first time³⁻⁶. As an organometallic intermediate for the synthesis of other pentafluorophenyl compounds, it behaves in many respects as the pentafluorophenyllithium or pentafluorophenyl Grignard. However, unlike the latter organometallics, the copper reagent selectively displaces the higher halogens (Br and I)⁶ 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:



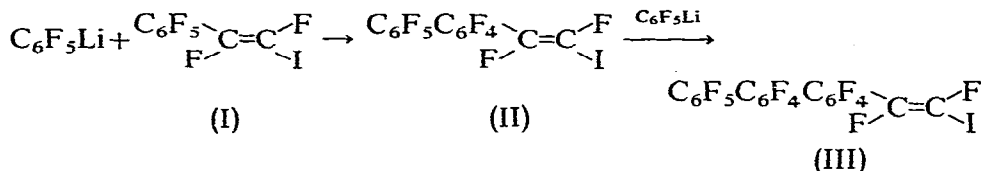
In addition, a small yield of iodopentafluorobenzene was indicated by VPC analysis. The presence of this compound indicates that copper-halogen interchange may take place, however, only to a minor extent.

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 Dixon⁷ 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

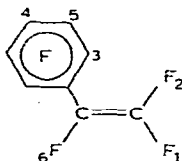
All organometallic preparations were carried out under an atmosphere of dry, oxygen-free nitrogen. Tetrahydrofuran was freshly distilled from sodium. VPC analysis were carried out on F&M Model 700 Gas Chromatograph using a 6' $\times$ 0.25" column, 20% Apiezon L on 60–80 mesh Chromasorb W. The mass spectral analysis were performed on a CEC-21-110B mass spectrometer. The ^{19}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° . After 0.5 h at -70° , 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

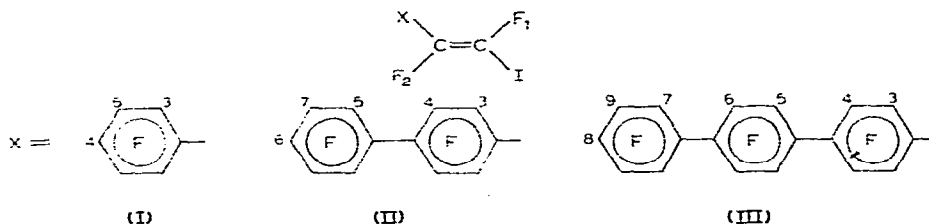
Freshly distilled trifluorovinyl iodide (8.7 g, 0.042 mole) was added to the above described THF solution of pentafluorophenylcopper (0.042 mole). The reaction flask, equipped with a methanol-ice condenser, was heated gradually from 25 – 55° . After 5 h at 55° , the reaction mixture was cooled and analyzed 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 (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 $\text{C}=\text{C}$ absorption in the infrared at $5.65\ \mu$. Its ^{19}F NMR spectrum (neat) showed multiplets at +97, +113, +138, +150, +162 and +171 ppm which were assigned the F_1 – F_6 , respectively. The experimentally derived coupling constants were: $J_{12}=63$, $J_{16}=36$, $J_{13}=2.5$, $J_{14}=1$, $J_{26}=117$, $J_{23}=10.5$, $J_{24}=1.5$, $J_{46}=3.5$, $J_{45}=20$ Hz. The mass spectrum indicates the parent ion at $m/e=$



248 ($C_8F_8^+$) and other principal fragmentation peaks in descending abundance at 179 ($C_7F_5^+$), 198 ($C_7F_6^+$), 229 ($C_8F_7^+$), 148 ($C_6F_4^+$).

Reaction of pentafluorophenyllithium with trifluorovinyl iodide

Freshly distilled trifluorovinyl iodide (20.8 g, 0.10 mole) was added to a -70° THF solution (~ 210 ml) of pentafluorophenyllithium (prepared from 16.8 g, 0.10 mole C_6F_5H and 0.10 mole $n-C_4H_9Li$) containing *n*-decane as the internal VPC standard. The reaction mixture was stirred at -70° for 16 h after which a sample was removed and analyzed by VPC. Very little reaction had occurred so the reaction mixture was allowed to warm gradually (2 h) to room temperature. The reaction mixture was hydrolyzed with 6 *N* HCl (60 ml), extracted with diethyl ether, phase separated and the organic layer dried ($MgSO_4$). VPC analysis indicated three major products I, II, III, in an area ratio of 1.4/2.1/1.2, respectively. Fractional distillation through a spinning band column yielded the first product I, b.p. $74^\circ/2$ mm. The pot residue contained products II and III. These two materials were separated by preparative VPC; II, m.p. $134-135^\circ$ and III, m.p. $173-175^\circ$. The products I, II and III were characterized by IR, mass spectrometric and NMR analysis.



The ^{19}F NMR chemical shifts (internal CFCl_3) and assignments are: I (neat) F_1 111, F_2 128 (J_{12} 152 Hz), F_3 136.5, F_4 149.5, F_5 161 ppm; II (THF solution) F_1 111, F_2 131 (J_{12} 152 Hz), F_3, F_4, F_5 138, F_6 151, F_7 162 ppm; III (Me_2CO solution) F_1 111, F_2 132 (J_{12} 151 Hz), F_3, F_4, F_5, F_6, F_7 138.5, F_8 152, F_9 163 ppm.

ACKNOWLEDGEMENT

We wish to express our appreciation to Lee D. Smithson of the Air Force Materials Laboratory for performing the mass spectral analysis.

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