O-21

USE OF 1,1-DICHLORO-2,2-DIFLUOROETHYLENE IN SYNTHESIS OF FLUORINE-CONTAINING ARYL ACETYLENES

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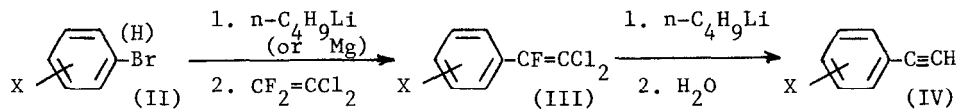
Recently polyfluoroacetylene and polydifluoroacetylene have been proposed as possible semiconducting meterials, particularly after doped with electron donors. Since their monomers are difficult to handle and their polymerization is unknown, polyphenylacetylene having fluorine atoms may be of considerable interest in evaluating the role of fluorine in this area. In connection with such a project, synthesis of some fluorine-containing phenylacetylenes was performed applying the method of introduction of the ethynyl group using $CF_2=CCl_2$ (I).



(II) (III) (IV)

X = m-, p-F; o-, m-, p-CF_3; 2,4-; 2,5-; 2,6-; 3,5-$(CF_3)_2$; F_5; (p-R-F_4)

The yields of III ranged from 50 to 80% except for the cases where m-bis(trifluoromethyl)benzene was used as the starting material. Lithiation of p-bis(trifluoromethyl)benzene and subsequent reaction with I occurred readily. In the cases where m- and p-fluoro- and m- and p-trifluoromethylbromobenzene were used, the route via Grignard reagents gave higher yields of III (by 11-32%). However, o-trifluoromethylphenylmagnesium bromide did not react with I. The reaction of pentafluorophenylmagnesium bromide with I was also very slow. The proportion of C_6F_5Cl and $C_6F_5CF=CCl_2$ obtained from the reaction of pentafluorophenyllithium with I was sensitive to the reaction conditions, the best yield of $C_6F_5CF=CCl_2$ being 59%. The conversion of III to IV was performed in high yield at low temperatures, though the yield of pentafluorophenylacetylene was only about 50% due to the concurrent substitution at the para position. p-$RC_6F_4C{\equiv}CH$ was obtained in ca 80% yield by treatment with 3 equiv of RLi.

$$C_6F_5CF=CCl_2 \longrightarrow C_6F_5C{\equiv}CLi \longrightarrow p\text{-}RC_6F_4C{\equiv}CLi$$

Some of the fluorine-containing diphenyldiacetylenes obtained by oxidative coupling from the stated terminal acetylenes showed solid-state polymerizability whereas the corresponding compounds containing no fluorine did not. Other acetylenic compounds such as $C_6F_5C{\equiv}C\text{-}C{\equiv}CH$ will also be reported.