

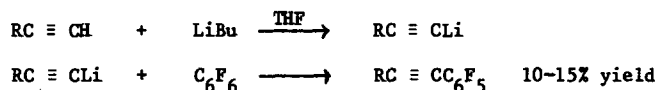
SYNTHESIS OF 1-PHENYLETHYNYL- 4-SUBSTITUTED TETRAFLUOROBENZENES

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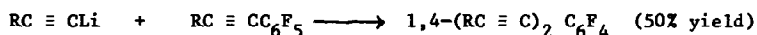
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We have recently described the preparation of several fluoroaromatic acetylene derivatives using the lithium salt of the corresponding mono-substituted alkynes¹:



The para fluorine atom in $\text{RC} \equiv \text{CC}_6\text{F}_5$ seems to be rather reactive and we found it difficult to arrest the reaction at this stage, the di-substituted compound being obtained in much the higher yield:



Attempts to block the para position by starting with pentafluorobenzene, bromo- or iodo- pentafluorobenzene gave rise to intractable mixtures of products when phenylethynyl-lithium is used possibly due to the formation of pentafluorophenyllithium, by lithium-hydrogen or lithium-halogen exchange reactions, which subsequently decomposed². However, decafluorobiphenyl on treatment with phenylethynyllithium gave good yields of 4-phenylethynyl-nonafluorobiphenyl, m.pt. 161-163° (Found C, 58.2; H, 1.1; F, 41.1. Calc. for $\text{C}_{20}\text{H}_5\text{F}_9$: C, 57.7; H, 1.2; F, 41.1%).

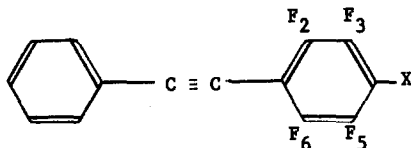
Similarly chloropentafluorobenzene, in a rather clean reaction, gave high yields of 1-phenylethynyl-4-chlorotetrafluorobenzene (I), m.pt. 95-96°, without the chlorine atom apparently either undergoing substitution with phenylethynyllithium or troublesome lithium-chlorine exchange reactions (Found: C, 58.9; H, 1.9; F, 26.8; Cl, 12.3. Calc. for $\text{C}_{14}\text{H}_5\text{ClF}_4$: C, 59.05; H, 1.8; F, 26.7; Cl, 12.5%). However, the reactivity of the chlorine atom in (I) makes it a useful synthetic intermediate since lithiation does occur via lithium-chlorine exchange with butyllithium in ether as shown by the formation of 1-phenylethynyl-2,3,5,6-tetrafluorobenzene, m.pt. 82-88°, on the addition of distilled water to the system (Found: C, 67.2; H, 2.5; F, 30.2. Calc. for $\text{C}_{14}\text{H}_6\text{F}_4$: C, 67.2; H, 2.4; F, 30.4). Treatment of the lithium reagent with bromine gives 1-phenylethynyl-4-bromotetrafluorobenzene, m.pt. 105-109°

(Found: C, 51.3, H, 1.6; F, 23.3; Br, 24.0. Calc. for $C_{14}H_5BrF_4$: C, 51.1; H, 1.5; F, 23.1; Br, 24.3%); whilst iodine gives the corresponding iodo-derivatives, m.pt. 118-120° (Found: C, 44.85; H, 1.3; F, 20.0; I, 33.55. Calc. for $C_{14}H_5IF_4$: C, 44.7; H, 1.3; F, 20.2; I, 33.8%). The reaction of the lithium derivative with halogen is relatively fast and if the calculated amount of halogen is used there is no significant addition to the triple bond. Treatment of 1-phenylethynyl-4-chlorotetrafluorobenzene with an excess of potassium fluoride in sulpholane at 180° for several hours yields only a trace of phenylethynylpentafluorobenzene; at 210-215° the yield increases to about 8% but appreciable charring causes some loss of product.

TABLE

^{19}F N.M.R. Chemical Shifts Recorded at 94.1 Mc/s

(± 0.5 ppm. relative to $CFCl_3$)



X	F _{2,6}	F _{3,5}	X
H *	136.3	139.9	
F	136.7	162.7	153.7
Cl	136.2	141.7	
Br	134.2	136.3	
I	121.2	136.0	

* In the 1H n.m.r. spectrum this proton has a chemical shift of 9.96 ppm relative to tetramethylsilane, with coupling constants of 9.8 and 7.5 c/s to the ortho and meta fluorine atoms respectively.

References

1. M. R. Wiles and A. G. Massey, *Chem. and Ind.* 663 (1967).
2. S. C. Cohen, A. J. Tomlinson, M. R. Wiles and A. G. Massey, *Chem. and Ind.* 877 (1967).