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PRELIMINARY NOTE

A Convenient Synthesis of Fluoro-Aromatic Acetylene Derivatives

YADONG ZHANG and JIANXUN WEN*

Shanghai Institute of Organic Chemistry, Academia Sinica,
345 Lingling Lu,Shanghai (China)

SUMMARY

The coupling reaction between polyfluoroiodobenzenes and terminal acetylenes under the catalysis of bis(triphenylphosphine)palladium dichloride and copper(I) iodide in triethylamine afforded a simple and effective method for the synthesis of fluoro-aromatic acetylene derivatives.

Poly(polyfluorophenyl)acetylenes and poly(dipolyfluorophenyl)diacetylenes derived from the fluoro-aromatic acetylenes can be used as various functional materials such as resists, electric conductors and nonlinear optical devices [1,2]. Recently there is great interest in the development of methods for introducing an acetylenic group into organic structures and much attention has been paid to the convenient synthesis of acetylenic compounds by the coupling reaction of arylhalides and terminal acetylenes in the presence of catalytic amounts of bis(triphenylphosphine)palladium dichloride and copper(I) iodide [3,4]. However, little work has been done on the synthesis of fluoro-aromatic acetylenes with this method. In this paper, we wish to report a convenient method for the synthesis of fluoro-aromatic acetylenes.

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$$\underset{1\text{-}2}{p\text{-}R\text{-}C_6F_4\text{-}I} \quad + \quad \underset{a\text{-}d}{H\text{-}C\equiv C\text{-}R'} \xrightarrow[Et_3N,\ 30\text{-}35^{o}C]{[(C_6H_5)_3P]_2PdCl_2/CuI} \underset{1a\text{-}d,\ 2a}{p\text{-}R\text{-}C_6F_4\text{-}C\equiv C\text{-}R'}$$

1, R = F- ; 2, R = N-.
a, R′ = C_6H_5- ; b, R′ = Me_3Si- ; c, R′ = p-CH_3OOC-C_6H_4- ;
d, R′ = p-O_2N-C_6H_4-.

Typical procedure: (Coupling of C_6F_5I with $HC\equiv CSiMe_3$)

To a mixture of trimethylsilylacetylene (b, 20 g, 0.20 mol) and pentafluoroiodobenzene (1, 53 g, 0.18 mol) in triethylamine (200 ml, dried over powdered potassium hydroxide) were added bis(triphenylphosphine)palladium dichloride (2 g, 2.8 mmol) and copper(I) iodide (0.5 g, 2.6 mmol). The reaction mixture was stirred at 30-35°C for 48h under nitrogen. Then 100 ml of ether was added to the suspension. The salt was filtered off on a sintered-glass funnel and rinsed well with ether. The solution was washed with water (small amounts of Et_3NHI were removed in this way). After drying over Na_2SO_4, the solution was distilled to give [(pentafluorophenyl)-ethynyl]trimethylsilane(1b, 43 g, 90.5 %).

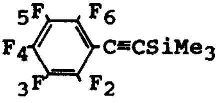
B.p. 106°C/25 mmHg.

^{1}H-NMR($CDCl_3$, TMS): 0.21(s) ppm.

^{19}F-NMR ($CDCl_3$, CF_3COOH): 59.67 (2F, d-d, $J_{23}=J_{65}=22.6$ Hz, $J_{25}=J_{63}=8.3$ Hz); 76.31 (1F, t, $J_{43}=J_{45}=22.6$ Hz); 85.67 (2F, d-d-d, $J_{32}=J_{34}=J_{54}=J_{56}=22.6$ Hz, $J_{36}=J_{52}=8.3$ Hz) ppm.

IR (film): 2169(m) ($C\equiv C$); 1518(vs), 1500(vs) (C_6F_5) cm^{-1}.

Elem. anal. for $C_{11}H_9F_5Si$ Calcd.: C, 50.00; H, 3.14; F, 35.99.
Found: C, 49.88; H, 3.38; F, 36.35.



(1b)

Synthesis of compounds 1a, 1c ,1d and 2a was followed by a similar procedure, the solvent was removed under reduced pressure. The residue was purified by chromatography on silica gel using petroleum ether as an eluent. The products were recrystallized from acetone-water or methanol-water. All had correct elemental analyses and approriate NMR and/or spectral data. Some of the results are shown in Table 1.

TABLE 1

Fluoro-Aromatic Acetylenes (1a-d, 2a) from Terminal Acetylenes

Polyfluoro-iodobenzenes	Terminal acetylenes	Temp. (°C)	Time (h)	Product	M.p./ B.p. (°C)	Yield (%)[a]
1	a	r.t.	12	1a	93	93.3
1	b	30-35	48	1b	106[b]	90.5
1	c	45-50	12	1c	116	78.7
1	d	45-50	16	1d	138	85.4
2	a	r.t.	12	2a	75	95.2

a) isolated yield.
b) b.p. under 25 mmHg.

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