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PRELIMINARY NOTE

Synthesis of (p-Substituted-tetrafluorophenyl)ethynes and Diacetylene Monomers Containing Fluoro-Aromatic Rings by Nucleophilic Substitution on [(Pentafluorophenyl)ethynyl]-trimethylsilane

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SUMMARY

Substitutions on [(pentafluorophenyl)ethynyl]trimethylsilane (**1**) with nucleophiles, Nu-X (**2**) give the corresponding [(p-substituted-tetrafluorophenyl)ethynyl]trimethylsilanes (**3**) or (p-substituted-tetrafluorophenyl)ethynes (**4**). The trimethylsilyl group of (**3**) can be easily removed by treatment with dilute alkali to give [(p-substituted-tetrafluorophenyl)-ethynes (**4**). Diacetylenes containing fluoro-aromatic rings are prepared by the Chodkiewiez-Cadiot and the Hay coupling of the corresponding terminal acetylenes (**4**).

Acetylenic compounds, especially terminal acetylenes, are valuable synthetic intermediates and there is great interest in the development of methods for introducing an ethynyl group into organic aromatic rings [1-4]. Up to now, several methods for introducing an acetylenic group into fluoro-aromatic compounds have been reported [5-7]. Previously we have reported

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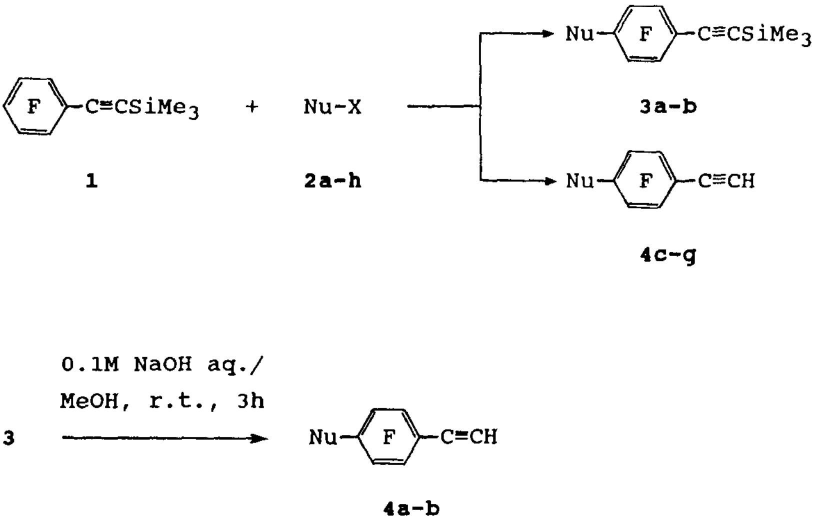
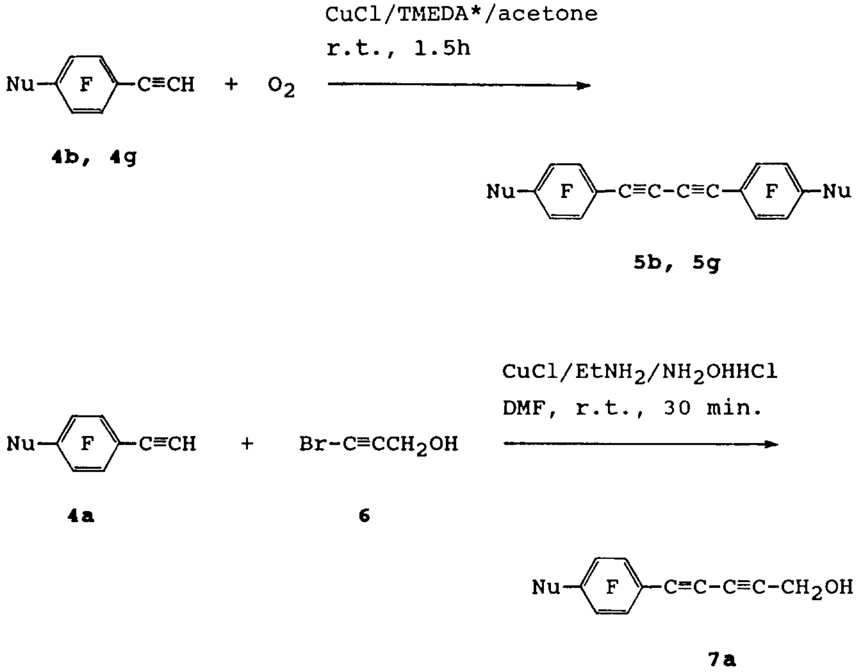
that a Pd catalyzed coupling reaction of a slight excess of trimethylsilylacetylene with pentafluoroiodobenzene afforded [(pentafluorophenyl)ethynyl]trimethylsilane in good yield [8]. Solid-state polymerization of some diacetylenes is known to give peculiar single crystals of conjugated polymers [9] which has attracted attention on their physical properties, such as conductivity [10, 11] and optical nonlinearity [12, 13]. Now quite a lot of diacetylenes have been synthesized and their solid-state polymerization reactivities have been extensively studied [9]. However, little work has been done on the synthesis of diacetylene monomers containing fluoro-aromatic rings. In this paper, we wish to report a convenient method for the synthesis of (p-substituted-tetrafluorophenyl)ethynes and diacetylene monomers containing fluoro-aromatic rings from [(pentafluorophenyl)ethynyl]trimethylsilane (**1**). Solid-state polymerization behaviour and nonlinear optical properties of these diacetylenes are now under study.



Scheme 1.



Scheme 2.

Starting material (**1**) was prepared by the method reported previously [8]. [(Pentafluorophenyl)ethynyl]trimethylsilane(**1**) reacted smoothly with nucleophiles to give the p-substituted products (**3**) or (**4**) in good yield and then (p-substituted-tetrafluorophenyl)ethynes were obtained after the removal of the trimethylsilyl group from (**3**). Nucleophilies, such as phenoxides, methanol and amines reacted with (**1**) to give directly (p-substituted-tetrafluorophenyl)ethynes (**4**). Representative examples are shown in Tables 1 and 2. Symmetric and unsymmetric diacetylene monomers containing fluoro-aromatic rings shown in Tables 3 and 4 were obtained by the Hay coupling of terminal acetylenes or the Chodkiewiez-Cadiot coupling of (p-substituted-tetrafluorophenyl)ethynes and bromopropargyl alcohol respectively as shown in Scheme 2 [14,15].

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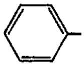
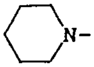
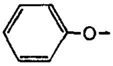
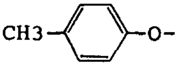
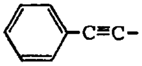
*N,N,N',N'-tetramethylethylenediamine.

TABLE 1

[(p-Substituted-tetrafluorophenyl)ethynyl]trimethylsilane **(3)** and (p-Substituted-tetrafluorophenyl)ethynes **(4)** from [(Pentafluorophenyl)ethynyl]trimethylsilane **(1)**

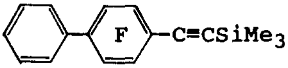
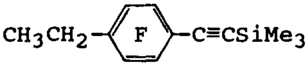
	Nu-X **2**		Reaction conditions	Product **3, 4**			
No	Nu	X	solvent/temp./time/base	No	m.p. (°C)	b.p. (°C)	yield (%)[a]
2a		MgBr	THF/62 C/11h/-	**3a**	93.4		92.3
2b	CH_3CH_2-	MgBr	THF/r.t./3.5h/-	**3b**		102.3[b]	85.7
2c	CH_3CH_2NH-	H	DMF/r.t./1.5h/K_2CO_3	**4c**		oil	88.5
2d		H	DMF/r.t./1.5h/K_2CO_3	**4d**	31.5		90.4
2e		K	DMF/r.t./1h/-	**4e**	73.3		97.4
2f		K	DMF/r.t./1h/-	**4f**	81.5		93.2
2g	CH_3O-	H	Methanol/r.t./KOH	**4g**	58.0		89.7
2h		MgBr	THF/rfl./10h/-	no reaction			

[a] Isolated yield.

[b] B.p under 5mmHg.

TABLE 2

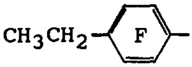
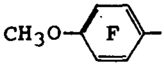
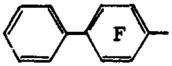
(p-Substituted-tetrafluorophenyl)ethynes (**4**) from [(p-Substituted-tetrafluorophenyl)ethynyl]trimethylsilane (**3**)[a]

No	Product **3**	Reaction condition temp./time/base	Product **4**			
			No	m.p. (^{o}C)	b.p. (^{o}C)	yield (%)[b]
3a		r.t./3h/NaOH	**4a**	76.5		89.4
3b		r.t./3h/NaOH	**4b**		50.0[c]	82.5

[a] The reactions were carried out in methanol.
[b] Isolated yield.
[c] B.p. under 5mmHg.

TABLE 3

Symmetric and Unsymmetric Diacetylene Monomers Containing Fluoro-Aromatic Rings (**5**),(**7**) (R^1-C≡C-C≡C-R^2) from Products(**4**)

Diacetylene No	R^1	R^2	Yield (%)[a]	M.p. (^{o}C)	Molecular formula
5b		R^1	90.8	137.2	$C_{20}H_{10}F_8$ (402.2)
5g		R^1	92.0	137.6	$C_{18}H_6F_8O_2$ (406.2)
7a		$-CH_2OH$	85.5	98.3	$C_{17}H_8F_4O$ (304.2)

[a] Isolated yield.

TABLE 4

Spectroscopic and Analytic Data of Diacetylenes **(5)**, **(7)**

No	IR[a] (KBr) ν(cm^{-1})	Raman[b] (neat) ν(cm^{-1})	^{1}H NMR[c] (CDCl$_3$/TMS) δ(ppm)	^{19}F NMR[d] (CDCl$_3$/CF$_3$COOH) δ(ppm)	MS[e] m/e (M$^+$)	Analysis Found (Calc.)
5b	1490 1480 1400 1323 1100 950	2227	1.23 (t, 6H, CH_3, J=7.2Hz); 2.76 (q, 4H, CH_2, J=7.2Hz)	58.7 (m, 4F, F_{arom}); 68.3 (m, 4F, F_{arom})	402	C 59.71 (59.70) H 2.28 (2.49) F 38.01 (37.81)
5g	1510 1500 1420 1195 1140 995	2224	4.08 (s, OCH_3)	59.2 (m, 4F, F_{arom}); 80.4 (m, 4F, F_{arom})	406	C 53.21 (53.20) H 1.36 (1.48) F 37.52 (37.44)
7a	3350 2210 1485 1440 1325 980	2244	7.38 (s, 5H, H_{arom}); 4.33 (s, 2H, OCH_2); 2.00(s, 1H, OH)	59.2 (m, 2F, F_{arom}); 66.6 (m, 2F, F_{arom})	304	C 66.99 (67.11) H 2.63 (2.43) F 25.11 (25.00)

[a] Recorded on a Shimadzu IR-440 spectrometer.

[b] Recorded on a JY-T 800 spectrometer.

[c] Recorded on a Varian EM 360A spectrometer.

[d] Recorded on a Varian EM 360L spectrometer.

[e] Recorded on a Finnigan-4021 spectrometer.

A typical procedure for nucleophilic substitution : To a solution of [(pentafluorophenyl)ethynyl]trimethylsilane (**1**; 5 g, 18.9 mmol) in dry THF (10 ml) was added phenylmagnesium bromide (20 ml of a 1.67 M solution in THF) at room temperature with stirring under nitrogen and then the reaction mixture was heated at 62°C. After 11 h the mixture was acidified with dilute hydrochloric acid and extracted with ether. The ether layer was dried over Na_2SO_4. After the removal of ether, a pale yellow solid product was collected. Recrystallization from acetone-water gave white crystals of [(p-phenyltetrafluorophenyl)ethynyl]trimethylsilane **(3a)** nc 5.6 g (92.3%) m.p. 93.4°C. IR (KBr): ν 2920, 2115, 1485, 1475, 1440, 1318, 1250, 1040, 1020, 980, 860, 840, 760, 725, 695, 643, 500 cm^{-1}; ^1H NMR ($CDCl_3$/TMS): δ 0.02 (s, 9H, $Si(CH_3)_3$), 7.08 (s, 5H, H_{arom}); ^{19}F NMR ($CDCl_3$/CF_3COOH): δ 59.5 (m, 2F, F_{arom}), 67.2 (m, 2F, F_{arom}); MS m/e 322 (M^+), 307 (base peak).

$C_{17}H_{14}F_4Si$ Calc. C 63.35 H 4.35 F 23.60
(322.2) Found C 63.18 H 4.25 F 23.71

A typical procedure for the removal of trimethylsilyl group: To a solution of 3a (5 g, 15.5 mmol), in methanol (200 ml), 0.1 M aqueous sodium hydroxide solution (25 ml) was added and the mixture was kept at room temperature. After 3 h, the mixture was acidified with dilute hydrochloric acid, and a yellow solid appeared. The crude product was recrystallized from methanol-water to afford white crystal of p-phenyl-tetrafluorophenylethyne **(4a)** nc 3.5 g (89.4%) m.p. 76.5°C. IR (KBr): ν 3300, 1483, 1475, 1440, 1315, 1280, 1025, 977, 915, 840, 795, 745, 695, 643, 500 cm^{-1}; ^1H NMR ($CDCl_3$/TMS): δ 3.23 (s, 1H, C≡C-H), 7.20 ppm (s. 1H, H_{arom}); ^{19}F NMR ($CDCl_3$/CF_3COOH): δ 59.3 (m, 2F, F_{arom}), 66.3 ppm (m, 2F, F_{arom}); MS m/e 250 (M^+).

$C_{14}H_6F_4$ Calc. C 67.20 H 2.40 F 30.40
(250.2) Found C 66.92 H 2.15 F 30.17

The reactions of [(pentafluorophenyl)ethynyl]trimethylsilane **(1)** with excess nucleophiles, Nu-X **(2c-g)** yielded directly (p-substituted-tetrafluorophenyl)ethynes **(4c-g)** in one step. Symmetric and unsymmetric diacetylenes containing fluoro-aromatic rings **(5)**, **(7)** were prepared according to the Hay method [14] and the Chodkiewiez-Cadiot method [15] from the corresponding terminal fluoro-aromatic acetylenes **(4)**.

1 R. D. Stephens and C. E. Gastro, J. Org. Chem., 28 (1963) 3313.

2 K. Sonogashira, Y. Tohda and N. Hagihara, Tetrahedron Lett. , (1975) 4467

3 R. Oliver and D. R. M. Watlton, Tetrahedron Lett., (1972) 5209.

4 D. E. Ames, D. Bull and C. Takundwa, Synthesis, (1981) 364.

5 P. L. Coe, R. G. Plevey and J. C. Tatlow, J. Chem. Soc. [C] (1966) 597; P.L. Coe, J.C. Tatlow and R.C. Terrell, J. Chem. Soc. [c] (1967) 2626.

6 F. Wangh and D. R. M. Walton, J. Organomet. Chem., 39 (1972) 275.

7 I. Barrow and A. E. Pedler, Tetrahedron, 32 (1976) 1829.

8 Y. Zhang and J. Wen, J. Fluorine Chem., 47 (1990) 533.

9 H.J. Cantow (ed.), 'Polydiacetylene', Advances in Polymer Science, 63, Springer-Verlag, 1984.

10 H. Nakanishi, H. Matsuda and M. Kato., Mol. Cryst. Liq. Cryst., 105 (1984) 77.

11 K. Lochner, B. Reimer and H. Bassler, Chem. Phys. Lett., 41 (1976) 388.

12 C. Sauteret, J.P. Hermann, R. Frey, F. Pradere, J. Ducuring, R. H. Baughman and R.R. Chance, Phys. Rev. Lett., 36 (1976) 956.

13 H. Matsuda, H. Nakanishi, N. Minami and M. Kato, Mol. Cryst. Liq. Cryst., 160 (1988) 241.

14 A. S. Hay, J. Org. Chem., 27 (1962) 3320.

15 W. Chodkiewicz and P. Cadiot, Compt. Rend., 241 (1955) 1055.