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SYNTHESIS OF SUBSTITUTED POLYFLUORO-AROMATIC ACETYLENES

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SUMMARY

Reaction of pentafluoro-aromatic acetylene compounds with large excesses of nucleophilic agents using K_2CO_3 as base gave polysubstituted and monosubstituted polyfluoro-aromatic acetylenes.

INTRODUCTION

It is well known that nucleophilic substitutions on polyfluoro-aromatic compounds are efficient methods for introducing substituents into the polyfluoro-arene rings [1-5]. In our previous notes, we reported a palladium-catalyzed coupling reaction of polyfluoroiodobenzenes and terminal acetylenes to give polyfluoro-aromatic acetylenes [6] and substitutions on 1-pentafluorophenyl-2-trimethylsilylacetylene with nucleophiles to give para-monosubstituted products [7]. Recently we found that 1,4-bis(pentafluorophenyl)butadiyne reacted with nucleophiles to give 1,4-bis(p-substituted-tetrafluorophenyl)butadiynes in tetrahydrofuran and to give 1,4-bis(2,4,6-trisubstituted-difluorophenyl)butadiynes in dimethylformamide [8-10]. In our laboratory, polyfluoro-aromatic acetylenes with extended π-conjugation are being prepared as the precursors of symmetric and asymmetric fluoro-diacetylene monomers for uses in nonlinear optics [7,11] and the monomers of poly(polyfluorophenylacetylene)s for electric conductors and nonlinear optics [12,13]. In this paper, we would like to report in full our methods for the synthesis of substituted polyfluoro-aromatic acetylenes from the corresponding pentafluoro-aromatic acetylene compounds.

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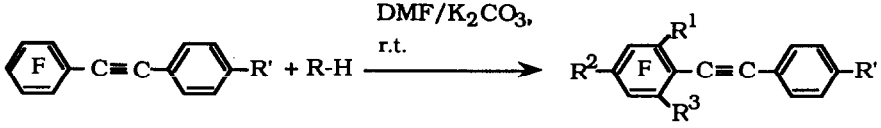
RESULTS AND DISCUSSION

All reactions were carried out in DMF at room temperature using K_2CO_3 as base as shown in Schemes 1 and 2.



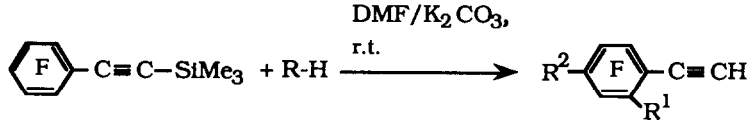
1-2 a-d 1a-d; 2a-c

1; R'=O_2N
2; R'=H

a; R=PhO
b; R=4-$MeOC_6H_4O$
c; R=MeO
d; R=Et_2N

1a; R^1=R^2=R^3=PhO
1b; R^1=R^2=R^3=4-$MeOC_6H_4O$
1c; R^1=R^2=MeO, R^3=F
1d; R^2=Et_2N, R^1= R^3=F
2a; R^1=R^2=PhO, R^3=F
2b; R^1=R^2=4-$MeOC_6H_4O$, R^3=F
2c; R^1=R^2= MeO, R^3=F

Scheme 1.



3 a-c 3a-c; 4a-c

a; R=PhO
b; R=4-$MeOC_6H_4O$
c; R=MeO

3a; R^1=F, R^2=PhO
3b; R^1=F, R^2=4-$MeOC_6H_4O$
3c; R^1=F, R^2=MeO
4a; R^1=R^2=PhO
4c; R^1=R^2=4-$MeOC_6H_4O$

Scheme 2.

Starting materials (1-3) were prepared by the coupling reaction of pentafluoroiodobenzene with the corresponding terminal acetylenes [6]. We found that the reaction of 1-pentafluorophenyl-2-p-nitro-phenylacetylene (1) with nucleophiles (a-c) in DMF using K_2CO_3 as base gave 2,4,6-trisubstituted difluoro-aromatic-acetylene derivatives (1a-b) and a 2,4-disubstituted trifluoro-aromatic acetylene (1c) due to the large π-

conjugation and acceptor properties (NO_2) of this pentafluoro-aromatic acetylene (1). (1) Reacted with diethylamine (d) to give only a 4-monosubstituted product (1d), in which a strong donor group (Et_2N) was introduced. This strong donor group would reduce the reactivities for further nucleophilic substitution on (1d) (Scheme 1). 1-Pentafluorophenyl-2-phenylacetylene (2) with significant π-conjugation reacted with nucleophiles (a-c) to give mainly 2,4-disubstituted products (2a-c) (Scheme 1). Nucleophilic substitutions on 1-pentafluorophenyl-2-trimethylsilylacetylene (3) with nucleophiles (a-b) gave 4-monosubstituted products (3a-b) and 2,4-disubstituted products (4a-b). (3) Reacted with MeOH (c) to give only the 4-monosubstituted product (3c) (Scheme 2). These results are in accordance with patterns of nucleophilic substitutions on polyfluoro-aromatic compounds [1-5].

TABLE 1

Substituted Polyfluoro-Aromatic Acetylenes (1a-d; 2a-c; 3a-c; 4a-b) from Pentafluoro-Aromatic Acetylene Compounds

Acetylene compound 1-3	Nucleophilic agent a-d	Reaction[a] time (h)	Product No	Product Yield[b] (%)
1	a	10	1a	96
1	b	8	1b	92
1	c	24	1c	78
1	d	24	1d	82
2	a	15	2a	86
2	b	12	2b	74
2	c	36	2c	88
3	a	24	3a	33
			4a	56
3	b	24	3b	27
			4b	64
3	c	24	3c	73

[a] All reaction were carried out in DMF at room temperature using K_2CO_3 as base.

[b] Isolated yields.

EXPERIMENTAL

IR spectra were recorded on a Shimadzu IR-400 spectrometer. ^{1}H-NMR spectra were recorded on a Varian EM 360A instrument (60 MHz). ^{19}F-NMR spectra were recorded on a Varian EM 360L instrument (60 MHz) (high field is positive). MS spectra were recorded on a Finnigan-4021 spectrometer.

Pentafluoro-aromatic acetylene compounds (1-3) were prepared by the coupling reaction reported previously [6]. The IR, ^{1}H-NMR, ^{19}F-NMR, MS and elemental analyses data of (1-2) were shown below.

1-Pentafluorophenyl-2-p-nitro-phenylacetylene (1): m.p. 137-138°C. IR (KBr): 1590, 1520, 1500, 1446, 1347, 1100, 995, 980, 850, 760, 742, 680 cm^{-1}; ^{1}H NMR ($CDCl_3$/TMS): δ= 7.80 (d, 2H, H_{arom}, J=8.2 Hz), 8.38 (d, 2H, H_{arom}, J=8.2 Hz) ppm; ^{19}F NMR ($CDCl_3$/CF_3COOH): δ= 58.42 (m, 2F, F_{arom}), 75.00 (t, 1F, F_{arom}), 83.78 (m, 2F, F_{arom}) ppm; MS: m/z 313 (M^+); Analysis, Found: C 53.38%, H 1.10%, N 4.30%, F 30.39%; Calc. for $C_{14}H_4F_5NO_2$: C 53.67%, H 1.28%, N 4.47%, F 30,35%.

1-Pentafluorophenyl-2-phenylacetylene (2): m. p. 93-94°C (ref. [14] m.p. 93°C). IR (KBr): 1520, 1500, 1445, 1120, 985, 975, 760, 695, 530 cm^{-1}; ^{1}H NMR ($CDCl_3$/TMS); δ=7.40 (s, H_{arom}) ppm; ^{19}F NMR ($CDCl_3$/CF_3COOH): δ=57.23 (m, 2F, F_{arom}), 75.00 (t, 1F, F_{arom}), 83.78 (m, 2F, F_{arom}) ppm; MS: m/z 268 (M^+).

1-Pentafluorophenyl-2-trimethylsilylacetylene (3) gave satisfactory IR, ^{1}H-NMR, ^{19}F-NMR, MS and elemental analysis [6].

1-(2,4,6-Triphenoxy-3,5-difluorophenyl)-2-p-nitro-phenylacetylene (1a) (nc): A Typical Procedure: 1-Pentafluorophenyl-2-p-nitro-phenylacetylene (1; 100mg, 0.32mmol), phenol (a; 0.8g, 8.5mmol) and K_2CO_3 (1.2g, 8.5mmol) were combined in DMF (4ml) at room temperature. After 7h, the mixture was

diluted with water (20ml) and extracted with ether. The solvent was removed, the residue was purified by chromatography on silica gel using petroleum ether (bp 60-90°C)/ethyl acetate (20:1) as an eluent to afford a pale yellow solid. Recrystallization from methanol-water gave pale yellow crystals of (1a): m.p. 121-122°C. IR (KBr): 3061, 1590, 1510, 1487, 1462, 1411, 1371, 1338, 1310, 1287, 1191, 1169, 1123, 1101, 1073, 1022, 991, 968, 896, 849, 811, 749, 728, 686, 566, 517 cm^{-1}; ^1H NMR ($CDCl_3$/TMS): δ=7.04-7.64 (m, 17H, H_{arom}), 8.23 (d, 2H, H_{arom}) ppm; ^{19}F NMR ($CDCl_3/CF_3COOH$): δ=66.73 (s, F_{arom}) ppm; MS: m/z 535 (M^+); Analysis, Found: C 71.65%, H 3.39%, N 2.38%, F 6.98%; Calc. for $C_{32}H_{19}F_2NO_5$: C 71.78%, H 3.55%, N 2.62%, F 7.10%.

Nucleophilic substitutions on pentafluoro-aromatic acetylene compounds (1-3) were performed by procedures similar to that described above. Specific reaction conditions are given in the Table 1. The following products were obtained:

1-[2,4,6-Tri(4-methoxy-Phenoxy)-3,5-difluorophenyl]-2-(4-nitro-phenyl)acetylene (1b) (nc): m.p. 149-150°C. IR (KBr): 2926, 1589, 1504, 1460, 1371, 1339, 1287, 1256, 1196, 1101, 1030, 996, 853, 765, 748, 708, 648, 511 cm^{-1}; ^1H NMR ($CDCl_3$/TMS): δ=3.80 (s, 9 H, 3xCH_3), 6.50-7.30 (m, 14H, H_{arom}), 8.12 (d, 2H, H_{arom}) ppm; ^{19}F NMR ($CDCl_3/CF_3COOH$): δ= 67.82 (s, F_{arom}) ppm; MS: m/z 625 (M^+); Analysis, Found: C 67.35%, H 3.97%, N 2.44%, F 6.28%; Calc. for $C_{35}H_{25}F_2NO_8$: C 67.20%, H 4.00%, N 2.24%, F 6.08%.

1-(2,4-Dimethoxy-3,5,6-trifluorophenyl)-2-(4-nitro-phenyl)acetylene (1c) (nc): m.p. 131-132°C. IR (KBr): 2950, 2217, 1628, 1590, 1502, 1480, 1429, 1404, 1372, 1341, 1285, 1196, 1131, 1106, 1023, 938, 900, 855, 750, 685 cm^{-1}; ^1H NMR ($CDCl_3$/TMS): δ= 4.00 (s, 6H, 2xCH_3), 7.36 (d, 2H, H_{arom}, J=8.7Hz), 8.20 (d, 2H, H_{arom}, J=8.7Hz) ppm; ^{19}F NMR ($CDCl_3/CF_3COOH$): δ=61.30 (q, 1F, F_{arom}, J_{65}=22.6Hz, J_{63}=10.2Hz), 75.77 (d, 1F, F_{arom}, J_{36}=10.2Hz), 82.75 (d, 1F, F_{arom}, J_{56}=22.6Hz) ppm; MS: m/z 337 (M^+); Analysis, Found: C 57.30%, H 2.86%, N 3.90%, F 16.72%; Calc. for $C_{16}H_{10}F_3NO_4$: C56.79%, H 2.79%, N 4.15%, F 16.91%.

1-(4-Diethylamino-2,3,5,6-tetrafluorophenyl)-2-(4-nitro-phenyl)acetylene (1d) (nc): m.p. 167-168°C. IR (KBr): 2981, 2211, 1640, 1588, 1528, 1510, 1490, 1472, 1447, 1381, 1349, 1335, 1309, 1286, 1195, 1099, 1013, 978, 918, 859, 785, 753, 678, 635 cm^{-1}; ^1H NMR ($CDCl_3$/TMS): δ=1.13 (t, 6H, 2xCH_3, J=6.0Hz), 3.33 (q, 4H, 2xCH_2, J=6.0Hz), 7.70 (d, 2H, H_{arom}, J=8.8Hz), 8.27 (d, 2H H_{arom}, J=8.8Hz) ppm; ^{19}F NMR ($CDCl_3$/CF_3COOH): δ=62.00 (m, 2F, F_{arom}), 73.78 (m, 2F, F_{arom}) ppm; MS: m/z 366 (M^+); Analysis, Found: C 59.33%, H 3.87%, N 7.47%, F 20.54%; Calc. for $C_{18}H_{14}F_4N_2O_2$: C 59.02%, H 3.83%, N 7.65%,F 20.77%.

1-(2,4-Diphenoxy-3,5,6-trifluorophenyl)-2-phenylacetylene (2a) (nc): m.p. 97-98°C. IR (KBr): 2220, 1580, 1478, 1423, 1234, 1206, 1165, 1104, 1072, 1024, 991, 986, 921, 807, 756, 687, 568, 529, 487 cm^{-1}; ^1H NMR ($CDCl_3$/TMS): δ=6.70-7.50 (m, H_{arom}) ppm; ^{19}F NMR ($CDCl_3$/CF_3COOH): δ=60.00 (q, 1F, F_{arom}, J_{65}=21.4Hz, J_{63}=11.3Hz), 69.00 (d, 1F, F_{arom}, J_{36}=11,3Hz), 76.33 (d, 1F, F_{arom}, J_{56}=21.4Hz) ppm; MS: m/z 416 (M^+); Analysis, Found: C 75.23%, H 3.57%, F 13.31%; Calc. for $C_{26}H_{15}F_3O_2$: C 75.00%, H 3.61%, F 13.70%.

1-[2,4-Di(4-methoxy-phenoxy)-3,5,6-trifluorophenyl]-2-phenylacetylene (2b) (nc): m.p. 95-96°C. IR (KBr): 2218, 1499, 1479, 1433, 1291, 1245, 1191, 1165, 1109, 1070, 990, 969, 829, 793, 756, 742, 690, 600, 521 cm^{-1}; ^1H NMR ($CDCl_3$/TMS): δ=3.76 (s, 6H, 2xCH_3), 6.90 (s, 8H, H_{arom}), 7.33 (s, 5H, H_{arom}) ppm; ^{19}F NMR ($CDCl_3$/CF_3COOH): δ=59.78 (q, 1F, F_{arom}, J_{65}=22.3Hz, J_{63}=10.7Hz), 69.33 (d, 1F, F_{arom}, J_{36}=10.7Hz), 76.72 (d, 1F, F_{arom}, J_{56}=22.3Hz) ppm; MS: m/z 476 (M^+); Analysis, Found: C 70.57%, H 3.79%, F 12.32%; Calc. for $C_{28}H_{19}F_3O_4$: C 70.59%, H 3.99%, F 11.97%.

1-(2,4-dimethoxy-3,5,6-trifluorophenyl)-2-phenylacetylene (2c) (nc): m.p. 44-45°C. IR (KBr): 2946, 2217, 1629, 1595, 1498, 1479, 1449, 1429, 1408, 1315, 1196, 1120, 1027, 1006, 994, 945, 756, 690, 555, 528 cm^{-1}; ^1H NMR ($CDCl_3$/TMS): δ=4.00 (s, 6H, 2xCH_3), 7.30-7.70 (m, 5H, H_{arom}) ppm; ^{19}F NMR ($CDCl_3$/CF_3COOH): δ=61.97 (q, 1F, F_{arom}, J_{65}=22.3Hz, J_{63}=10.4Hz), 77.33 (d, 1F, F_{arom}, J_{36}=10.4Hz), 83.00 (d, 1F, F_{arom}, J_{56}=22.3Hz) ppm; MS: m/z 292 (M^+); Analysis, Found: C 65.83%, H 3.56%, F 19.49%; Calc. for $C_{16}H_{11}F_3O_2$: C 65.75%, H 3.77%, F 19.52%.

(3) Reacted with phenol (a) to give a yellow solid which was chromatographed on a silica gel column. Elution with petroleum ether (60-90°C) initially gave 4-phenoxy-2,3,5,6-tetrafluorophenylacetylene (3a) which gave satisfactory IR, ^{1}H, NMR, ^{19}F NMR, MS and elemental analysis [7,15], followed by 2,4-diphenoxy-3,5,6-trifluorophenylacetylene (4a) (nc).

(4a): m.p. 99-100°C. IR (KBr): 3290, 1588, 1479, 1413, 1206, 1167, 1114, 1072, 1022, 990, 891, 807, 753, 683, 640, 487 cm^{-1}; ^{1}H NMR ($CDCl_3$/TMS): δ=3.50(s, 1H, C≡C-H), 6.90-7.60 (m, 10H, H_{arom}) ppm; ^{19}F NMR ($CDCl_3$/CF_3COOH): δ=60.72 (q, 1F, F_{arom}, J_{65}=22.5Hz, J_{63}=11.3Hz), 68.32 (d, 1F, F_{arom}, J_{36}=11.3Hz), 76.68 (d, 1F, F_{arom}, J_{56}=22.5Hz) ppm; MS: m/z 340 (M^+); Analysis, Found: C 70.47%, H 3.24%, F 16.19%; Calc. for $C_{20}H_{11}F_3O_2$:; C 70.59%, H 3.23%, F 16.76%.

(3) Reacted with p-hydroxy anisole (b) to give a brown solid which was chromatographed on a silica gel column. Elution with petroleum ether (60-90°C)/ethyl acetate (10:1) initially gave 4-(4-methoxy-phenoxy)-2,3,5,6-tetrafluorophenylacetylene (3b) (nc) and 2,4-di(4-methoxy-phenoxy)-3,5,6-trifluorophenylacetylene (4b) (nc).

(3b): m.p. 100-101°C. IR (KBr): 3306, 2959, 1640, 1489, 1456, 1440, 1297, 1250, 1192, 1118, 1102, 1030, 986, 953, 834, 809, 728, 676, 649, 597 cm^{-1}; ^{1}H NMR ($CDCl_3$/TMS): δ=3.60 (s, 1H, C≡C-H), 3.78 (s, 3H, CH_3), 6.89 (s, 4H, H_{arom}) ppm; ^{19}F NMR ($CDCl_3$/CF_3COOH): δ=60.72 (m, 2F, F_{arom}), 78.32 (m, 2F, F_{arom}) ppm; MS: m/z 296 (M^+); Analysis, Found: C 60.67% H 2.74%, F 25.48%; Calc. $C_{15}H_8F_4O_2$: C 60.81%, H 2.70%, F 25.68%.

(4b): m.p. 103-104°C. IR (KBr): 3263, 3009, 2957, 1861, 1629, 1593, 1501, 1480, 1442, 1295, 1248, 1198, 1113, 1102, 1030, 997, 951, 823, 771, 746, 717, 692, 672, 654, 597, 552, 507 cm^{-1}; ^{1}H NMR ($CDCl_3$/TMS): δ=3.50 (s, 1H, C≡C-H), 3.72 (s, 6H, 2xCH_3), 6.80 (s, 8H, H_{arom}) ppm; ^{19}F NMR ($CDCl_3$/CF_3COOH): δ=60.00 (q, 1F, F_{arom}, J_{65}=21.8Hz, J_{63}=10.9Hz), 68.77 (d, 1F, F_{arom}, J_{36}=10.9Hz), 77.00 (d, 1F, F_{arom}, J_{56}=21.8Hz) ppm; MS: m/z 400 (M^+); Analysis, Found: C 65.74%, H 3.72%, F 14.51%; Calc. for $C_{22}H_{15}F_3O_4$: C 66.00%, H 3.75%, F 14.25%.

4-Methoxy-2,3,5,6-tetrafluorophenylacetylene (3c) [7]: m.p. 58-59°C. IR (KBr): 3283, 2957, 2123, 1711, 1638, 1491, 1424, 1309, 1194, 1334, 988, 908, 649 cm^{-1}; ^1H NMR ($CDCl_3$/TMS): δ=3.32 (s, 1H, C≡C-H), 3.98 (s, 3H, CH_3) ppm; ^{19}F NMR ($CDCl_3$/CF_3COOH): δ=61.22 (m, 2F, F_{arom}), 82.34 (m, 2F, F_{arom}) ppm; MS: m/z 204 (M^+); Analysis, Found: C 52.89%, H 2.04%, F 37.58% ; Calc. for $C_9H_4F_4O$: C 52.94%, H 1.96%, F 37.25%.

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