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A FACILE SYNTHESIS OF PERFLUORO- AND POLYFLUORO-ALKYL THIENYL ACETYLENES

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SUMMARY

Perfluoro- and polyfluoro-alkyl thienyl acetylenes were conveniently prepared by the following reaction sequence: Thienylmethylenetriphenylphosphorane (generated from the corresponding chloride and phenyllithium without isolation) was acylated by the addition of perfluoroacyl chloride or polyfluoroacyl chloride, respectively, to give the corresponding perfluoroacyl or polyfluoroacyl phosphoranes in 82-94% yields and pyrolysis of these latter compounds under reduced pressure gave perfluoro- and polyfluoro-alkyl thienyl acetylenes <u>4</u> in 52-94% yields: These acetylenes would be expected to be good dipolarophiles and dienophiles.

INTRODUCTION

Pyrolysis of 1-acylalkylidenetriphenylphosphoranes is a useful method for the synthesis of acetylenes especially fluorinated species [1].

$$(C_6H_5)_3\overset{+}{P}-\underset{\underset{\bar{O}-C-R^2}{\|}}{C}-R^1 \longrightarrow R^1-C\equiv C-R^2$$

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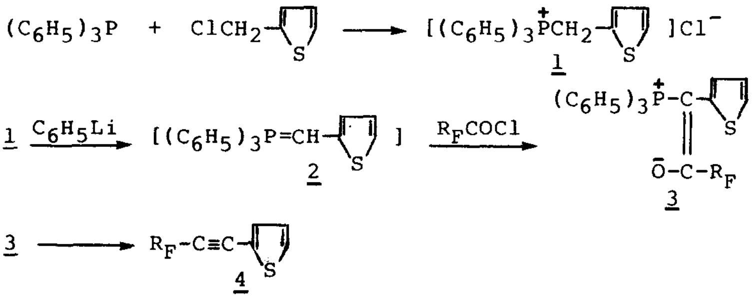
However, the thermolysis reaction proceeds satisfactorily only when R^1 is electron-withdrawing such as an ester, cyano or aryl group [2]. Recently this reaction has been extended to the synthesis of thioacetylenes [2], arylselenoacetylenes [3] and diphenoxyphosphonylacetylenes [4], and also to the synthesis of aliphatic non-terminal and terminal acetylenes but flash vacuum pyrolysis had to used in the latter case [5]. Now we extend this reaction to the synthesis of fluoroalkyl heterocyclyl acetylenes. In addition, perfluoro- and polyfluoro-alkyl thienyl acetylenes would expected to be good dipolarophiles and dienophiles and a useful species for the synthesis of heterocyclic compounds having biological properties, thus, the preparation of the title compounds is of interest. But the method for the preparation of heterocyclyl fluoro- and polyfluoroalkyl acetylenes have not been reported previously.

RESULTS AND DISCUSSION

In continuation of our investigation of the applicability of the intramolecular Wittig reaction to the synthesis of fluoroalkynes [1], we now prepared the title compounds successfully by the following reaction sequences:



Thienylmethyltriphenylphosphonium chloride was easily prepared from chloromethyl thiophene and triphenylphosphine in absolute benzene under nitrogen [6]. Thienylmethylenetriphenylphosphorane generated from thienylmethyltriphenylphosphonium chloride and phenyllithium in ether [6], without isolation, was acylated by the addition of perfluoroacyl chloride or polyfluoroacyl chloride to give the corresponding perfluoroacyl or polyfluoroacyl phosphoranes 3 in good to excellent yields (Table 1).

TABLE 1

Physical Constants and the Yields of 3.

Compound	R_F	m.p. (°C)	Yield (%)
3a	CF_3	170-171	82
3b	C_2F_5	161-162	88
3c	$n\text{-}C_3F_7$	152-153	90
3d	$Cl(CF_2)_3$	149-150	94
3e	$n\text{-}C_3F_7OCF(CF_3)$	112-113	84

Compounds 3 were isolated and submitted to vacuum pyrolysis (220-280°C/ 3-30 mmHg) to afford the expected perfluoro- and polyfluoro-alkyl thienyl acetylenes in moderate to excellent yields (Table 2). The structures of all products were ascertained by their i.r., MS and NMR spectra and by microanalyses which were satisfactorily consistent with the calculated values.

TABLE 2

Reaction conditions, Physical Constants and the Yields of 4.

Compound	R_F	Reaction Condition (°C/mmHg)	b.p. (°C)	Yield (%)
4a	CF_3	220-240/30	136	55
4b	C_2F_5	240-260/27	154	94
4c	$n-C_3F_7$	260-280/25	186-187	92
4d	$Cl(CF_2)_3$	260-280/25	207-208	72
4f	$n-C_3F_7OCF(CF_3)$	240-260/3	228-229	69

EXPERIMENTAL

All melting points and boiling points were uncorrected. Infrared spectra of solid products were obtained as KCl disks and liquid products as films on a Shimadzu IR-440 Spectrometer. ^{19}F and ^{1}H NMR spectra were obtained on a EM-360 Spectrometer at 60 MHz using TFA as external reference and TMS as internal reference, Mass spectra were obtained on a Finnigan GC-MS 4021 Mass Spectrometer.

Preparation of trifluoroacetylthienylmethylenetriphenylphosphorane (3a)

Phenyllithium (10 mmol) in absolute ether (25 ml) was added dropwise over 30 min, to a stirred suspension of a thienylmethyltriphenylphosphonium chloride (3.94g, 10 mmol) in absolute ether (75 ml). After the addition the reaction mixture was stirred at 25°C for 4 h and cooled to -78°C. A solution of perfluoroacetyl chloride (0.66g, 5 mmol) in ether (5 ml) was added. The mixture was allowed to warm to 25°C, stirred for 5 h and left at room temperature overnight. The precipitate was filtered off, the filtrate was evaporated and the residue was recrystallized from methanol-water (9:1) to give the product 3a; yield 1.86g (82%); mp 170-171°C; IR(KCl): 1580(s) cm^{-1}; ^1H NMR ($CDCl_3$): δ 6.49-7.05(m,3H); 7.15-7.83 (m,15H); ^{19}F NMR ($CDCl_3$): δ -9.4(s) ppm; MS m/e 454(M^+), 385 (M^+-CF_3). Analysis: Calcd for $C_{25}H_{18}F_3OPS$: C,66.08, H,3.99, F,12.54; Found: C,66.48, H,4.20, F,11.75.

Similar procedures were used to obtain the following products:
3b: 88% yield; mp 161-162°C; IR(KCl): 1560(s) cm^{-1}; ^1H NMR ($CDCl_3$): δ 6.40-7.09(m,3H); 7.11-7.83(m,15H); ^{19}F NMR ($CDCl_3$): δ 3.2(s,3F); 36.1(s,2F) ppm; MS m/e 504(M^+), 385(M^+-C_2F_5). Analysis: Calcd for $C_{26}H_{18}F_5OPS$: C,61.91, H,3.60, F,18.83; Found: C,61.71, H,3.41, F,18.03.

3c: 90% yield; mp 152-153°C; IR(KCl): 1590(s) cm^{-1}; ^1H NMR ($CDCl_3$): δ 6.31-7.07(m,3H); 7.17-7.86(m,15H); ^{19}F NMR ($CDCl_3$): δ 1.9(t,3F,J=10Hz); 33.9(q,2F,J=10Hz); 46.4(s,2F) ppm; MS m/e 554(M^+), 385(M^+-C_3F_7). Analysis: Calcd for $C_{27}H_{18}F_7OPS$: C, 58.49, H,3.27, F,23.98; Found: C,58.53, H,3.16, F,24.19.

3d: 94% yield; mp 149-150°C; IR(KCl): 1560(s) cm^{-1}; ^1H NMR ($CDCl_3$): δ 6.41-7.11(m,3H); 7.12-7.78(m,15H); ^{19}F NMR ($CDCl_3$): δ -11.4(t,2F,J=16Hz); 32.2(t,2F,J=16Hz); 40.1(br.s,2F)ppm; MS m/e 570(M^+), 385[M^+-$(CF_2)_3Cl$]. Analysis: Calcd for $C_{27}H_{18}F_6ClOPS$: C,56.80, H,3.18, F,19.97; Found: C,56.99, H,3.10, F,19.60.

3e: 84% yield; mp 112-113°C; IR(KCl): 1560(s) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 6.42-7.06(m,3H); 7.17-7.86(m,15H); ^{19}F NMR ($CDCl_3$): δ 2.5(t,3F,J=2Hz); 3.0(d,2F,J=2Hz); 4.3(AB,2F); 47.6-48.2(m, 1F); 51.0(br.s,2F) ppm; MS m/e 670(M^+),385[M^+-n-$C_3F_7OCF(CF_3)$]. Analysis: Calcd for $C_{29}H_{18}F_{11}O_2PS$: C,51.95, H,2.71, F,31.17; Found: C,52.00, H,2.40, F,30.34.

Preparation of trifluoromethyl thienyl acetylenes (4a)

The phosphorane 3a (0.9g 2 mmol), admixed with pumice stone (100 mg) was pyrolyzed under nitrogen at reduced pressure (220-240°C/30mmHg). The pyrolysate collected in traps cooled with Dry Ice/ethanol was redistilled to give 4a; yield: 0.19g (55%); bp 136°C; IR (film): 2260(w) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 6.60-7.00(m,1H); 7.08-7.80(m,2H); ^{19}F NMR ($CDCl_3$): δ 27.8(s) ppm; MS m/e 176(M^+), 157(M^+-F), 126(M^+-CF_2). Analysis: Calcd for $C_7H_3F_3S$: C,47.73, H,1.72, F,32.36; Found: C,47.03, H,1.55, F,32.57.

Similar procedure were used to obtained the following products:

4b: 94% yield; bp 154°C; IR (film): 2240(w) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 6.90-7.33(m,1H); 7.40-7.82(m,2H); ^{19}F NMR ($CDCl_3$): δ 7.3(t,3F,J=6Hz); 22.9(q,2F,J=6Hz) ppm; MS m/e 226(M^+), 207 (M^+-F), 157(M^+-CF_3); Analysis: Calcd for $C_8H_3F_5S$: C,42.49, H,1.34, F,42.00; Found: C,42.55, H,1.23, F,42.42.

4c: 92% yield; bp 186-187°C; IR (film): 2200(w) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 6.40-7.03(m,1H); 7.05-7.82(m,2H); ^{19}F NMR ($CDCl_3$): δ 2.3(t,3F,J=14Hz); 19.9-21.3(m,2F); 48,4(t,2F,J=6Hz) ppm; MS m/e 276(M^+), 257(M^+-F), 157(M^+-C_2F_5). Analysis: Calcd for $C_9H_3F_7S$: C,39.14, H,1.10, F,48.15; Found: C,39.38, H,1.11, F,48.13.

4d: 72% yield; bp 207-208°C; IR (film): 2230(w) cm^{-1}; ^1H NMR ($CDCl_3$): δ 6.36-7.07(m,1H); 7.10-8.10(m,2H); ^{19}F NMR ($CDCl_3$): δ -11.2(t,2F,J=13Hz); 17.3-18.5(m,2F); 43.2(t,2F,J=7Hz) ppm; MS m/e 292(M^+), 257(M^+-Cl), 157[M^+-Cl(CF_2)$_2$]. Analysis: Calcd for $C_9H_3ClF_6S$: C.36.95, H,1.03, F,38.95; Found: C,37.34, H,1.13, F,39.28.

4e: 69% yield; bp 228-229°C; IR(film): 2220(w) cm^{-1}; ^1H NMR ($CDCl_3$): δ 6.46-6.93(m,1H); 6.98-7.56(m,2H); ^{19}F NMR ($CDCl_3$): δ 4.2(t,3F,J=6Hz); 7.3(d,2F,J=5Hz); 6.3(AB,2F); 31.0-32.2 (m,1F); 52.3(br.s,2F) ppm; MS m/e 392(M^+), 373(M^+-F), 157 [M^+-n-$C_3F_7OCF(CF_3)$)]. Analysis: Calcd for $C_{11}H_3F_{11}OS$: C,33.69, H,0.77, F,53.29; Found: C,33.81, H,0.71, F,52.89.

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