Journal of Fluorine Chemistry, *41* (1988) 363–369
Received: March 23, 1988; accepted: June 7, 1988

A CONVENIENT SYNTHESIS OF CHLOROFLUORO- AND PERFLUOROXY-ALKYNENITRILES

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SUMMARY

Chlorofluoro- and perfluoroxy-alkynenitriles were conveniently prepared by the following reaction sequence: cyanomethylenetriphenylphosphorane was acylated by the addition of chlorofluoroalkanoyl chlorides or perfluoroxy-alkanoyl chloride, respectively, to the corresponding fluorinated phosphoranes and the latter compounds submitted to vacuum pyrolysis to afford the title compounds in 53-85% yields.

INTRODUCTION

An intramolecular Wittig reaction is a well known method for the synthesis of acetylenes [1].

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

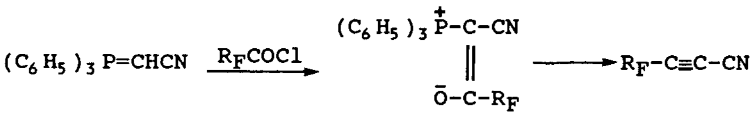
0022-1139/88/$3.50

However, investigation has been made only on the influence of R[1] upon this reaction and is limited to the cases where R[1] is an electron-withdrawing group such as 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 be used in the latter case [5].

To the best of our knowledge, no report has appeared in the literature concerning the influence of R[2] upon this reaction. In the present work, we investigated the influence of R[2] and the synthesis of chlorofluoro- and perfluoroxy- alkynenitriles.

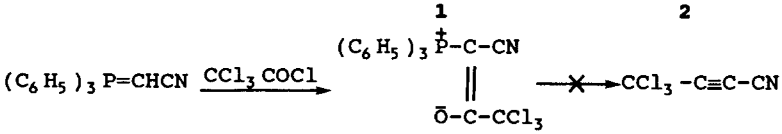
RESULTS AND DISCUSSION

In our continuing investigations on new applications of the intramolecular Wittig reaction in the synthesis of functionalised fluoroacetylenes [6], we found that while R[2] was a chlorofluoroalkyl or perfluoroxyalkyl group, this reaction proceeded smoothly to give acetylenes; when R[2] was a trichloromethyl group no acetylene was obtained.



$$(C_6H_5)_3P{=}CHCN \xrightarrow{R_FCOCl} \begin{array}{c}(C_6H_5)_3\overset{+}{P}-C-CN\\ \| \\ \bar{O}-C-R_F\end{array} \longrightarrow R_F-C\equiv C-CN$$

1 **2**



$$(C_6H_5)_3P{=}CHCN \xrightarrow{CCl_3COCl} \begin{array}{c}(C_6H_5)_3\overset{+}{P}-C-CN\\ \| \\ \bar{O}-C-CCl_3\end{array} \not\longrightarrow CCl_3-C\equiv C-CN$$

1e

Cyanomethylenetriphenylphosphorane was easily prepared from cyanomethyltriphenyl phosphonium chloride and aqueous sodium hydroxide solution [7] and was acylated by the addition of chlorofluoroalkanoyl chlorides or perfluoroxyalkanoyl chloride to give the corresponding fluorinated phosphoranes (**1**) in 77-90% yields. Fluorinated phosphoranes (**1**) were isolated and submitted to vacuum pyrolysis (280°C/1 mmHg) to afford the chlorofluoro- and perfluoroxy- alkynenitriles in 53-85% yields. The results are summarized in Tables 1 and 2.

TABLE 1
Physical Constants and the Yields of **1**.

Compound	R_F	m.p. (°C)	Yield (%)
1a	$ClCF_2$	170-172	85
1b	$Cl(CF_2)_3$	168-170	81
1c	$Cl(CF_2)_5$	150-151	90
1d	$n\text{-}C_3F_7OCF(CF_3)$	123-125	77
1e	CCl_3	238-239	80

TABLE 2
Physical Constants and the Yields of **2**.

Compound	R_F	m.p. (°C)	Yield (%)
2a	$ClCF_2$	55	53
2b	$Cl(CF_2)_3$	88	83
2c	$Cl(CF_2)_5$	128	85
2d	$n\text{-}C_3F_7OCF(CF_3)$	96	77
2e	CCl_3	—	0

EXPERIMENTAL

All melting points and boiling points were uncorrected. Infrared spectra of solid products were determined as KCl disks and liquid products as films on a Shimadzu IR-440 Spectrometer. NMR spectra (chemical shifts in ppm from TMS for ^{1}H NMR and from external TFA for ^{19}F NMR, positive for upfield shifts) were obtained on a EM-360 Spectrometer at 60 MHz. Mass spectra were recorded on a Finnigan GC-MS 4021 Mass Spectrometer.

Preparation of chlorodifluoroacetylcyanomethylenetriphenylphosphoranes (**1a**)

Cyanomethylenetriphenylphosphorane (19.0g, 63 mmol) and absolute benzene (550 mL) were placed in a flask with a Dry Ice/ ethanol cooled condenser. The mixture was stirred at 20°C while chlorodifluoroacetyl chlorides (5.0g,34 mmol) was bubbled into the solution. After stirring the mixture at 20°C for 2 h and standing overnight, the white precipitate was collected and washed with absolute benzene to give cyanomethyltriphenylphosphonium chloride; yield:10.0g(94%). Evaporation of the combined benzene solution gave a solid which is recrystallized from methanol to give chlorodifluoroacetylcyanomethylenetriphenylphosphorane (**1a**);yield 11.0g (85%); mp 170-171°C. IR(KCl): 2200(w),1620(s),1110(s) cm^{-1} ; ^{1}H NMR($CDCl_3$): δ 7.53-7.67(m); ^{19}F NMR($CDCl_3$): δ -16.1(s) ppm; MS m/e 413(M^+), 328(M^+-$CClF_2$). Analysis: Calcd for $C_{22}H_{15}ClF_2NOP$: C,63.86, H,3.65; Found: C,63.40, H,3.61.

Similar procedures were used to obtain the following products:

1b: 81% yield; mp 168-170°C; IR(KCl): 2200(w), 1620(s), 1110(s) cm^{-1}; ^{1}H NMR($CDCl_3$): δ 7.50-7.63(m); ^{19}F NMR ($CDCl_3$): δ -(11.5-11.8)(m,2F); 35.5-35.8(m,2F); 41.3 (br.s,2F) ppm; MS m/e 513(M$^+$), 328[M$^+$-Cl$(CF_2)_3$]. Analysis: Calcd for $C_{24}H_{15}ClF_6NOP$: C,56.10, H,2.94; Found: C,56.11, H,2.79.

1c: 90% yield; mp 150-151°C; IR(KCl): 2180(w), 1600(s), 1110(s) cm^{-1}; ^{1}H NMR($CDCl_3$): δ 7.50-7.63(m); ^{19}F NMR ($CDCl_3$): δ -(11.7-12.0)(m,2F); 35.3-35.7(m,2F); 40.7-42.1(m,6F) ppm; MS m/e 613(M$^+$), 328[M$^+$-Cl$(CF_2)_5$]. Analysis: Calcd for $C_{26}H_{15}ClF_{10}NOP$: C,50.88, H,2.46; Found: C,50.81, H,2.29.

1d: 77% yield; mp 123-125°C; IR(KCl): 2190(w), 1650(s), 1220(s) cm^{-1}; ^{1}H NMR($CDCl_3$): δ 7.55-7.60(m); ^{19}F NMR ($CDCl_3$): δ 2.7(t,3F,J=2Hz); 3.0(d,3F,J=2Hz);3.8(AB,2F); 49.1-50.8(m,1F); 51.1(br.s,2F) ppm; MS m/e 613(M$^+$), 328 [M$^+$-n-$C_3F_7OCF(CF_3)$]. Analysis: Calcd for $C_{26}H_{15}F_{11}NOP$: C,50.91, H,2.47; Found: C,51.13, H,2.39.

1e: 80% yield; mp 238-239°C; IR(KCl): 2200(w), 1600(s), cm^{-1}; ^{1}H NMR($CDCl_3$): δ 7.47-7.68(m) ppm; MS m/e 445(M$^+$), 328[M$^+$-CCl_3]. Analysis: Calcd for $C_{22}H_{15}Cl_3NOP$: C,59.15, H,3.39; Found: C,59.23, H,3.42.

Preparation of chlorodifluoro-2-butynenitrile (**2a**):

The phosphorane **1a** (0.8g, 1.9 mmol) admixed with pumice stone (100 mg) was pyrolyzed under nitrogen at reduced pressure (280°C/10 mmHg). The pyrolysate collected in traps cooled with Dry Ice/ethanol was redistilled to give **2a**; yield 0.14g (53%); bp 55°C; IR(film): 2350(w), 2180(w), 1160(s) cm^{-1}; ^{19}F NMR($CDCl_3$): δ -35.3(s) ppm; MS m/e 135 (M^+), 116(M^+-F).

Similar procedures were used to obtain the following products:

2b: 83% yield; bp 88°C; IR(film): 2300(w), 2170(w), 1170(s) cm^{-1}; ^{19}F NMR($CDCl_3$): δ -(8.7-9.1)(m,2F); 23.8-24.3 (m,2F); 44.2(br.s,2F); MS m/e 235(M^+), 200(M^+-Cl). Analysis: Calcd for C_6ClF_6N: C,30.60; Found: C,30.46.

2c: 85% yield; bp 128°C; IR(film): 2340(w), 2170(w), 1180(s) cm^{-1}; ^{19}F NMR($CDCl_3$): δ -(8.3-10.3)(m,2F); 22.8-25.8(m,2F); 42.0-46.7(m,6F); MS m/e 335(M^+), 300 (M^+-Cl). Analysis: Calcd for $C_8ClF_{10}N$: C,28.64; Found: C,28.52.

2d: 77% yield; bp 96°C; IR(film): 2300(w), 2170(w), 1160(S) cm^{-1}; ^{19}F NMR($CDCl_3$): δ 5.5(t,3F,J=8Hz); 8.4(d,3F,J=6Hz) ;7.3(AB,2F), 31.8-32.6(m,1F); 54.0(br.s,2F) ppm; MS m/e 335(M^+), 150(M^+-C_3F_7O). Analysis: Calcd for $C_8F_{11}NO$: C,28.68; Found: C,29.02.

ACKNOWLEDGEMENT

Thanks are due to National Natural Science Foundation of China and Academia Sinica for financial support.

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