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A CONVENIENT SYNTHESIS OF PERFLUORO- AND POLYFLUORO-ACETYLENIC THIOLESTERS

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SUMMARY

An intramolecular Wittig reaction has been successfully applied to the synthesis of perfluoro- and polyfluoro-acetylenic thiolesters in excellent yields. These thiolesters would be expected to be good dipolarophiles and dienophiles and useful species for the synthesis of fluorinated heterocyclic compounds.

INTRODUCTION

Fluoroalkynes, such as hexafluorobutyne-2 are good dipolarophiles and dienophiles and valuable species for the synthesis of various trifluoromethylated compounds [1]. In our studies of fluoroalkynes as dipolarophiles for the synthesis of fluorinated heterocyclic compounds the fluorinated species were also found to be good dipolarophiles [2]. For the extension of these studies, the preparation of perfluoro- and polyfluoro-acetylenic thiolesters is of interest, since none of these compounds have been prepared previously. Furthermore, perfluoro- and polyfluoro- thiol-

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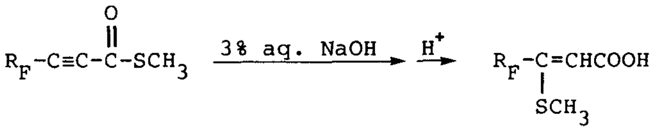
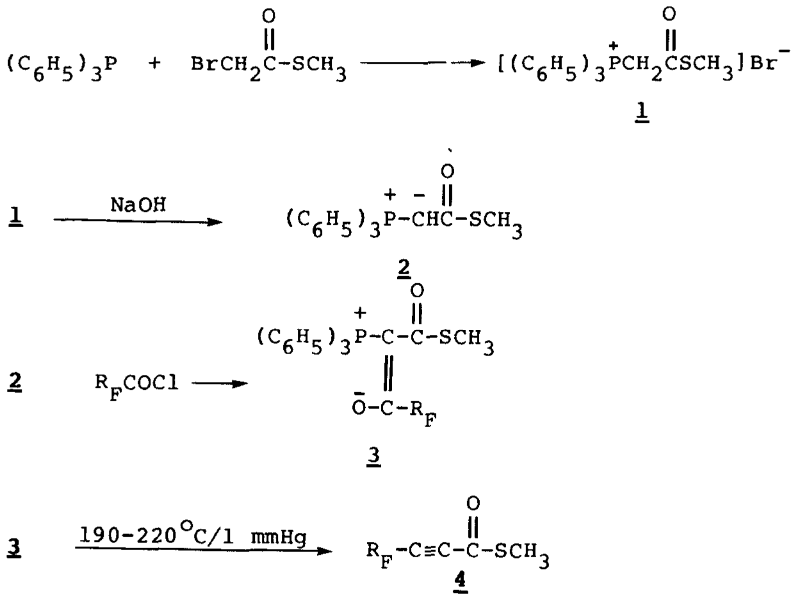
esters could undergo an unprecedented novel rearrangement in which the methylthio group would migrate to the β-carbon [3].



$$R_F\text{-}C{\equiv}C\text{-}\overset{\overset{O}{\|}}{C}\text{-}SCH_3 \xrightarrow{3\%\ \text{aq. NaOH}} \xrightarrow{H^+} R_F\text{-}\underset{\underset{SCH_3}{|}}{C}{=}CHCOOH$$

RESULTS AND DISCUSSION

Pyrolysis of acetylated phosphoranes is a useful method for the synthesis of acetylenes especially fluorinated species [4]. In the present work , we investigated the application of the intramolecular Wittig reaction in the synthesis of perfluoro- and polyfluoro- acetylenic thiolesters. The reaction sequence is as follows:



$$(C_6H_5)_3P + BrCH_2\overset{\overset{O}{\|}}{C}\text{-}SCH_3 \longrightarrow [(C_6H_5)_3\overset{+}{P}CH_2\overset{\overset{O}{\|}}{C}SCH_3]Br^- \quad \underline{1}$$

$$\underline{1} \xrightarrow{NaOH} (C_6H_5)_3\overset{+}{P}\text{-}\overset{-}{C}H\overset{\overset{O}{\|}}{C}\text{-}SCH_3 \quad \underline{2}$$

$$\underline{2} \quad R_FCOCl \longrightarrow (C_6H_5)_3\overset{+}{P}\text{-}\underset{\underset{\overset{-}{O}\text{-}C\text{-}R_F}{\|}}{C}\text{-}\overset{\overset{O}{\|}}{C}\text{-}SCH_3 \quad \underline{3}$$

$$\underline{3} \xrightarrow{190\text{-}220^{\circ}C/1\ mmHg} R_F\text{-}C{\equiv}C\text{-}\overset{\overset{O}{\|}}{C}\text{-}SCH_3 \quad \underline{4}$$

Carbomethylthiomethylenetriphenylphosphoranes(2) have been prepared previously, but the method of preparation is troublesome and the yield poor (46%) [5]. Our method using bromoacetic thiolester as starting material was convenient and the yields were excellent (for 1, 92%; for 2, 98%). The perfluoroacyl and polyfluoroacyl phosphoranes 3 were prepared in good to excellent yields by reaction of phosphoranes 2 with perfluoroacyl and polyfluoroacyl chlorides (Table 1). Pyrolysis of perfluoroacyl and polyfluoroacyl phosphoranes 3 under vacuum at 190-220°C gave the expected perfluoro- and polyfluoro-acetylenic thiolesters 4 in 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 1

Physical Constants and the yields of 3.

Compound	R_F	m.p. (°C)	Yield (%)
3a	C_2F_5	129-130	97
3b	$n\text{-}C_3F_7$	135-136	90
3c	$n\text{-}C_7F_{15}$	100-101	80
3d	$Cl(CF_2)_3$	151-152	90
3e	$Cl(CF_2)_5$	144-145	91
3f	$n\text{-}C_3F_7O\underset{CF_3}{\underset{\vert}{C}}F$	113-114	81

TABLE 2

Physical Constants and the Yields of 4.

Compound	R_F	b.p. (^oC)	Yield (%)
4a	C_2F_5	122	92
4b	$n\text{-}C_3F_7$	139	95
4c	$n\text{-}C_7F_{15}$	202	93
4d	$Cl(CF_2)_3$	168	95
4e	$Cl(CF_2)_5$	198	90
4f	$n\text{-}C_3F_7O\underset{CF_3}{\underset{\mid}{C}}F$	172	94

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 ^1H 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 carbomethylthiomethyl triphenylphosphonium bromide (1)

To a solution of triphenylphosphine (175g, 0.67 mol) in absolute benzene (60 ml) methyl α-bromothioacetate (112g 0.67 mol) was slowly added.After addition,the reaction mixture was stirred at room temperature for 6 h and then allowed to stand overnight. The precipitate formed was collected and washed with absolute benzene to give 1 which was recrystallized from methanol/ether; yield: 262g(92%); mp 164-165°C; IR(KCl); 1650 (s) cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.25(s,3H), 6.02 (d, 2H, J=14 Hz), 7.50-8.20(m,15H) ppm. Analysis: Calcd for $C_{21}H_{20}BrOPS$: C, 58.47; H, 4.67, Found: C, 58.55; H,4.67.

Preparation of carbomethylthiomethylenetriphenylphosphorane(2)

A suspension of carbomethylthiomethyl triphenylphosphonium bromide (43g, 0.1 mol) in 800 ml of water was stirred at room temperature while a 5% sodium hydroxide solution (80 ml) was slowly added. After addition the reaction mixture was further stirred at room temperature for 30 min.The precipitate formed was filtered, washed with ice water until neutral and dried over P_2O_5 under vacuum to give 2 which was recrystallized from chloroform/ ethyl acetate; yield: 34.5g (98%); mp 170°C (decomposition); IR (KCl): 1570 (s) cm^{-1}; ^1H NMR ($CDCl_3$); δ 2.20(s,3H),3.67(d,1H,J=20Hz)7.48-8.00(m,15H) ppm. Analysis: Calcd for $C_{21}H_{19}OPS$: C, 71.98, H, 5.47, Found: C, 71.62, H, 5.38.

Preparation of pentafluoropropionylcarbomethylthiomethylene triphenylphosphorane (3a)

To a stirred suspension of 2 (9.5g, 0.027 mol) in a absolute benzene (300 ml) placed in a flask with a Dry

Ice/ethanol cooled condenser, pentafluoropropionyl chloride (3.3g, 0.018 mol) was slowly added. After stirring the mixture at room temperature for 4 h and standing overnight,the precipitate was collected and washed with absolute benzene to give carbomethylthiomethyltriphenylphosphonium chloride; yield: 5.0g (96%). Evaporation of the combined benzene solution gave a solid which was recrystallized from methanol to give 3a; yield 6.5g (97%); mp 129-130°C; IR (KCl): 1610 (s) 1550(s) cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.05(s,3H); 7.45-7.95(m, 15H); ^{19}F NMR ($CDCl_3$): δ 4.0 (t, 3F, J=2Hz), 37.0(q,2F,J=2Hz) ppm. Analysis: Calcd for $C_{24}H_{18}F_5O_2PS$:C, 58.07, H, 3.66: Found: C, 58.47, H, 3.41.

Similar procedures were used to obtain the following products:

3b: 90% yield; mp 135-136°C; IR(KCl): 1630(s) 1550(s) cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.05(s,3H); 7.40-7.90 (m, 15H); ^{19}F NMR ($CDCl_3$): δ 5.0(t,3F, J=9Hz), 26.1-26.7(m, 2F), 51.0(t, 2F, J=4Hz) ppm; MS m/e 546(M^+), 499(M^+-SCH_3), 262[$(C_6H_5)_3P^+$]. Analysis: Calcd for $C_{28}H_{18}F_7O_2PS$: C, 54.95, H, 3.32; Found: C, 54.89, H, 3.24.

3c: 80% yield; mp 100-101°C; IR(KCl): 1650(s), 1560(s) cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.00 (s, 3H), 7.25-7.85 (m, 15H); ^{19}F NMR ($CDCl_3$): δ 2.9(t,3F, J=7Hz); 32.2-34.4(m,2F); 41.2-45.2(m,8F), 47.2-49.0 (m, 2F) ppm; MS m/e 746(M^+), 699 (M^+-SCH_3), 262 [$(C_6H_5)_3P^+$]. Analysis: Calcd for $C_{29}H_{18}F_{15}O_2PS$: C, 46.66, H, 2.43; Found: C, 46.57, H, 2.67.

3d: 90% yield; mp 151-152°C; IR (KCl): 1640(s), 1560(s) cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 1.98(s,3H), 7.38-7.78(m,15H); ^{19}F NMR (CDCl$_3$): δ -11.5(t,2F, J=14Hz), 32.3(t,2F, J=14Hz), 40.1-40.7(m,2F) ppm MS m/e 562(M$^+$), 515(M$^+$-SCH$_3$), 262[(C$_6$H$_5$)$_3$P$^+$]; Analysis: Calcd for $C_{25}H_{18}F_6ClO_2PS$: C,53.35, H,3.22; Found: C, 53.38, H, 3.33.

3e: 91% yield; mp 144-145°C; IR (KCl): 1650(s), 1560(s) cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 2.00(s,3H), 7.27-7.83(m,15H): ^{19}F NMR (CDCl$_3$): δ -10.7(t,2F, J=12Hz), 32.1-33.7(m,2F), 41.7-43.3(m,6F) ppm; MS m/e 662(M$^+$), 615(M$^+$-SCH$_3$), 262[(C6H5)3P$^+$]; Analysis: Calcd for $C_{27}H_{18}F_{10}ClO_2PS$: C, 48.92, H, 2.74; Found: C, 48.98, H, 2.84.

3f: 81% yield; mp 113-114°C; IR (KCl): 1650(s), 1570(s) cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 1.95(s,3H), 7.15-7.85(m,15H); ^{19}F NMR (CDCl$_3$): δ 2.5(t,3F,J=2Hz), 2.8(d,3F,J=2Hz), 3.6(AB,2F), 47.3-48.6(m,1F), 51.7(br.s,2F) ppm; MS m/e 662(M$^+$), 615(M$^+$-SCH$_3$), 262[(C$_6$H$_5$)$_3$P$^+$]; Analysis: Calcd for $C_{27}H_{18}F_{11}O_3PS$: C, 48.95, H,2.74; Found: C, 48.72, H, 2.73.

Preparation of methyl pentafluorothiopent-2-ynoate (**4**a)

After heating at 70°C under nitrogen for 2 h, **3**a (3.0g, 6 mmol) was pyrolyzed under N$_2$ at reduced pressure (190-220°C/1 mmHg) and the pyrolysate collected in Dry Ice/ethanol trap was redistilled to give **4**a; yield: 1.2g (92%); bp 122°C; IR (film): 2200(w), 1650(s) cm^{-1}; ^{1}H NMR δ (CDCl$_3$): 2.10(s); ^{19}F NMR (CDCl$_3$): δ 9.7(t, 3F, J=4Hz), 28.6(q,2F,J=4Hz) ppm; MS m/e 218(M$^+$), 171(M$^+$-SCH$_3$), 143[M$^+$-C(O)SCH$_3$]; Analysis: Calcd for $C_6H_3F_5OS$: C, 33.04, H,1.39; Found: C, 33.22, H, 1.46.

Similar procedures were used to obtain the following products:

4b: 95% yield; bp 139°C; IR (film): 2200(w), 1620(s) cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.10(s); ^{19}F NMR ($CDCl_3$): δ 3.0(t,3F,J=10Hz), 34.7(q,2F, J=10Hz), 47.1(br.s, 2F) ppm; MS m/e 268(M^+), 221 (M^+-SCH_3), 193[M^+-C(O)SCH_3]; Analysis: Calcd for $C_7H_3F_7OS$: C, 31.36, H, 1.13; Found: C, 31.31, H, 1.17.

4c: 93% yield; bp 202°C; IR (film): 2260(w), 1660(s) cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.45(s); ^{19}F NMR ($CDCl_3$): δ 4.2(t,3F,J=9Hz), 23.1-24.2(m,2F); 42.6-46.8(m,8F), 48.7-49.9(m,2F) ppm; MS m/e 468(M^+), 453(M^+-CH_3), 421(M^+-SCH_3); Analysis: Calcd for $C_{11}H_3F_{15}OS$: C, 28.22, H, 0.65; Found: C, 27.88, H, 0.59.

4d: 95% yield; bp 168°C; IR (film): 2250(w), 1660(s) cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.20(s); ^{19}F NMR ($CDCl_3$): δ -10.3(t,2F,J=12Hz), 21.7-22.9(m,2F); 43.0-44.0(m,2F) ppm MS m/e 284(M^+), 269(M^+-CH_3), 237(M^+-SCH_3); Analysis: Calcd for $C_7H_3F_6ClOS$: C, 29.54, H, 1.06; Found: C, 29.56, H, 1.12.

4e: 90% yield; bp 198°C, IR (film): 2250(w), 1660(s) cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.13(s); ^{19}F NMR ($CDCl_3$): δ -9.3(t,2F,J=12Hz), 22.8-24.0(m,2F), 42.8-44.0(m,6F) ppm; MS m/e 384(M^+), 369 (M^+-CH_3), 337(M^+-SCH_3); Analysis: Calcd for $C_9H_3F_{10}ClOS$: C, 28.11, H, 0.79; Found: C, 27.66, H, 0.78.

4f: 94% yield; bp 172°C; IR (film): 2250(w), 1660(s) cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.53(s); ^{19}F NMR ($CDCl_3$): δ 5.1(t,3F,J=6Hz), 8.0(d,2F,J=5Hz), 6.4(AB,2F), 30.8-32.0(m,1F); 53.5(br.s, 2F) ppm; MS m/e 384(M^+), 337(M^+-SCH_3), 99(M^+-n-$C_3F_7O\underset{CF_3}{\underset{|}{C}}F$)

Analysis: Calcd for $C_9H_3F_{11}O_2S$: C, 28.14,H, 0.79; Found: C, 28.11, H, 0.64.

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This paper is the 45th report on studies of the application of elemento-organic compounds of the fifth and sixth groups in organic synthesis.

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