Synthesis of 1-Aryloxyperfluoro-1-alkynes[1]

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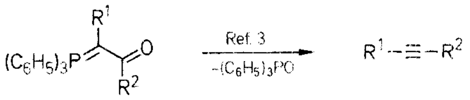
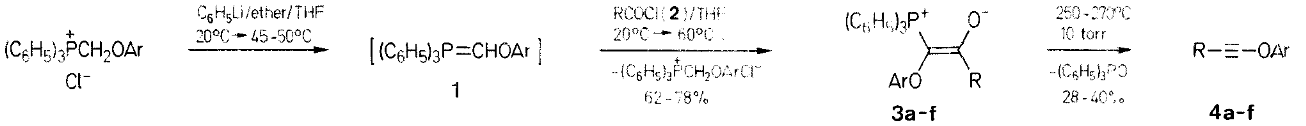
1-Aryloxyperfluoro-1-alkynes, a kind of "push-pull" acetylenes, are conveniently synthesized by intramolecular Wittig reaction.

Fluorinated acetylenic compounds are valuable starting materials for the synthesis of various other fluorinated compounds; for example, they are good dipolarophiles and dienophiles.[2] Thus the preparation of 1-aryloxyperfluoro-1-alkynes, a kind of "push-pull" acetylenes, is of interest. The Wittig reaction applied to carboxylic acid chlorides has proven useful for the preparation of alkynes.[3]



However, it is limited to cases where R^1 is an electron-withdrawing group, such as an ester, cyano, or aryl group.[4] This reaction has been extended to the synthesis of thioacetylenes,[4] arylselenoacetylenes,[5] and diphenoxyphosphonylacetylenes,[6] and also to the synthesis of aliphatic non-terminal and terminal acetylenes but flash vacuum pyrolysis had to be used in the latter case.[7]

We report here that the synthesis of alkynes via the Wittig reaction can also be applied to alkynes having a non-electron-withdrawing group and that this method can be extended to the synthesis of "push-pull" perfluoroalkynes. The reaction sequen-



3, 4	Ar	R
a	C_6H_5	C_2F_5
b	C_6H_5	$n{-}C_3F_7$
c	C_6H_5	$n{-}C_3F_7OCF(CF_3)-$
d	$4{-}ClC_6H_4$	C_2F_5
e	$4{-}ClC_6H_4$	$n{-}C_3F_7$
f	$4{-}ClC_6H_4$	$n{-}C_3F_7OCF(CF_3)-$

ce is as follows: Aryloxymethylenetriphenylphosphoranes **1**[8] are generated from aryloxymethyltriphenylphosphonium chlorides and phenyllithium in ether and are acylated by the addition of a perfluoroacyl chloride[9] **2** to give the corresponding 1-aryloxy-2-oxoperfluoroalkylidenetriphenylphosphorane **3** in 62–78% yields. Compounds **3** are isolated and submitted to vacuum pyrolysis to afford the expected 1-aryloxyperfluoro-1-alkynes **4** in 28–40% yields.

Table 1. 1-Aryloxy-2-oxoperfluoroalkylidenetriphenylphosphoranes **3** Prepared

Product	Yield (%)	m.p. (°C)	Molecular Formula[a]	MS[b] m/e	IR (KBr)[c] ν (cm⁻¹)	¹H-NMR[d] ($CDCl_3/TMS_{int}$) δ (ppm)	¹⁹F-NMR[d] ($CDCl_3/CF_3CO_2H_{ext}$) δ (ppm)
3a	74	146	$C_{28}H_{20}F_5O_2P$ (514.4)	514 (M^+), 437, 183	1580 (s), 1560 (s), 1210 (s)	7.01–8.05 (m, 15H); 6.62–7.13 (m, 5H)	3.0 (t, 3F, J = 1.3 Hz); 41.5 (q, 2F, J = 1.3 Hz)
3b	72	160	$C_{29}H_{20}F_7O_2P$ (564.4)	564 (M^+), 487, 183	1580 (s), 1570 (s), 1210 (s)	7.20–7.81 (m, 15H); 6.63–7.12 (m, 5H)	2.8 (t, 3F, J = 10 Hz); 39.0–40.2 (m, 2F); 48.3 (br.s, 2F)
3c	62	91	$C_{31}H_{20}F_{11}O_3P$ (680.5)	680 (M^+), 603, 183	1580 (s), 1560 (s), 1240 (s)	7.23–7.87 (m, 15H); 6.68–7.12 (m, 5H)	2.7 (t, 3F, J = 2 Hz); 3.0 (d, 2F, J = 2 Hz); 4.1 (AB, 2F); 49.5–51.6 (m, 1F); 54.6 (br.s, 2F)
3d	72	185	$C_{28}H_{19}ClF_5O_2P$ (548.9)	548 (M^+), 437, 183	1580 (s), 1570 (s), 1210 (s)	7.22–7.93 (m, 15H); 6.62–7.27 (m, 4H)	3.1 (t, 3F, J = 2 Hz); 40.9 (q, 2F, J = 2 Hz
3e	78	165	$C_{29}H_{19}ClF_7O_2P$ (598.9)	598 (M^+) 487, 183	1580 (s), 1560 (s), 1220 (s)	7.24–7.95 (m, 15H); 6.61–7.23 (m, 4H)	2.1 (t, 3F, J = 10 Hz); 38.1–39.2 (m, 2F); 47.6 (br.s, 2F)
3f	65	122	$C_{31}H_{19}ClF_{11}O_3P$ (714.9)	714 (M^+), 603, 183	1580 (s), 1560 (s), 1220 (s)	7.23–7.82 (m, 15H); 6.63–7.09 (m, 4H)	2.8 (t, 3F, J = 2 Hz); 3.1 (d, 2F, J = 2 Hz); 4.3 (AB, 2F) 50.1–51.4 (m, 1F); 55.0 (br. s, 2F)

[a] Satisfactory microanalyses obtained: C ± 0.31, H ± 0.15.
[b] The mass spectra were taken on a Finnigan 4021 spectrometer.
[c] The IR spectra were recorded on a Schmadzu IR-440 spectrometer.
[d] The NMR spectra were recorded with a Varian EM-360 spectrometer.

Table 2. 1-Aryloxyperfluoro-1-alkynes **4** Prepared

Product	Yield (%)	b.p. (°C/torr)	Molecular Formula[a]	MS[b] m/e	IR (film)[c] ν (cm⁻¹)	¹H-NMR[d] ($CDCl_3/TMS_{int}$) δ (ppm)	¹⁹F-NMR[d] ($CDCl_3/CF_3CO_2H_{ext}$) δ (ppm)
4a	28	166	$C_{10}H_5F_5O$ (236.1)	236 (M^+) 217, 77	2290 (w), 1590 (s), 1220 (s)	6.40–7.35 (m)	9.0 (t, 3F, J = 4 Hz); 21.4 (q, 2F, J = 4 Hz)
4b	35	40/2	$C_{11}H_5F_7O$ (286.2)	286 (M^+) 267, 77	2290 (w), 1600 (s), 1220 (s)	6.62–7.37 (m)	3.0 (t, 3F, J = 10 Hz); 17.1–18.3 (m, 2F); 49.1 (t, 2F, J = 4 Hz)
4c	38	78/2	$C_{13}H_5F_{11}O_2$ (402.2)	402 (M^+) 383, 333	2280 (w), 1600 (s), 1230 (s)	6.70–7.30 (m)	4.8 (t, 3F, J = 6 Hz); 7.3 (AB, 2F); 8.7 (d, 3F, J = 5 Hz); 23.2–24.6 (m, 1F); 52.1–52.9 (m, 2F)
4d	31	185 (dec.)	$C_{10}H_4ClF_5O$ (270.6)	270 (M^+), 251, 111	2260 (w), 1590 (s), 1220 (s)	6.80–7.41 (m)	8.0 (t, 3F, J = 4 Hz); 21.6 (q, 2F, J = 4 Hz);
4e	36	63/2	$C_{11}H_4ClF_7O$ (320.6)	320 (M^+), 301, 111	2260 (w), 1590 (s), 1220 (s)	6.72–7.30 (m)	2.6 (t, 3F, J = 9 Hz); 16.8–17.9 (m, 2F); 48.2 (t, J = 5 Hz)
4f	40	91/2	$C_{13}H_4ClF_{11}O_2$ (436.6)	436 (M^+) 417, 111	2290 (w), 1590 (s), 1230 (s)	6.69–7.32 (m)	4.5 (t, 3f, J = 7 Hz); 7.0 (AB, 2F); 8.3 (d, 3F, J = 6 Hz); 23.4–24.9 (m, 1F); 51.8–53.3 (m, 2F)

[a] Satisfactory microanalyses obtained: C ± 0.38; H ± 0.28, except for **4d** (C − 0.50).
[b, c, d] see Table 1.

All Products were characterized by microanalyses, IR, NMR, and mass spectroscopy.

The yields of "push-pull" perfluoroalkynes **4** are lower (28–40%) than those of 1-alkynes bearing an electron-withdrawing group;[4,6] nevertheless, the present reaction represents a new entry to 1-alkynyl ethers.[10]

1-Aryloxy-2-oxoperfluoroalkylidenetriphenylphosphoranes 3; General Procedure:

Phenyllithium (12 mmol) in absolute ether (25 ml) is added dropwise, over 30 min, to a stirred suspension of a 1-aryloxymethylenetriphenylphosphonium chloride[8] (12 mmol) in dry tetrahydrofuran (30 ml) at 20 °C under nitrogen. The mixture is heated at 45–50 °C, stirred for 30 min, then cooled to 20 °C. A slight excess of perfluoroacyl chloride[9] or perfluoroalkanoic anhydride[11] (6.6 mmol) in tetrahydrofuran (5 ml) is added. The resulting mixture is stirred for 1 h, heated to 60 °C, stirred for a further 30 min, cooled to 20 °C, and allowed to stand overnight. The mixture is filtered, the filtrate is evaporated, and the residue is purified by column chromatography on silica gel [elution with petroleum ether (b.p. 30–60 °C)/ethyl acetate (95:5)] or recrystallized from methanol/water (9:1).

1-Aryloxyperfluoro-1-alkynes 4; General Procedure:

The temperature of a silicone oil bath is maintained at 250–270 °C, the phosphorane **3** (1.6 mmol), admixed with pumice stone (~ 80 mg), is placed in the bath, and the pyrolysis is performed under nitrogen at reduced pressure (10 torr). The pyrolysate is collected in traps cooled with Dry Ice/ethanol and purified by column chromatography on silica gel (elution with petroleum ether) to give product **4**.

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(1) This paper is the 51st report on our studies of the application of elementoorganic compounds of the fifth and sixth groups to organic synthesis.
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