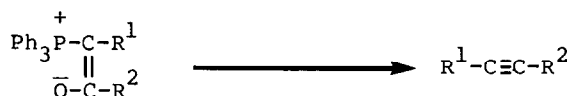


SYNTHESIS OF 1-PERFLUOROALKYNYL PHOSPHONATES¹

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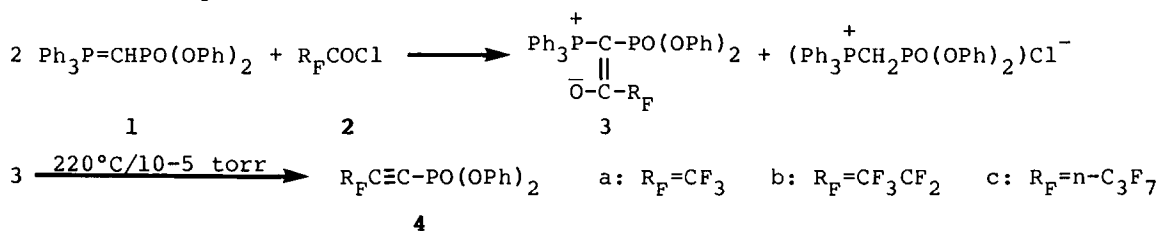
Summary. Intramolecular Wittig reaction is extended to the synthesis of 1-perfluoroalkynyl phosphonates.

An intramolecular Wittig reaction is a useful method for the synthesis of acetylenes especially fluorinated species².



However, this reaction is limited to the cases where R¹ is CO₂R, CN or Ar³. When R¹ is hydrogen or an alkyl group no acetylene results. Recently, Comasseto et al extended the intramolecular Wittig reaction to the synthesis of thioacetylenes³ and arylselenoacetylenes⁴.

In this paper we report that the intramolecular Wittig reaction can be applied to the synthesis of 1-perfluoroalkynyl phosphonates. The synthesis of alkynyl phosphonates has been reported, some involved the preparation of explosive alkynyl bromides⁵, others gave low yields⁶, or alkynyl magnesium bromides had to be used⁷, but no perfluoroalkynyl phosphonates have been prepared previously. In view of the biological activity of some phosphonic acids and their derivatives⁸, the preparation of these compounds is of interest which are found to be a good dipolarophile and a useful species for the synthesis of fluorinated heterocyclic phosphonates⁹. The reaction sequence is as follows:



In a general experiment, an excess of perfluoroacetyl chlorides (2, 2 mmol) is bubbled into a solution of diphenoxyphosphorylmethylenetriphenylphosphorane (1, 1 mmol) in absolute benzene (10 ml) while the reaction mixture is maintained at 50°C under nitrogen. After stirring of the mixture at 50°C for one hour, the precipitate formed is filtered and the solvent evaporated. The residue is purified by column chromatography on silica gel eluting with 1:1 petroleum ether (b.p. 60-90°C)/dichloromethane to give perfluoroacyldiphenoxyphosphorylmethylenetriphenylphosphorane (3). 3 (0.8 mmol) admixed with boiling stone is pyrolyzed under nitrogen at reduced pressure (220°C/10⁻⁵ torr) and the pyrolyzate collected in Dry Ice/ethanol

trap is redistilled to give diphenyl perfluoroalkynyl phosphonates (4).

The results are summarized in Table 1. All products are characterized by microanalyses, IR, NMR and mass spectroscopy. Thus, the scope of application of intramolecular Wittig reaction is extended and this methodology provides a convenient synthesis of the title compounds.

Table 1. Yields and Physical Constant of 3 and 4

Compound	Yield (%)	m.p.(°C) or b.p.(°C/torr)	MS (m/e)	IR ν (cm ⁻¹)	¹ H-NMR ^a δ (ppm)	¹⁹ F-NMR ^a δ (ppm)
3a	80	209-210	604, 535, 277, 77.	1560(s), 1270(s), 1150(s), 1040(m).	6.80-7.75(m)	-5.3(s)
3b	60	178-179	654, 535, 277, 77.	1570(s), 1280(s), 1150(s), 1020(m).	6.79-7.90(m)	1.5(s,3F); 36.0(s,2F).
3c	98	170-171	705, 535, 277, 77.	1570(s), 1280(s), 1160(s), 1060(m).	6.85-7.90(m)	1.0(t,3F,J=8Hz); 33.0(q,2F,J=8Hz); 45.0(s,2F)
4a	84	80/0.2	326, 257, 94, 77.	2240(w), 1260(s), 1160(s), 1020(m).	6.50-6.98(m)	-25.0(s)
4b	78	96/0.2	376, 257, 94, 77.	2230(w), 1220(s), 1160(s), 1020(m).	6.98-7.36(m)	6.5(s,3F) 26.8(s,2F).
4c	85	109/0.2	426, 257, 94, 77.	2240(w), 1240(s), 1180(s), 1020(m).	6.48-6.82(m)	3.0(t,3F,J=8Hz); 24.7(m,2F); 49.2(t,2F,J=3Hz).

^aCDCl₃ was used as solvent. For ¹⁹F-NMR TFA was used as external reference, and for ¹H-NMR TMS was used as internal reference.

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References and Notes

1. This paper is the 39th report on the studies of the application of elemento-organic compounds of the fifth and sixth groups in organic synthesis.
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