SYNTHESIS OF PERFLUORO-2-ALKYNENITRILES¹

Yaozeng Huang (Y.Z.Huang)², Yanchang Shen, Weiyu Ding³ and Jianhua Zheng Shanghai Institute of Organic Chemistry, Academia Sinica 345 Lingling Lu, Shanghai, China

Summary. Intramolecular Wittig reaction has been applied to the synthesis of perfluoro-2alkynenitriles (4a, b, c).

Perfluoroacetylenes and their polymers have been found to possess unique properties.⁴ Bieri et al.⁵ reported that perfluoro-2-butynenitrile (4a) was obtained from perfluoropyridine by plasma reaction in 0.1% yield. Just as the intramolecular Wittig reaction has been applied to the syntheses of perfluoroalkylactylenic acid esters⁶, the trifluoro-2-butynenitrile (4a), perfluoro-2-pentynenitrile (4b) and perfluoro-2-hexynenitrile (4c) were also successfully synthesized by the following sequence of reactions.

$$Ph_{3}P=CHCN + R_{F}COC1 \longrightarrow Ph_{3}P-CH-CN \qquad Ph_{3}P-CHCN \qquad [Ph_{3}P-CH_{2}CN]C1 + Ph_{3}P=C-CN \qquad (Ph_{3}P-CH_{2}CN]C1 + Ph_{3}P=C-CN \qquad (Ph_{3}P-CH_{2}CN]C1 + Ph_{3}P=C-CN \qquad (Ph_{3}P-CH_{2}CN]C1 + (Ph_{3}P-CH_{2}CN]C1 + (Ph_{3}P-CH_{2}CN)C1 \qquad (Ph_{3}P-CH_{2}CN]C1 + (Ph_{3}P-CH_{2}CN)C1 \qquad (Ph_{3}P-$$

In a typical experiment, the heptafluoro-n-butryl chloride (2c) (4.7 g, 20 mmol) was added slowly to a lukewarm solution of cyanomethylene triphenylphosphorane (1) (12.0 g, 40 mmol) in benzene (360 ml) under stirring. The mixture was stirred at room temperature for 2 hr, and 80° for 1 hr. After cooling, the white ppt. (6.0 g) of cyanomethyl triphenylphosphonium chloride was collected, washed three times with 20 ml. portions of benzene and recrystallized from methanol-ether, mp. 234-244°. Evaporation of the combined benzene solution gave a yellowish solid which was recrystallized from methanol to furnish heptafluoro-n-butyryl cyanomethylene triphenylphosphorane (3c) (9.0 g).

The above product was heated $(220-240^{\circ}/10 \text{ mmHg})$ for 40 min. under N₂ and the pyrolyzate collected in solid CO₂-alcohol traps was redistilled and identified as heptafluoro-2-hexynenitrile (4c).

The yields and physical constants are shown in the Table.

Compound	Yield %	Мр ([°] С)	MS -	Nucleus	<u>NMR</u> ** δ(ppm)	J(Hz)	— IR(cm ⁻¹)
(3a)	85	187–188	397, 328, 183, 77	19 _F 1 _H	-3.7(s) 7.52-7.60(m)		2200(s), 1618(s), 1130(s), 1200(s)
(3b)	82	151-152	447, 328, 183, 77	19 _F 1 _H	4.5(t) (3F) 40.2(q) (2F) 7.60-7.70(m)	J, 1.2	2200(s), 1610(s), 1140(s), 1210(s)
(3c)	90	164-165	497, 328, 183, 77	19 _F 1 _H	$37.6(q) (COCF_{2})$ $47.4(s) (CF_{2}CF_{3})$ $3.0(t) (\overline{CF_{2}CF_{3}})$ $7.55-7.69(m)$	⁴ J, 7.5	2200(s), 1608(s), 1100(s), 1200(s)
Compound	Yield %	Bp (°C)	MS	1 δ(ppm)	9 _{F NMR} J(Hz)	- IR(cm ⁻¹)****	
(4a)	50	-6 ~-5	*** 119, 100	-21.3(s)			(s), 2175(s), 1936(w), (s), 1235(s)
(4b)	82	37-38	169, 150, 100, 69	9.7(t)(3F) 29.0(q)(2F)	J, 3.3		(s), 2175(s), 1960(w), (s), 1200(s)
(4c)	80	57.5-58	219, 200, 100, 69	5.0(t)(CF_3 50.0(t)($\overline{CF_3}$ 26.3(tq)(CF	(CF_2) $^3J_{CF_2CF_2}$		(s), 2180(s), 1960(w), (s), 1200(s)

Table: Yields and Physical Constants of (3) and (4)

* All elemental analyses were consistent with the calculated values.

** For¹⁹F NMR, TFA was used as external reference, and for ¹H NMR, TMS was used as internal reference.

*** MS date were obtained by chemical ionization method.

**** Gas sample.

References and Notes

- 1. This paper is the 20th report on the studies of the application of elemento-organic compounds of the fifth and sixth groups in organic syntheses.
- 2. Formerly spelled as Yao-Tseng Huang.
- 3. Department of Chemistry, Shanghai University of Science and Technology, Shanghai, China.
- 4. H. C. Brown and H. L. Gewanter, J. Org. Chem., <u>25</u>, 2071 (1960);
- H. C. Brown, H. L. Gewanter, D. M. White and W. G. Woods, ibid, <u>25</u>, 634 (1960); J. F. Harris, R. J. Harder Jr. and G. N. Sausen, ibid, <u>25</u>, 633 (1960); Huang Yaozeng, Tao Wentian, Chen Jinghong, Li Jisen, Zhou Jianqiang and Wu Longdi, Gaofenzi Tongxun (Polymer Communication) 1981, 130.
- 5. G. Bieri, J. P. Stadelmann, F. Thommen and J. Vogt, Helv. Chim Acta, 61, 357 (1978).
- 6. Huang Yao-Tseng, Shen Yen-Chang, Chen Kuo-Tun and Wang Cho-Ching, Acta Chimica Sinica, <u>37</u>, 47 (1979); Huang Yaozeng, Shen Yanchang, Xin Yuankang, Wang Qiwen and Wu Wenchao, Scientia Sinica (Chinese Ed.) 1981, 973; ibid. (English Ed.), in press.