Heteroatom Chemistry
Volume 8, Number 1, 1997

1,1,3,3,3-Pentafluoro-2-pentafluorophenylpropene Oxide. Precursor for Novel Phosphonates and Ylides

Alexander A. Kadyrov*

A. N. Nesmeyanov Institute of Organo-Element Compounds, Russian Academy of Sciences, 28 Vavilova, 117813 Moscow, Russia

Gerd-Volker Röschenthaler*

Institut für Anorganische und Physikalische Chemie, Universität Bremen, Leobener Strasse, D-28334 Bremen, Germany

Received 3 June 1996

ABSTRACT

1,1,3,3,3-Pentafluoro-2-pentafluorophenylpropene oxide reacted with triethyl phosphite to give the ylide $C_6F_5(CF_3)C{=}P(OEt)_3$. *Hydrolysis yielded the phosphonate* $C_6F_5(CF_3)CHP(O)(OEt)_2$, *which was dehydrofluorinated using* $Et_3N\cdot BF_3$ *to form the vinyl phosphonate* $C_6F_5(CF_2{=})CP(O)(OEt)_2$, *a compound available also directly from the starting epoxide and diethyl trimethylsilyl phosphite. The vinyl phosphonate and diethyl trimethylsilyl phosphite furnished a 2:1 mixture of (Z) and (E) bisphosphonates together with fluorotrimethylsilane. Thermolylsis of the ylide gave diethyl phosphorofluoridate and 1,1-difluoro-2-pentafluorophenyl-but-1-ene.*

INTRODUCTION

Epoxides of a few terminal perfluoroolefins $CF_3(R^1)C{=}CF_2$ [R^1 = CF_3, C(O)OEt, $P(O)(OMe)_2$] reacted with trialkyl phosphites $P(OR^2)_3$ (R^2 = Me, Et) under C–C and C–O bond cleavage to give the ylides $CF_3(R^1)C{=}P(OR^2)_3$ and decomposition products of the thermally unstable phosphorane intermediate $FC(O)P(F)(OR^2)_3$, namely, difluorophosphoranes $F_2P(OR^2)_3$ and carbon monoxide [1]. Diethyl trimethylsilyl phosphite, $Me_3SiOP(OEt)_2$, and perfluoroisobutene oxide gave fluorotrimethylsilane, the fluorophosphate $FP(O)(OEt)_2$, and the perfluorovinyl phosphonate $CF_2{=}C(CF_3)P(O)(OEt)_2$, which could be prepared by different routes [2,3]. Dimeric hexafluorothioacetone and triethyl phosphite gave the ylide $(CF_3)_2C{=}P(OEt)_3$ [4], which was hydrolyzed to furnish $(CF_3)_2CHP(O)(OEt)_2$ [4] and dehydrofluorinated using $Et_3N\cdot BF_3$ to form $CF_2{=}C(CF_3)$-$P(O)(OEt)_2$ [2]. We report here the reactions of the title compound with triethyl and diethyl trimethylsilyl phosphite.

RESULTS AND DISCUSSION

On reaction of 1,1,3,3,3-pentafluoro-2-pentafluorophenyl-propene oxide [6] (**1**) with triethyl phosphite in a 1:2 ratio, the ylide **2** is formed as a colorless liquid besides carbon monoxide, triethoxydifluorophosphorane [8], and diethyl phosphorofluoridate. Hydrolysis using concentrated hydrogen chloride afforded phosphonate **4**, which could be dehydrofluorinated by $Et_3N\cdot BF_3$ to furnish vinylphosphonate **5**.

---

*To whom correspondence should be addressed.

1042-7163/97/010059-03

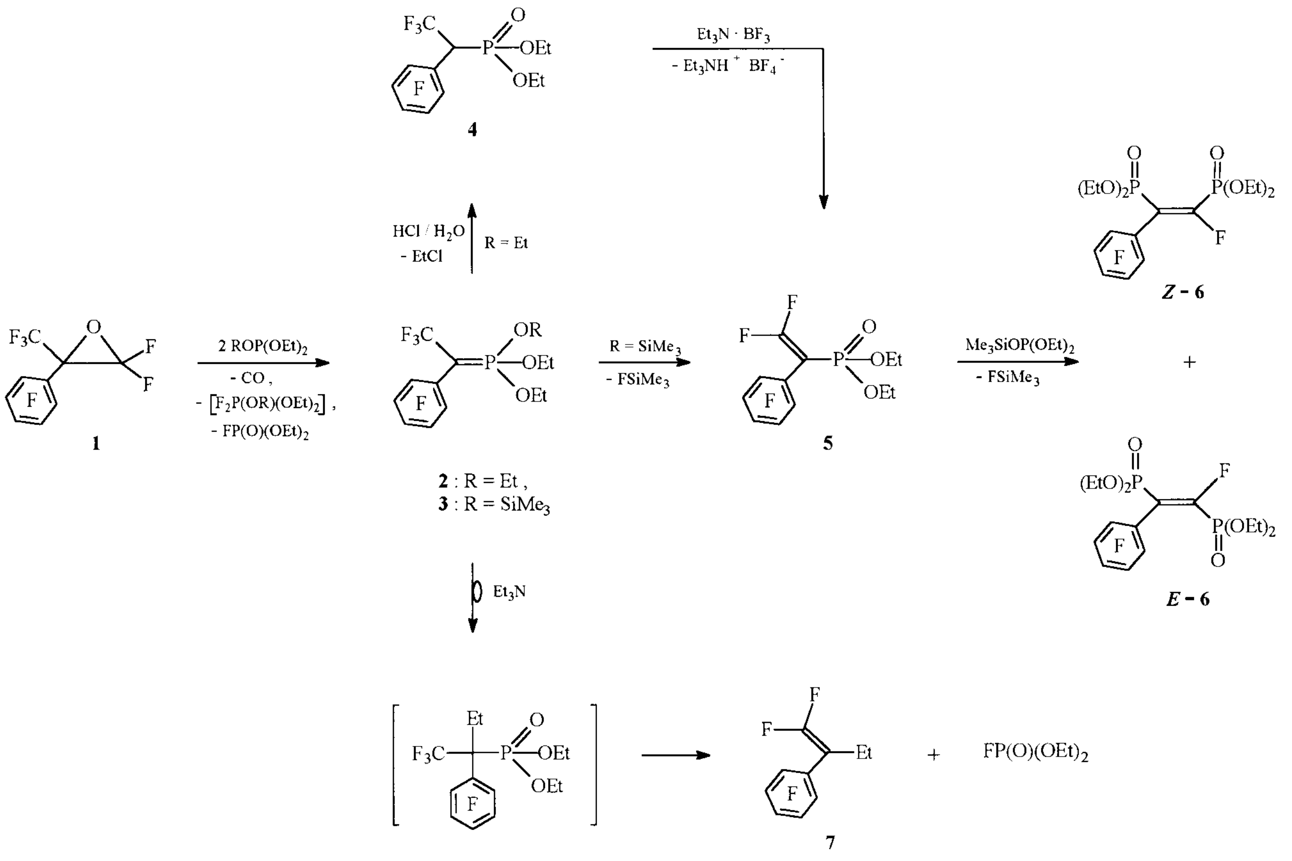
The latter compound was also obtained when epoxide **1** was reacted with diethyl trimethylsilyl phosphite. In this case, fluorotrimethylsilane, diethyl phosphorofluoridate, and carbon monoxide were observed. The ^{31}P-NMR spectrum of the reaction mixture showed a signal at $\delta = 40.5$, characteristic for the ylide $CF_3(C_6F_5)C{=}P(OSiMe_3)(OEt)_2$, **3**, besides other signals. In a second step, diethyl trimethylsilyl phosphite and the vinylphosphonate **5** gave a 2:1 mixture of (*Z*) and (*E*) bisphosphonates **6**. On heating ylide **2** to 100°C in the presence of a catalytic amount of triethylamine, diethyl phosphorofluoridate and 1,1-difluoro-2-pentafluorophenyl-but-1-ene (**7**) were formed in low yield. (Butene **7** could be characterized by mass spectrometry only.) The O-ethyl group probably was transferred to the ylide carbon forming an intermediate, in which the P–C bond was cleaved. In the case of $(CF_3)_2C{=}P(OMe)_3$, a rearrangement took place to give the thermally stable phosphonate $(CF_3)_2CMeP(O)(OMe)_2$ [4]. All new compounds were colorless liquids (Scheme 1).

The NMR data of the ylide [1,4,9] and the phosphonates [1,2] were consistent with the constitution proposed. The larger $^3J_{PF}$ value of 28.1 Hz was assigned to the *trans* vinylic fluorine nuclei in phosphonate **5** as in $CF_2{=}C(CF_3)P(O)(OSiMe_3)_2$ [3]. The same assumption was made for bisphosphonate **6**, where the larger *trans* coupling constant ($^3J_{PF} = 40.9$ Hz) is due to the (*Z*) form.

EXPERIMENTAL

The appropriate precautions in handling moisture and oxygen-sensitive compounds were observed throughout this work. Elemental analysis: Mikroanalytisches Laboratorium Beller, Göttingen. MS: MAT 8222 (EI, electron energy 70 eV). NMR: AC 80, operating at 80.13 MHz (^{1}H, internal standard TMS), 75.39 MHz (^{19}F, internal standard CCl_3F), and 32.44 MHz (^{31}P, external standard 85% H_3PO_4). Compound **1** [6] and $Me_3SiOP(OEt)_2$ [7] were prepared according to literature procedures.

1-Pentafluorophenyl-2,2,2-trifluoroethylidene-triethoxyphosphorane (**2**). Triethyl phosphite (14.8 g, 89 mmol) and 14.0 g (44.5 mmol) of **1** were heated at 60°C for 20 hours. Distillation gave 11.5 g (62%) of **2** (bp 86–88°C/0.01 Torr). MS: *m/e* (%): 414 (M$^+$,



SCHEME 1

20), 395 ($M^+ - F$, 4), 369 ($M^+ - OC_2H_5$, 12), 341 ($M^+ - OC_2H_5 - C_2H_4$, 4), 338 ($M^+ - HF - 2\,C_2H_4$, 6), 331 ($M^+ - 2\,C_2H_4 - C_2H_3$, 14), 313 ($M^+ - 2\,C_2H_4 - OC_2H_5$, 25), 290 ($M^+ - CF_3 - C_2H_4 - C_2H_3$, 100), 230 ($C_3F_3P(O)(OC_2H_5)_2^+$, 14), 179 ($CF_3P(OH)_2(OC_2H_5)^+$, 14), 167 ($C_6F_5^+$, 1), 69 ($CF_3^+$, 2), and other fragments. NMR: ^{1}H: $\delta = 1.12$ (CH_3, t, $^3J_{HH} = 7.0$ Hz), 4.1 (CH_2, m); ^{19}F: $\delta = -47.0$ (CF_3, 3 F, dt, $^3J_{PF} = 8.3$, $^5J_{FF} = 5.5$ Hz), −141.8, −144.6 (F^1, F^2, m), −166.5 (F^5, m), −168.5, −171.0 (F^3, F^4, m); ^{31}P: $\delta = 41.2$. Anal. calcd for $C_{14}H_{15}F_8O_3P$ (414.23): C, 40.59; H, 3.65; F, 36.69; P, 7.48. Found: C, 40.10; H, 3.73; F, 36.70; P, 7.72.

1-Pentafluorophenyl-2,2,2-trifluoroethyl Diethyl Phosphonate (**4**). Conc. hydrochloric acid (5 mL) was added dropwise to 4.14 g (10 mmol) of phosphorane **2**, and the mixture was stirred for 3 hours. After three extractions with 10 mL of diethyl ether each time, distillation gave 3.44 g (89%) phosphonate **4** (bp 101–103°C/10 Torr). MS: *m*/*e* (%): 386 (M^+, 16), 367 ($M^+ - F$, 14), 340 ($M^+ - F - C_2H_3$, 22), 313 ($M^+ - OC_2H_5 - C_2H_4$, 10), 276 ($M^+ - CF_3 - C_2H_3 - CH_2$, 12), 230 ($C_3F_3P(O)(OC_2H_5)_2^+$, 100), 199 ($C_2F_2P(O)(OC_2H_5)_2^+$, 23), 109 ($C_2H_5OP(O)OH^+$, 81), 84 ($FP(OH)(O)H^+$, 56), and other fragments. NMR: ^{1}H: $\delta = 1.3$ (CH_3, 6 H, q, $^3J_{HH} = 7.2$ Hz), 3.9–4.4 (CH_2, AB-parts of 2 ABM_3X-systems, 4 H, and CH, 1 H); ^{19}F: $\delta = -65.3$ (CF_3, 3 F, dd, $^3J_{PF} = 17.5$, $^3J_{HF} = 7.8$ Hz), −138.5, −145.3 (F^1, F^2, m), −156.3 (F^5, m), −165.5 (F^3, F^4, m). ^{31}P: $\delta = 3.5$. Anal. calcd for $C_{12}H_{11}F_8O_3P$ (386.18): C, 37.32; H, 2.87; F, 39.36; P, 8.02. Found: C, 37.22; H, 3.03; F, 39.00; P, 7.54.

1-Pentafluorophenyl-2,2-difluoroethenyl Diethyl Phosphonate (**5**). Phosphonate **4** (3.50 g, 9 mmol) and 1.52 g (9 mmol) $Et_3N \cdot BF_3$ in 5 mL diethyl ether were refluxed for 5 hours. After filtration to remove $Et_3NH^+ \cdot BF_4^-$ distillation of the filtrate gave 2.80 g (80%) of **5** (bp 77–79°C/0.1 Torr). In a separate experiment, diethyl trimethylsilyl phosphite (4.20 g, 20 mmol) and 3.14 g (10 mmol) of **1** were stirred at ambient temperature for 3 hours. Distillation gave 3.11 g (85%) of **5**. MS: *m*/*e* (%): 366 (M^+, 51), 340 ($M^+ - C_2H_2$, 12), 338 ($M^+ - C_2H_4$, 7), 318 ($M^+ - C_2H_5 - F$, 38), 293 ($M^+ - OC_2H_5 - C_2H_4$, 7), 290 ($M^+ - CF_2 - C_2H_2$, 100), 199 ($M^+ - C_6F_5$, 7), 179 ($M^+ - C_6F_5 - HF$, 17), 109 ($C_2H_5OP(O)OH^+$, 9), 81 ($C_2F_3^+$, 13), and other fragments. ^{1}H: $\delta = 1.80$ (CH_3, 6 H, t, $^3J_{HH} = 6.9$ Hz), 4.69 (CH_2, 4 H, $^3J_{PH} = 7.1$ Hz); ^{19}F: $\delta = -68.1$ ($=CF_2$, *trans* to phosphorus, 1 F, dd, $^2J_{FF} = 12.2$, $^3J_{PF} = 28.1$ Hz), −69.2 ($=CF_2$, *cis* to phosphorus, 1 F, dd, $^3J_{PF} = 12.2$ Hz), −143.2, −144.0 (F^1, F^2, m), −159.2 (F^5, m), −168.6 (F^3, F^4, m); ^{31}P: $\delta = 7.9$. Anal. calcd for $C_{12}H_{10}F_7O_3P$ (366.17): C, 39.36; H, 2.75; F, 36.32; P, 8.46. Found: C, 39.30; H, 2.89; F, 36.50; P, 8.36.

(*Z*/*E*)*-1,2-bis*(*Diethylphosphonato*)*-1-fluoro-2-pentafluorophenylethene* (**Z/E-6**). Diethyl trimethylsilyl phosphite (0.40 g, 1.9 mmol) and 0.68 g (1.9 mmol) of **5** were allowed to react for 4 hours at 60°C. Distillation gave 0.70 g (78%) of **Z/E-6** (*Z*:*E* = 2:1) (bp 153–154°C/0.01 Torr). MS: *m*/*e* (%): 484 (M^+, 100), 439 ($M^+ - OC_2H_5$, 95), 347 ($M^+ - P(O)(OC_2H_5)_2$, 30), and other fragments. *Z*-isomer: ^{19}F: $\delta = -82.5$ ($=CF$, 1 F, ddt, $^2J_{PF} = 105.6$, $^3J_{PF} = 40.9$, $^5J_{FF} = 4.7$ Hz), −143.2 (F^1, F^2, m), 157.0 (F^5, m), 166.3 (F^3, F^4, m); ^{31}P: $\delta = -3.0$ ($PC(C_6F_5)$), 4.9 (PCF). *E*-isomer: $\delta = -91.3$ ($=CF$, 1 F, dd, $^2J_{PF} = 102.6$, $^3J_{PF} = 11.1$ Hz), −142.3, (F^1, F^2, m), −157.0 (F^5, m), −167.2 (F^3, F^4, m); Anal. calcd for $C_{16}H_{20}F_6O_6P_2$ (484.30): C, 39.68; H, 4.16; F, 23.54; P, 12.79. Found: C, 38.81; H, 4.01; F, 22.90; P, 11.57.

1,1-Difluoro-2-pentafluorophenyl-but-1-ene (**7**). Compound **1** (0.62 g, 2 mmol) was heated in the presence of 0.01 g Et_3N at 100°C for 1 hour. From GC/MS investigation, diethyl phosphorofluorodate and butene **7** could be detected. MS: *m*/*e* (%): 258 (M^+, 69), 243 ($M^+ - CH_3$, 100), 223 ($M^+ - CH_3 - HF$, 8), 193 ($M^+ - CH_3 - CF_2$, 48), 181 ($M^+ - C_2H_3 - CF_2$, 15), 143 ($C_4F_5^+$, 7), and other fragments.

ACKNOWLEDGMENT

The authors acknowledge gratefully the financial support by the Deutsche Forschungsgemeinschaft.

REFERENCES

[1] A. A. Kadyrov, G. G. Bargamov, E. M. Rokhlin, *J. Fluorine Chem., 65,* 1993, 195.
[2] A. A. Kadyrov, E. M. Rokhlin, *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1981, 2583.
[3] J. Heine, G.-V. Röschenthaler, *Chemiker-Ztg., 110,* 1986, 91.
[4] W. J. Middleton, W. H. Sharkey, *J. Org. Chem., 30,* 1965, 1384.
[5] A. A. Kadyrov, E. M. Rokhlin, *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1983, 1353.
[6] R. A. Bekker, G. V. Asratyan, B. I. Dyatkin, *Zh. Org. Chem., 9,* 1973, 1635.
[7] M. Sekine, K. Okimoto, K. Yamada, T. Hata, *J. Org. Chem., 46,* 1981, 2097.
[8] S. M. Williamson, O. D. Gupta, J. M. Shreeve, *Inorg. Synth., 24,* 1986, 62.
[9] O. I. Kolodyazhnyi, *Tetrahedron, 52,* 1996, 1855.