

Brief Communications

Reaction of salicyl phosphites with hexafluoroacetone imine

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Benzo-1,3,2-dioxaphosphorin-4-ones react with hexafluoroacetone imine to form 2-R-2,5-dioxo-3,3-bis(trifluoromethyl)-6,7-benzo-1,4,2-oxazaphosphhepanes.

Key words: 2-R-5,6-benzo-1,3,2-dioxaphosphorin-4-ones, 2-R-2,5-dioxo-3,3-bis(trifluoromethyl)-6,7-benzo-1,4,2-oxazaphosphhepanes, hexafluoroacetone imine.

Mixed esters-anhydrides of salicylic and phosphorous acids, the so-called salicyl phosphites, 2-R-5,6-benzo-1,3,2-dioxaphosphorin-4-ones, react readily with both electrophiles and nucleophiles and are used in the synthesis of various heterocycles.¹⁻³ Reactions with carbonyl compounds give 1,3,2-dioxaphosphhepanes^{4,5} and 1,4,2-dioxaphosphhepanes,⁶ while reactions with imines yield 1,4,2-oxazaphosphhepanes.⁷ At the first stage of reactions of salicyl phosphites with carbonyl compounds, nucleophilic attack of the P atom occurs on the carbonyl C atom, whereas the first stage of reactions with imines involves nucleophilic attack of the N atom of imine on the carbonyl group of salicyl phosphite.⁶

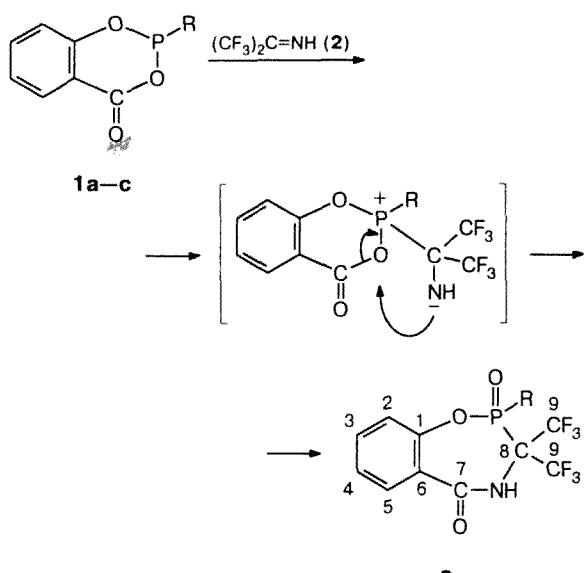
In the present work, it was demonstrated that the reactions of salicyl phosphites (**1a-c**) containing donor or acceptor substituents (R) at the P atom with

hexafluoroacetone imine (**2**), which contains a weakly nucleophilic nitrogen atom, occur through the attack of P on the imine C atom to form 2-R-2,5-dioxo-3,3-bis(trifluoromethyl)-6,7-benzo-1,4,2-oxazaphosphhepanes (**3a-c**) (Scheme 1).

The nucleophilic role of the P atom was confirmed by comparing the reactivities of salicyl phosphites **1a** and **1c**: the reaction of compound **1a** at 20 °C was completed in one day, whereas a mixture of phosphite **1c** with imine **2** remained unchanged for 2 months.

Our results differ from those observed in the reactions of salicyl phosphites with hexafluoroacetone, which gave 1,3,2-dioxaphosphhepanes.⁴ It should be also noted that trimethyl phosphite does not add to a derivative of compound **2**, hexafluoroacetone ethoxycarbonylimine, which only fluorinates this phosphite to form fluorophosphate.⁸

Scheme 1



R = OMe (1a, 3a); NEt₂ (1b, 3b); OCH₂CF₂CHF₂ (1c, 3c)

The structures of phosphepanes 3a-c were confirmed by the ¹H, ¹³C, ¹⁹F, and ³¹P NMR and IR spectral data. The compositions of these compounds were established by elemental analysis. The ¹³C NMR spectral data for compounds 3a-c are given in Table 1 from which it is evident that 1,4,2-oxazaphosphepanes containing the P—C—N fragment (¹J_{P,C} was 113, 138.7, and 141.7 Hz, respectively) formed.

Experimental

The ¹H, ¹³C-^{1}H, ¹⁹F, and ³¹P-^{1}H NMR spectra were recorded on a Varian Unity 300 instrument (300, 75.43, 282.2, and 121.42 MHz, respectively) in CDCl₃ (3a), a CDCl₃-DMF-d₇ mixture (1 : 1) (3b), and acetone-d₆. Me₄Si and CF₃CO₂H (inner capillary), and H₃PO₄ were used as standards. Chemical shifts δ_F were referenced to CFCl₃. The IR spectra were recorded on a Specord M-80 instrument (Nujol mulls).

2-Methoxy-2,5-dioxo-3,3-bis(trifluoromethyl)-6,7-benzo-1,4,2-oxazaphosphepane (3a). A mixture of hexafluoroacetone imine 2 (10 mmol) and CH₂Cl₂ (3 mL) was frozen in a tube at -100 °C, and then phosphite 1a (10 mmol) was added. The reaction mixture was kept in a sealed tube for 3 days (after one day, the reaction mixture crystallized out). The tube was

Table 1. Parameters of the ¹³C-^{1}H NMR spectra of compounds 3a-c*

Carbon atom	3a		3b		3c	
	δ_C	J/Hz	δ_C	J/Hz	δ_C	J/Hz
C(1)	146.74 d	7.5 (POC(1))	150.70 d	7.5 (POC)	144.48 d (m)	7.3 (POC)
C(2)	122.15 d	4.5 (POCC)	122.30 d	4.5 (POCC)	121.21 d (br.dd)	2.6 (POCC) 7.0-8.0 (HCCC) 166.8 (HC)
C(3)	135.77 s		134.11 s		134.89 s (dd)	8.5 (HCCC) 163.7 (HC)
C(4)	127.64 d	1.5 (POCCCC)	124.23 s		127.25 s (dd)	164.1 (HC) 7.0-7.5 (HCCC)
C(5)	133.11 s		132.34 s		131.50 s (dd)	7.5 (HC) 166.3 (HC)
C(6)	124.88 br.s	1.0-1.5 (POCC)	125.58 d	2.0 (POCC)	124.99 br.s (br.m)	
C(7)	167.24 br.s		168.42 s		165.63 s (br.s)	
C(8)	67.12 d.sept	138.7 (PC) 30.0 (FCC)	65.97 d.sept	113.0 (PC) 27.1 (FCC)	66.69 d.sept (d.sept)	141.3 (PC) 29.7 (FCC)
C(9)	122.32 qm	288.4 (FC) 2.0 (PCC) 1.8-2.0 (FCCC)	123.53 qm	287.0 (FC) 2.0-3.0 (PCC) 1.0-2.0 (FCCC)	121.41 q (q) 121.51 q (qd)	288.1 (FC) 288.0 (FC) 5.7 (PCC)
C(10)	57.01 d	7.0 (POC)	42.54 br.s		64.08 td (td)	155.0 (HC) 28.0 (FCC) 5.3-5.5 (POC)
C(11)			11.03 br.s		113.50 dttd (br.tt)	250.8 (FC) 27.6 (FCC) 6.8-7.0 (POCC)
C(12)					109.15 tt (tdt)	249.0 (FC(12)) 34.1 (FCC(12)) 196.3 (HC(12))

* OC(10)H₃ (3a), N(C(10)H₂C(11)H₃)₂ (3b), and OC(10)H₂C(11)F₂C(12)HF₂ (3c); for compound 3c, the types of signals in the ¹³C NMR spectrum are given in parentheses.

opened, and the content was diluted with a 1 : 1 ether-pentane mixture. The crystals were filtered off, washed with the same mixture, and dried *in vacuo*. The yield of phosphepane **3a** was 93%, m.p. 121–123 °C, δ_p 7.2 (br.s), δ_F –70.32 and –71.53 (2 br.q, $^4J_{F,F}$ = 11.3 Hz). 1H NMR, δ : 7.99 (dd, 1 H, H(5), $^3J_{H(4),H(5)}$ = 7.8 Hz, $^4J_{H(3),H(5)}$ = 1.7 Hz); 7.66 (dddd, 1 H, H(3), $^3J_{H(2),H(3)}$ = 8.0 Hz, $^3J_{H(3),H(4)}$ = 7.2 Hz, $^4J_{H(3),H(5)}$ = 1.7 Hz, $^5J_{H(3),P}$ = 0.7–0.8 Hz); 7.56 (br.d, 1 H, NH, $^3J_{PCNH}$ = 16.2 Hz); 7.44 (dddd, 1 H, H(4), $^3J_{H(4),H(5)}$ = 7.8 Hz, $^3J_{H(3),H(4)}$ = 7.2 Hz, $^4J_{H(2),H(4)}$ = 1.2 Hz, $^6J_{H(4),P}$ = 1.2 Hz); 7.28 (ddd, 1 H, H(2), $^3J_{H(2),H(3)}$ = 8.0 Hz, $^4J_{H(2),H(4)}$ = 1.2 Hz, $^4J_{H(2),P}$ = 1.0 Hz); 4.92 and 5.06 (both m, 2 H, OCH₂, ABM₂X spectrum, $^3J_{POCH}$ = 9.5 Hz, $^3J_{FCCH}$ = 13.0 Hz); 6.45 (tt, 1 H, $^2J_{FCCH}$ = 52.3 Hz, $^3J_{FCCH}$ = 4.6 Hz). IR, ν/cm^{-1} : 3240, 3150, 3100, 1680, 1625, 1590, 1560, 1520, 1490, 1475, 1390, 1325, 1310, 1270, 1215, 1185, 1175, 1165, 1160, 1115, 1100, 1065, 1035, 990, 960, 930, 870, 830, 800, 780, 760, 750, 720. Found (%): C, 33.74; H, 1.54; P, 6.78. $C_{11}H_8F_6NO_4P$. Calculated (%): C, 33.36; H, 1.73; P, 6.69.

2-Diethylamino-2,5-dioxo-3,3-bis(trifluoromethyl)-6,7-benzo-1,4,2-oxazaphosphepane (3b). The reaction was carried out analogously (12 mmol each of the initial compounds and 5 mL of CH₂Cl₂). The mixture was kept for 7 days, and then the yellowish liquid was diluted with a 4 : 1 ether-pentane mixture and kept at –5 °C for 3 days. A crystalline precipitate of phosphepane **3b** formed. This precipitate was filtered off and dried *in vacuo*. The filtrate was kept further under the same conditions, which made it possible to obtain three more portions of crystals of **3b**. The total yield was 43–47%, m.p. 159–160 °C, δ_p 1.7 (br.s), δ_F –68.56 (br.s, the half width of the signal was 5.6 Hz). 1H NMR, δ : 7.91 (br.dd, 1 H, H(5), $^3J_{H(4),H(5)}$ = 7.9 Hz, $^4J_{H(3),H(5)}$ = 1.6 Hz); 7.85 (br.d, 1 H, NH, $^3J_{PCNH}$ = 16.0 Hz); 7.46 (dddd, 1 H, H(3), $^3J_{H(2),H(3)}$ = 7.1 Hz, $^3J_{H(3),H(4)}$ = 7.3 Hz, $^4J_{H(3),H(5)}$ = 1.6 Hz, $^5J_{H(3),P}$ = 0.6–0.7 Hz); 7.15 (br.dd, 1 H, H(4), $^3J_{H(4),H(5)}$ = 7.9 Hz, $^3J_{H(3),H(4)}$ = 7.3 Hz); 7.04 (br.d, 1 H, H(2), $^3J_{H(2),H(3)}$ = 7.1 Hz); 2.73 (br.m, 4 H, NCH₂, $^3J_{H,H}$ = 7.2 Hz); 1.76 (br.t, 6 H, Me, $^3J_{H,H}$ = 7.2 Hz). IR, ν/cm^{-1} : 3210, 3120, 1618, 1580, 1485, 1465, 1290, 1258, 1240, 1220, 1180, 1170, 1150, 1110, 1090, 1072, 1048, 1021, 992, 970, 945, 920, 865, 811, 793, 770, 745, 720. Found (%): C, 41.84; H, 3.54; P, 7.59. $C_{14}H_{15}F_6N_2O_3P$. Calculated (%): C, 41.60; H, 3.74; P, 7.66.

2,5-Dioxo-2-(2,2,3,3-tetrafluoropropoxy)-3,3-bis(trifluoromethyl)-6,7-benzo-1,4,2-oxazaphosphepane (3c). The reaction of **1c** with **2** (31 mmol each of the initial reagents and 5 mL of CH₂Cl₂) was carried out in a sealed tube for 4 months. As a result, a crystalline precipitate was obtained. The tube was opened, and the content was diluted with a 4 : 1 ether-pentane mixture. The crystals were filtered off, washed with the same mixture, and dried *in vacuo*. The yield of phosphepane

3c was 82%, m.p. 52–54 °C, δ_p 7.45 (CD₃CN). 1H NMR, δ : 7.92 (dd, 1 H, H(5), $^3J_{H(4),H(5)}$ = 7.8 Hz, $^4J_{H(3),H(5)}$ = 1.5 Hz); 7.78 (dd, 1 H, H(3), $^3J_{H(2),H(3)}$ = 8.1 Hz, $^3J_{H(3),H(4)}$ = 7.3 Hz, $^4J_{H(3),H(5)}$ = 1.5 Hz, $^5J_{H(3),P}$ = 0.7–0.8 Hz); 7.56 (ddd, 1 H, H(4), $^3J_{H(4),H(5)}$ = 7.8 Hz, $^3J_{H(3),H(4)}$ = 7.3 Hz, $^4J_{H(2),H(4)}$ = 1.2 Hz); 7.42 (ddd, 1 H, H(2), $^3J_{H(2),H(3)}$ = 8.1 Hz, $^4J_{H(2),H(4)}$ = 1.2 Hz, $^4J_{H(2),P}$ = 1.0 Hz); 4.92 and 5.06 (both m, 2 H, OCH₂, ABM₂X spectrum, $^3J_{POCH}$ = 9.5 Hz, $^3J_{FCCH}$ = 13.0 Hz); 6.45 (tt, 1 H, $^2J_{FCCH}$ = 52.3 Hz, $^3J_{FCCH}$ = 4.6 Hz). IR, ν/cm^{-1} : 3240, 3150, 3100, 1680, 1625, 1590, 1560, 1520, 1490, 1475, 1390, 1325, 1310, 1270, 1215, 1185, 1175, 1165, 1160, 1115, 1100, 1065, 1035, 990, 960, 930, 870, 830, 800, 780, 760, 750, 720. Found (%): C, 33.74; H, 1.54; P, 6.78. $C_{13}H_8F_{10}NO_4P$. Calculated (%): C, 33.96; H, 1.73; P, 6.69.

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