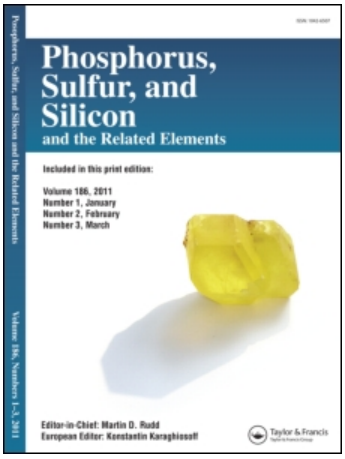

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THE EASY P—C-BOND CLEAVAGE OF FLUORINATED PHOSPHINE OXIDE

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Communication

THE EASY P—C-BOND CLEAVAGE OF FLUORINATED PHOSPHINE OXIDE

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Treatment of (1-acetamido-1-trifluoromethyl-2,2,2-trifluoroethyl)diphenyl phosphine oxide by OH-nucleophiles leads to the P—C(sp^3) bond cleavage.

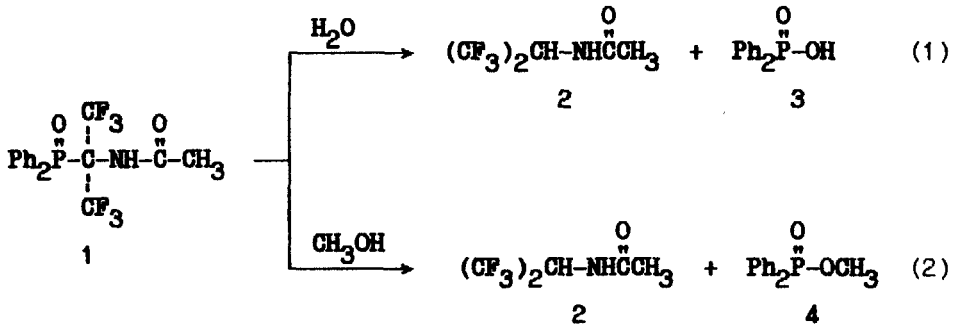
Key words: (1-Acetamido-1-trifluoromethyl-2,2,2-trifluoroethyl)diphenyl phosphine oxide; hydrolysis; methanolysis; P—C bond cleavage.

It is known that nucleophilic substitution on the phosphorus atom of phosphine oxides needs hard conditions: a strong nucleophilic reagent or a slackening of the P—C bond under the influence of substituents.[1] In this paper we report the unusual case of cleavage of a P—C(sp^3) bond in (1-acetamido-1-trifluoromethyl-2,2,2-trifluoroethyl)diphenylphosphine oxide **1** with OH-nucleophiles.

Phosphine oxide **1** was synthesized by the addition of diphenylphosphinous acid to the N-acetylimine of hexafluoroacetone. We found that treatment of **1** by water or methanol results in the cleavage of a P—C(sp^3) bond, yielding acetamide **2**, phosphinic acid **3** or phosphinate **4**, respectively.

The initial investigation of this reaction was done by NMR. We have established that heating of a solution of **1** for a short time in CD_3CN with H_2O or CH_3OH at 60°C leads to complete P—C bond cleavage yielding **2**, **3**, and **4**, respectively, with no other products.

In a preparative scale amide **2** and acid **3** were isolated as pure substances, but in the second case amide **2** and ester **4** were obtained as mixture 1:1 (according to the NMR data). The ^{19}F and $^{31}P\{H\}$-NMR spectra of this mixture showed only one signal as well as the ^1H NMR spectrum showed the only typical signals of $CH(CF_3)_2$ proton and the only signal CH_3O ester group as doublet with J_{HP} = 10 Hz.



Recently we have published the X-ray analysis of **1** which has shown the strain and energy disadvantageous conformation of substituents along the bonds P—C(sp^3), C(sp^3)-CF_3, the considerable lengthening of covalent bond P—C(sp^3) up to 1.94 Å (the longest P—C bond, as authors know at this time) and the strong internal hydrogen bond P=O . . . H—N. All these, from our point of view, as well as two electron withdrawing CF_3-groups, is the cause of slackening of P—C(sp^3) bond and its easy cleavage.

EXPERIMENTAL

^1H-, $^{13}C\{H\}$-, ^{19}F- and $^{31}P\{H\}$-NMR spectra were recorded on a Bruker CXP-200 instrument operating at 200.13, 50.0, 188.3 and 81.0 MHz, respectively. Chemical shifts are downfield relative to tetramethylsilane (internal), CF_3COOH and 85% H_3PO_4 (external) as standards, and have a positive sign. Satisfactory microanalyses obtained for all compounds: C ± 0.3, H ± 0.3, P ± 0.2.

(1-Acetamido-1-trifluoromethyl-2,2,2-trifluoroethyl)diphenyl phosphine oxide **1**. The N-acetylimine of hexafluoroacetone (1.50 g 7.2 mmol) in 10 ml anhydrous diethyl ether was added dropwise to diphenylphosphinic acid (1.23 g 7.2 mmol) in 15 ml diethyl ether at room temperature, stirred during 2 hours and stood overnight. The precipitate formed was filtered, washed by pentane and dried. Yield of **1** 2.5 g (92%), m.p. 116–118°C. The NMR spectra of **1** are summarized in Tables I and II. Calcd. for $C_{17}H_{14}F_6NO_2P$: C, 35.21; H, 3.45; P, 7.57. Found: C, 35.12; H, 3.56; P, 7.55.

Hydrolysis of **1**. The 0.1 ml water was added to **1** (0.5 g 1.3 mmol) in 5 ml anhydrous acetonitrile. The mixture was heated 5 min at 50°C. The crystals of **3** formed during 2 weeks were filtered, filtrate was evaporated and the residue was washed by diethyl ether yielding **2**. Yield of **2** 0.25 g (86%), m.p. 114–115°C ^1H-NMR (CD_3CN): 2.05 (s, CH_3, 3H), 5.52 (d, sept, J_{HF} 7, J_{HH} 10, CH, 1H), 8.50 (d, J_{HH} 10, NH, 1H). ^{19}F-NMR (CD_3CN): 6.16 d J_{FH} 7. Yield of **3** 0.21 g (85%), m.p. 195–196°C. ^1H-NMR (CD_3OD), δ: 7.40–7.60 (m, *m*, *p*-Ph, 6H), 7.75–7.95 (m, *o*-Ph, 4H). ^{31}P-NMR (CD_3OD): 29.5 ppm.

Methanolysis of **1**. 0.5 g of **1** was dissolved in 5 ml of methanol. The resulted mixture was heated during 5 min at 50°C and left overnight. The methanol was evaporated and colorless admixture crystals were obtained. The slow crystallization of this mixture from CH_3CN yielded 90 mg of **4** with m.p. 56–57°C. ^1H-NMR of **4** (acetone-d_6), δ: 3.75 (d, J_{HP} 10, CH_3OP, 3H), 7.30–7.60 (m, Ph, 6H), 7.80–8.00 (m, Ph, 4H). ^{31}P-NMR of **4** (acetone-d_6): 33.00 ppm. The attempts to isolate **2** from the mixture were unsuccessful. ^{19}F-NMR of mixture (acetone-d_6), δ: 6.51 (d, J_{FH} 7).

TABLE I

^1H, ^{19}F and ^{31}P NMR date of **1**

Solvent	^1H NMR, (δ, ppm)	$^{19}F\{H\}$ (ppm)	$^{31}P\{H\}$ (ppm)
$CDCl_3$	2.25 s (3H,CH_3); 7.50–7.75 m (7H, *m,p*-Ph + NH); 8.00–8.20 m (4H, *o*-Ph)	14.97 d $^3J_{FP}$ 2.5	32.7
CD_3CN	2.10 s (3H); 7.50–7.80 m (7H, *m,p*-Ph + NH); 7.70–7.85 , (4H, *o*-Ph)	6.3 d $^3J_{FP}$ 2.1	29.3

TABLE II

^{13}C-chemical shifts (δ, ppm) and J (Hz) coupling constants of **1**

CH_3	C–O	P–C–N	CF_3	Ph			
				C–P	*o*	*m*	*p*
[a]24.09	168.27	67.72	121.97	125.57	128.58	132.81	133.70
[b]23.08	168.58	51.07	122.11	126.13	128.57	132.67	133.64
s	d	d sept	k	d	d	d	d
	$^3J_{CP}$ 7	$^1J_{CP}$ 50 $^2J_{CF}$ 31	$^1J_{CF}$ 286	$^1J_{CP}$ 104	$^2J_{CP}$ 14	$^3J_{CP}$ 10	$^4J_{CP}$ 3

[a]In $CDCl_3$

[b]In CD_3CN

REFERENCES

1. O. A. Erastov and G. N. Nikonov, "Functionally-substituted phosphines and their derivatives" (eds. "Nauka," Moscow, 1986), p. 210.
2. A. N. Chekhlov, A. Yu. Aksinenko, V. B. Sokolov and I. V. Martynov, *Dokl. Acad. Nauk (USSR)*, **319,** 1396 (1991).