Russian Chemical Bulletin, International Edition, Vol. 59, No. 5, pp. 1059—1060, May, 2010

# Letters to the Editor

## Cleavage of the P—C bond in the reactions of phosphoryl-substituted CH acids with 1-fluoro-2,4,6-trinitrobenzene in the presence of bases

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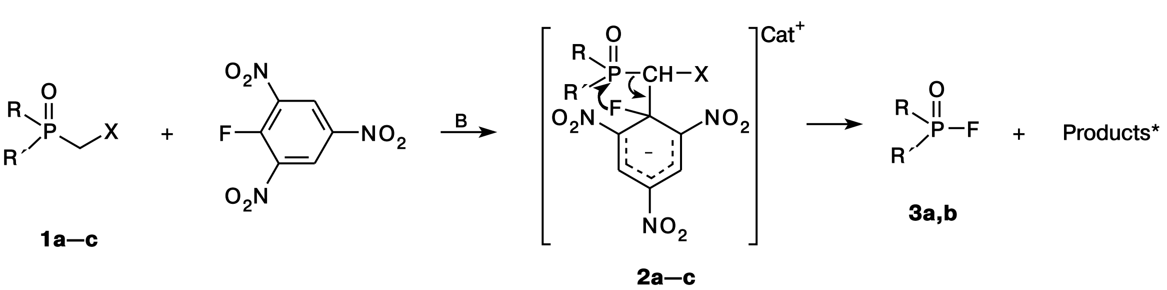
Formation and cleavage of the P—C bonds in the organophosphorus compounds are of fundamental importance. In our laboratory, base-assisted cleavage of the P—C bond, which occurred smoothly in the reactions of the phosphorus-containing CH acids **1** with 1-fluoro-2,4,6-trinitrobenzene, was discovered (Scheme 1).

Apparently, in the presence of sodium hydride or triethylamine the phosphoryl-substituted CH acids **1a—c** are converted into the corresponding carbanions, which react with 1-fluoro-2,4,6-trinitrobenzene to give σ-complexes **2a—c**. Fragmentation of intermediates **2a—c** results in phosphorus acid fluorides **3a,b** and salt-like

**Scheme 1**



Cat$^+$ = $Et_3NH^+$, $Na^+$
R = R′ = Ph, X = COOEt (**1a**), CN (**1b**); R = Ph, R′ = OEt, X = COOEt (**1c**); R = R′ = Ph (**3a**); R = Ph, R′ = OEt (**3b**)
*Products are compounds of unidentified structures.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 1034—1035, May, 2010.

compounds of unknown structure. In this case the P—F bond formation mechanism is probably similar to that of the P—C bond cleavage in the Horner—Wadsworth—Emmons reaction,[1] which is known to involve an intramolecular attack of the phosphorus atom by the negatively charged oxygen atom of the carbonyl counterpart. In our case, intramolecular attack of the phosphorus atom by the fluorine atom of the $\sigma^F$-complex **2** occurred. The possibility of the cleavage of the P—C bond under the action of the fluoride ion is documented.[2]

The structures of fluorides **3** were confirmed by $^{19}$F and $^{31}$P NMR spectroscopy. In the $^{19}$F and $^{31}$P NMR spectra of the reaction mixtures, the doublets with the spin-spin coupling constants $^1J_{P,F}$ of ~1000 Hz were observed. Compounds **3a,b** were isolated in the yields of ~50%. The chemical shifts for the phosphorus atom and observed coupling constants values are consistent with the published data on the resulting phosphorus acid fluorides.

One of the driving forces of the P—C bond cleavage, which proceeds so readily, is obviously a gain in the energy due to the bond P—F ($E$ = 126 kcal mol$^{-1}$) formation, which is more energetically favorable in respect of the P—C bond ($E$ = 65 kcal mol$^{-1}$).

The scope of the reactions under study is obviously defined by the CH acidity of the starting compounds bearing an active methylene group as well as the steric factors (a certain steric accessibility is required for the effective attack of the carbanion by 1-fluoro-2,4,6-trinitrobenzene). These issues and the nature of the resulting compounds as well will be covered later.

The reaction under consideration is of low synthetic interest as the phosphoryl fluorides can easily be prepared from the corresponding chlorides. However, this reaction is of importance for the understanding of the chemical properties of α-phosphorus-containing CH acids. The latter are of considerable interest as pharmaceuticals, extractants and complexing agents and for the synthesis of practically useful compounds as well.[3]

The $^{19}$F and $^{31}$P NMR spectra were recorded on a Bruker AMX-300 instrument at 282.4 MHz and 121.5 MHz, respectively. All reactions were carried out under dry nitrogen. Solvents were purified and dried prior to use. Starting compounds **1a—c** were synthesized by the known procedures,[4—5] their physicochemical characteristics coincided with published data.

**Synthesis of phosphorus acid fluorides 3a,b.** ***A.*** A solution of CH acid **1a—c** (0.5 mmol), 1-fluoro-2,4,6-trinitrobenzene (1 mmol) and triethylamine (1 mmol) in THF (5 mL) was kept at room temperature for 24 h. After mixing of the reactants, an intensive dark-cherry color of the mixture was observed. In the NMR spectra of all reaction mixtures, the signals characteristic of phosphoryl fluorides were observed.

**Diphenylphosphinic fluoride (3a).** $^{31}$P NMR, δ: 39.25, $J_{P,F}$ = 1015 Hz; $^{19}$F NMR, δ: 73.29, $J_{F,P}$ = 1015 Hz (*cf.* Ref 6: $^{31}$P NMR: 40.5 ppm, $J_{P,F}$ = 1010 Hz; $^{19}$F NMR, δ: 11.6 (relative to PhCF$_3$), $J_{F,P}$ = 1010 Hz).

***O*-Ethyl *P*-phenyl-*P*-fluorophosphinate (3b).** $^{31}$P NMR, δ: 16.94, $J_{P,F}$ = 1032 Hz; $^{19}$F NMR, δ: 63.52, $J_{F,P}$ = 1036 Hz (*cf.* Ref 6: $^{31}$P NMR, δ: 16.3, $J_{P,F}$ = 1035 Hz; $^{19}$F NMR, δ: 63.8 (relative to PhCF$_3$), $J_{F,P}$ = 1010 Hz).

***B.*** To a solution (or suspension) of CH acid **1a—c** (0.5 mmol) in THF (5 mL), equimolar amount of NaH (60% dispersion in mineral oil) was added. To the resulting homogenous mixture, a solution of 1-fluoro-2,4,6-trinitrobenzene (0.5 mmol) in THF (2—3 mL) was added. Immediately, the dark-red color of the mixture appeared. The reaction mixture was kept at room temperature for 24 h. The $^{19}$F and $^{31}$P NMR spectra of the resulting reaction mixtures were similar to that obtained by the method *A*.

This work was financially supported by the Russian Foundation for Basic Research (Grant No. 08-03-00196a).

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*Received July, 2009;*
*in revised form December, 28 2009*