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Reactions of N–P^{III}-Phosphorylated Trifluoroacetamides with (Ethoxycarbonyl)triphenylmethylide

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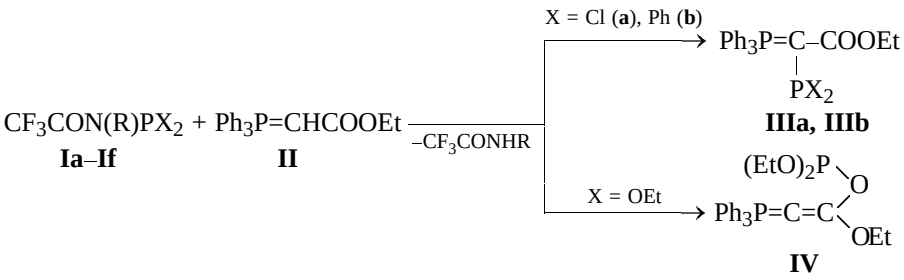
Abstract — N–P^{III}-Phosphorylated trihaloacetamides act as phosphorylating agents with respect to (ethoxycarbonyl)triphenylmethylide. The reactions give rise to C-phosphorylated ylides and *O*-(diethoxyphosphino)-phosphaketene acetals.

Our synthesized N–P^{III}-phosphorylated *N*-alkyltrifluoroacetamides **I** are ambident electrophilic reagents, and in reactions with nucleophiles they can act both as phosphorylating and trifluoroacetylating agents.

It is known that trifluoroacetamides and activated ylides enter the Wittig reaction to form enamines [2] and their subsequent cyclization products [3]. It might be expected that *N*-alkyl(aryl)trifluoroacetamides with the electron-acceptor phosphino group at the nitrogen atom would exhibit enhanced reactivity not only toward activated, but also toward stabilized ylides.

In view of the aforesaid and with the aim to study the properties of N–P^{III}-phosphorylated trihaloacetamides, we have studied reactions of *N*-alkyl- and *N*-phenyl-*N*-phosphinotrifluoroacetamides with (ethoxycarbonyl)triphenylmethylide (**II**).



I, R = Me, X = Cl (**a**), Ph (**b**), OEt (**c**); R = Bu, X = Cl (**d**), Ph (**e**), OEt (**f**). **III**, X = Cl (**a**), Ph (**b**).

It was found that amidophosphines **Ia**, **Ib**, **Id**, and **Ie** react with ylide **II** to form *C*-phosphinylides **IIIa** and **IIIb**, i.e. nucleophilic substitution at P^{III} takes place. An interesting feature of this reaction is the substitution of the amido group rather than chlorine in dichlorophosphinamide **Ia** (X = Cl). The structure of ylides **IIIa** and **IIIb** was proved by spectral data, as well as the identity of one of them (compound **IIIb**) to that obtained from chlorodiphenylphosphine with excess ylide **II** as HCl acceptor [4]. Attempted substitution of the chlorine atom in ylide **IIIa** under the action of amines results in C–P^{III} bond cleavage.

Substituents R in amidophosphines **I** have no substantial effect on the direction and facility of the reactions, unlike the nucleophilicty of the ylides. Thus, amidophosphines **I** fail to react with benzoyl(triphenylphosphino)methylide that is less nucleophilic than its alkoxycarbonyl analog **II**. The reactions of ylide **II** with diethyl trifluoroacetylphoshoramidites **Ic** and **If** take an unusual pathway to form heterocumulene **IV**. The IR spectrum of the latter display a band at 2225 cm^{-1}, characteristic of the P=C=C triad [5]. The ^{31}P NMR spectrum of heterocumulene **IV** shows signals at 18.2 and 180.4 ppm ($^4J_{PP}$ 9.2 Hz). Evidence for the presence in compound **IV** of *sp*- and sp^2-carbon atoms is provided by the ^{13}C NMR spectra (see Experimental) that are consistent with the spectra

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of ethoxyphosphaketene acetals [6]. Compound **IV** is a representative of previously unknown O–P^{III}-phosphorylated phosphaketene acetals [7].

$$\mathbf{IV} + HX \longrightarrow \mathbf{II} + \underset{\mathbf{V}}{(EtO)_2PX},$$

X = OH, AlkO, Alk_2N.

Ketene acetal **IV** readily reacts with water, alcohols, amines, and other compounds containing active hydrogen. The reactions provide ylide **II** and corresponding phosphorus acid derivatives **V**.

EXPERIMENTAL

The IR spectra were registered on a UR-20 spectrophotometer. The ^1H, ^{13}C, and ^{31}P NMR spectra were obtained on a Varian VXR-300 spectrometer at 299.15, 75.43, and 121.42 MHz, respectively, against internal HMDS (^1H, ^{13}C) and external 85% H_3PO_4 (^{31}P). All manipulations were carried out under dry argon.

N-(Dichlorophosphino)-*N*-methyltrifluoroacetamide (**Ia**) was prepared as described in [1].

N–P^{III}-Phosphorylated *N*-alkyltrifluoroacetamides Ib, Id, Ie, and If *(general procedure).* To a solution of 0.1 mol of *N*-alkyltrifluoroacetamide and 0.1 mol of triethylamine in 180 ml of ether, 0.1 mol of P(III) chloride was added dropwise with vigorous stirring over the course of 2 h so that the temperature of the reaction mixture was maintained below 10°C. The mixture was left overnight, and the triethylamine hydrochloride was filtered off and washed with ether (2 × 20 ml). The solvent was removed, and the reaction products were isolated by vacuum distillation or crystallization.

***N*-(Diphenylphosphino)-*N*-methyltrifluoroacetamide (Ib).** Yield 38%, mp 76–79°C (benzene–hexane, 1 : 2). IR spectrum (Nujol), ν, cm^{-1}: 1700 (C=O). ^{19}F NMR spectrum (C_6D_6), δ_F, ppm: –65.2 d ($^4J_{FP}$ 75.8 Hz). ^{31}P NMR spectrum (C_6D_6), δ_P, ppm: 60.1 q ($^4J_{FP}$ 75.8 Hz). Found P, %: 10.42. $C_{15}H_{13}F_3NOP$. Calculated P, %: 9.95.

***N*-Butyl-*N*-(dichlorophosphino)trifluoroacetamide (Id).** Yield 50%, bp 43–45°C (0.08 mm Hg), n_D^{15} 1.3842. IR spectrum (CCl_4), ν, cm^{-1}: 1750 (C=O). ^{19}F NMR spectrum (C_6D_6), δ_F, ppm: –68.5 d ($^4J_{FP}$ 100.9 Hz). 31P NMR spectrum (C_6D_6), δ_P, ppm: 169.8 q ($^4J_{FP}$ 100.9 Hz). Found P, %: 11.39. $C_6H_9Cl_2F_3NOP$. Calculated P, %: 11.47.

***N*-Butyl-*N*-(diphenylphosphino)trifluoroacetamide (Ie).** Yield 35% (oil), bp 142–146°C (0.07 mm Hg). IR spectrum (thin film), ν, cm^{-1}: 1720 (C=O). ^{19}F NMR spectrum (C_6D_6), δ_F, ppm: –65.8 d ($^4J_{FP}$ 77.8 Hz). 31P NMR spectrum (C_6D_6), δ_P, ppm: 60.7 q ($^4J_{FP}$ 77.8 Hz). Found P, %: 8.81. $C_{18}H_{19}F_3NOP$. Calculated P, %: 8.77.

***N*-Butyl-*N*-(diethoxyphosphino)trifluoroacetamide (If).** Yield 48%, bp 86–90°C (0.08 mm Hg), n_D^{15} 1.5372. IR spectrum (thin film), ν, cm^{-1}: 1740 (C=O). ^{19}F NMR spectrum (C_6D_6), δ_F, ppm: –66.7 d ($^4J_{FP}$ 93.7 Hz). ^{31}P NMR spectrum (C_6D_6), δ_P, ppm: 146.2 q ($^4J_{FP}$ 93.7 Hz). Found P, %: 10.38. $C_{10}H_{19}F_3NO_3P$. Calculated P, %: 10.71.

Ethyl (dichlorophosphino)(triphenylphosphoranylidene)acetate (IIIa). To a solution of 0.004 mol of *N*-methyl- (**Ia**) or *N*-butyl-*N*-(dichlorophosphino)-trifluoroacetamide (**Id**) in 10 ml of ether, a suspension of 0.004 mol of (ethoxycarbonylmethylene)triphenylphosphorane (**II**) in 10 ml of ether. The mixture was left overnight. The precipitate was filtered off, and the residue was kept for 8 h at 40–50°C (0.08 mm Hg). Yield 75–79% (dark red oil). IR spectrum (thin film), ν, cm^{-1}: 1650–1710, 1900, 1960. ^1H NMR spectrum (C_6D_6), δ, ppm: 0.79 t (3H, CH_3), 3.75 q (2H, CH_2), 7.07–7.19 m (9H, H_{arom}); 7.52–7.62 m (6H, H_{arom}). ^{13}C NMR spectrum (C_6D_6), δ_C, ppm: 14.24 s (CH_3), 33.76 d.d (PCP, $J_{CP^{IV}}$ 93.6 Hz, $J_{CP^{III}}$ 25.2 Hz), 59.50 s (CH_2), 125.32 d.d (C_{ipso}, $J_{CP^{IV}}$ 92.9 Hz, $J_{CP^{III}}$ 5.4 Hz), 129.00 s (C_p), 129.33 d (C_m, $^3J_{CP}$ 12.3 Hz), 129.42 d (Co, $^2J_{CP}$ 13.4 Hz), 167.33 d.d (C=O, $^2J_{CP^{IV}}$ 13.0 Hz, $^2J_{CP^{III}}$ 9.1 Hz). ^{31}P NMR spectrum (C_6D_6), δ_P, ppm: 21.9 d (Ph_3P, $^2J_{PP}$ 185.5 Hz), 166.3 d (PCl_2, $^2J_{PP}$ 185.5 Hz). Found P, %: 13.24. $C_{22}H_{20}Cl_2O_2P_2$. Calculated P, %: 13.79.

Ethyl (diphenylphosphino)(triphenylphosphoranylidene)acetate (IIIb). To a solution of 0.004 mol of *N*-methyl- (**Ia**) or *N*-butyl-*N*-(dichlorophosphino)-trifluoroacetamide (**Id**) in 5 ml of benzene, a suspension of 0.004 mol of (ethoxycarbonylmethylene)triphenylphosphorane (**II**) in 5 ml of benzene. The mixture was kept at 30–35°C for 4 h and left overnight. The solvent was removed, and the residue was washed with 20 ml of ether. Yield 71–74%, mp 151– 152°C. ^{31}P NMR spectrum (C_6D_6), δ_P, ppm: 28.7 d (Ph_3P, $^2J_{PP}$ 183.5 Hz), –14.1 d (Ph_2P, $^2J_{PP}$ 183.5 Hz), which corresponds to published data [4].

Diethyl 1-ethoxy-2-(triphenylphosphoranylidene)vinyl phosphite (IV). To a solution of 0.0074 mol of *N*-methyl- (**Ic**) or *N*-butyl-*N*-(diethoxyphosphino)trifluoroacetamide (**If**) in 10 ml of benzene, a suspension of 0.0074 mol of (ethoxycarbonylmethylene)triphenylphosphorane (**II**) in 20 ml of benzene was added with stirring. The mixture was kept for 1 h

at 50–60°C. The solvent was removed in a vacuum, and the residue was kept for 5 h at 70–75°C (0.08 mm Hg) to obtain a viscous yellow oil. Yield 60– 65%. IR spectrum (Nujol), ν, cm^{-1}: 2225 (P=C=C). ^{1}H NMR spectrum (C_6D_6), δ, ppm: 0.99 t (6H, $POCH_2CH_3$), 1.26 t (3H, CH_2CH_3),3.61–3.80 m (4H, $POCH_2CH_3$), 4.12 q (2H, CH_2CH_3), 6.98–7.07 m (9H, H_{arom}), 7.78–7.87 m (6H, H_{arom}). ^{13}C NMR spectrum (C_6D_6), δ_C, ppm: 14.85 s (OCH_2CH_3), 16.42 d (P=*C*=C, J_{CP} 133.1 Hz), 17.34 d ($POCH_2CH_3$, $^3J_{PC}$ 6.5 Hz), 58.18 s (OCH_2CH_3), 62.00 d ($POCH_2CH_3$, $^2J_{CP}$ 20.5 Hz), 128.80 d (C$_o$, $^2J_{CP}$ 12.1 Hz), 131.37 s (C_p), 133.29 d (C_m, $^3J_{CP}$ 9.9 Hz), 133.82 d (C_{ipso}, J_{CP} 90.4 Hz), 170.60 d.d (P=C=*C*, $^2J_{CP}$ 9.6, $^2J_{CP}$ 26.7 Hz). ^{31}P–{^{1}H} NMR spectrum (C_6D_6), δ_P, ppm: 18.2 d (Ph_3P, $^4J_{PP}$ 9.2 Hz), 180.4 d [$P(OEt)_2$, $^4J_{PP}$ 9.2 Hz]. Found P, %: 12.64. $C_{26}H_{30}O_4P_2$. Calculated P, %: 13.22.

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