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N-Substituted *N*-Phosphinotrifluoroactetamides in the Staudinger Reaction

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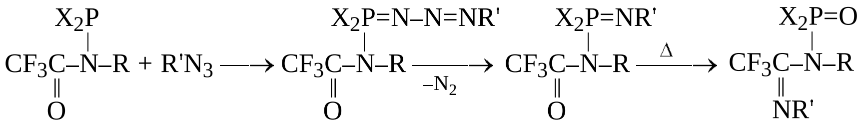
Abstract—Formerly unknown phosphazides with *N*-trifluoroacetamido groups at the phosphorus atom were obtained by the imination of *N*-(diphenylphosphino)-*N*-phenyltrifluoroacetamide with aryl azides. Stability of the phosphazides was found to depend on the nature of the radical at the amide nitrogen atom. The phosphazides were shown to readily eliminate nitrogen to yield phosphinimines that undergo the aza-Wittig thermal rearrangement into N-phosphorylated trifluoroacetamidines.

A few examples of stable phosphazides obtained by imination of P(III) derivatives with organic azides are known [1]. The structure of some of them have been proved by X-ray diffraction [2]. *N*-Arylphosphazides are stabilized by bulky and electron-acceptor substituents in the azide phenyl ring, as well as bulky and preferentially donor substituents on phosphorus. Thus, the phosphazide obtained from picryl azide and trimorpholino phosphite is so stable that it could not be converted into corresponding phosphazo compounds [3].

Proceeding with our research [4, 5] into the properties of N–P^{III}-phosphorylated trihaloacetamides and aiming at preparing formerly unknown types of phosphazides, we turned to reactions of *N*-methyl- and *N*-phenyl-*N*-phosphinotrifluoroacetamides with aryl azides.

It was found that amidophosphines **I** slowly react with azides **II** to give formerly unknown phosphazides **III** that have substituted *N*-trifluoroacetamido groups on phosphorus. Compounds **IIIa** and **IIIb** are the only phosphazides we could isolate individual as yellowish amorphous materials. In the absence of solvents, they can be stored for 7–10 days. Compounds **IIIc** and **IIId** converted into corresponding phosphinimides, gradually during reaction and fast on heating. Phosphazides **IIIa** and **IIIb** eliminated nitrogen on heating to 40–50°C.

Comparison of the properties of *N*-aryltriphenyl phosphazides [6] and our prepared compounds shows that replacement of even one phenyl group on phosphorus by the fairly bulky *N*-phenyl-*N*-trifluoroacetamide group renders phosphazides much more stable.



$$\mathrm{CF_3C(=O)N(R)PX_2} + \mathrm{R'N_3} \longrightarrow \mathrm{CF_3C(=O)N(R)PX_2{=}N{-}N{=}NR'} \xrightarrow[-N_2]{} \mathrm{CF_3C(=O)N(R)PX_2{=}NR'} \xrightarrow{\Delta} \mathrm{CF_3C(=NR')N(R)PX_2{=}O}$$

Ia–Ic **IIa–IIc** **IIIa–IIId** **IVa–IVd** **Va–Vd**

I, R = X = Ph (**a**); R = Me, X = Ph (**b**), OEt (**c**). **II**, R' = Ph (**a**), *p*-FC_6H_4 (**b**), *p*-$NO_2C_6H_4$ (**c**). **III**, R = X = Ph, R' = Ph (**a**), *p*-FC_6H_4 (**b**); R = Me, R' = *p*-$NO_2C_6H_4$, X = Ph (**c**), OEt (**d**). **IV**, R = Ph, R' = X = Ph (**a**), R' = *p*-FC_6H_4, X = Ph (**b**); R = Me, R' = *p*-$NO_2C_6H_4$, X = Ph (**c**), OEt (**d**). **V, R = X = Ph, R' = Ph** (**a**), *p*-FC_6H_4 (**b**); R = Me, R' = *p*-$NO_2C_6H_4$, X = Ph (**c**), OEt (**d**).

Phosphinimines **IV** undergo the aza-Wittig rearrangement, partially during their synthesis and completely under reflux in toluene or xylene, to form N-phosphorylated trifluoroacetamidines **V** (see [4]). This conversion suggests that the electron-acceptor iminophosphoryl and trifluoromethyl groups strongly favor polarization of the carbonyl group.

EXPERIMENTAL

The IR spectra were obtained on a UR-20 spec-

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trophotometer. The ^{1}H, ^{19}F, and ^{31}P NMR spectra were taken on a Varian VXR-300 spectrometer at 299.15, 282.20, and 121.42 MHz, respectively, against internal HMDS (^{1}H, ^{13}C) and $CFCl_3$ (^{19}F), and external 85% H_3PO_4 (^{31}P).

$N–P^{III}$-Phosphorylated trifluoroacetamides **I** were prepared according to [5].

***N*-(Diphenylphosphino)-*N*-phenyltrifluoroacetamide (Ia).** A solution of 0.0682 mol of chlorodiphenylphosphine in 20 ml of benzene was added to a solution of 0.0686 mol of *N*-phenyl-*N*-(trimethylsilyl)trifluoroacetamide [7] in 30 ml of benzene. The reaction mixture was kept for 3 h at 60°C. The solvent was removed in a vacuum, and the residue was treated at –5 to 10°C with hexane (2×30 ml). Yield 87%, mp 58–59°C. IR spectrum (Nujol), ν, cm^{-1}: 1690 (C=O). ^{19}F NMR spectrum (C_6D_6), δ_F, ppm: –67.1 d ($^{4}J_{FP}$ 16.7 Hz). $^{31}P–\{^{1}H\}$ NMR spectrum (C6D6), δ_P, ppm: 69.0 q ($^{4}J_{PF}$ 16.7 Hz). Found P, %: 8.18. $C_{20}H_{15}F_3\cdot NOP$. Calculated P, %: 8.29.

***N*-[Diphenyl(3-phenyl-2-triazenylidene)phosphoranyl]-*N*-phenyltrifluoroacetamide (IIIa).** A solution of 0.0016 mol of phenyl azide in 10 ml of hexane was added at 0°C to a suspension of 0.0016 mol of *N*-(diphenylphosphino)-*N*-phenyltrifluoroacetamide (**Ia**) in 30 ml of hexane. The mixture was left overnight, and the precipitate was filtered off and washed with 20 ml of hexane. Yield 98%, mp 110–112°C (decomp.). IR spectrum (KBr), ν, cm^{-1}: 1710 (C=O), 1380 (P=N), 2130 (P=N–N=N). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.85–7.15 m (5H, H_{arom}, NPh), 7.31–7.65 m (10H, H_{arom}, Ph_2P), 7.82–7.96 m (5H, H_{arom}, P=NPh). ^{19}F NMR spectrum (benzene), δ_F, ppm: –67.79. ^{31}P NMR spectrum (benzene), δ_P, ppm: –0.19 m. Found, %: N 10.97; P 6.43. $C_{26}H_{20}F_3N_4OP$. Calculated, %: N 11.38; P 6.29.

***N*-[[3-(4-Fluorophenyl)-2-triazenylidene]diphenylphosphoranyl]-*N*-phenyltrifluoroacetamide (IIIb).** A solution of 0.0027 mol of *p*-fluorophenyl azide in 10 ml of hexane was added at 0°C to a suspension of 0.0027 mol of compound **Ia** in 30 ml of hexane. The mixture was left overnight, and the precipitate was filtered off and washed with 20 ml of hexane. Yield 97%, mp 67–70°C (decomp.). IR spectrum (KBr), ν, cm^{-1}: 1715 (C=O), 1380 (P=N), 2120 (P=N–N=N). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.79–7.22 m (5H, H_{arom}, NPh), 7.39–7.66 m (10H, H_{arom}, Ph2P), 7.85 d (2H, H_{arom}), 7.89 d (2H, H_{arom}, *J* 7.5 Hz). ^{19}F NMR spectrum (benzene), δ_F, ppm: –67.99 (CF_3), –125.50 (F). ^{31}P NMR spectrum (benzene), δ_P, ppm: –0.58. Found, %: N 10.14; P 6.06. $C_{26}H_{19}F_4N_4OP$. Calculated, %: N 10.98; P 6.07.

***N*-Phenyl-*N*-(triphenylphosphorimidoyl)trifluoroacetamide (IVa).** Compound **IIIa**, 0.0056 mol, was refluxed in 10 ml of benzene for 20 min. The solvent was removed in a vacuum, and the residue was washed with 20 ml of hexane. Yield 90%, mp 116–117°C. IR spectrum (KBr), ν, cm^{-1}: 1690 (C=O), 1340–1370 (P=N). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.00–7.18 m (5H, H_{arom}, NPh), 7.35–7.55 m (10H, H_{arom}, Ph_2P), 7.84–7.93 m (5H, H_{arom}, P=NPh). ^{19}F NMR spectrum (benzene), δ_F, ppm: –74.43. ^{31}P NMR spectrum (benzene), δ_P, ppm: 16.20. Found, %: N 6.10; P 6.59. $C_{26}H_{20}F_3N_2OP$. Calculated, %: N 6.03; P 6.67.

***N*-[*N*-(4-Fluorophenyl)diphenylphosphorimidoyl]-*N*-phenyltrifluoroacetamide (IVb).** A solution of 0.0049 mol of compound **IIIb** in 10 ml of benzene was refluxed for 20 min. The solvent was removed in a vacuum, and the residue was washed with 20 ml of hexane. Yield 86%, mp 106–107°C. IR spectrum (KBr), ν, cm^{-1}: 1690 (C=O), 1340–1370 (P=N). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.98–7.20 m (5H, H_{arom}, NPh), 7.40–7.63 m (10H, H_{arom}, Ph2P), 7.72 d (2H, H_{arom}), 7.80 d (2H, H_{arom}, *J* 7.8 Hz). ^{19}F NMR spectrum (benzene), δ_F, ppm: –75.02 (CF_3), –122.52 (F). ^{31}P NMR spectrum (benzene), δ_P, ppm: 16.96. Found, %: N 5.74; P 6.37. $C_{26}H_{19}F_4N_2OP$. Calculated, %: N 5.81; P 6.42.

***N*-Methyl-*N*-[*N*-(4-nitrophenyl)diphenylphosphorimidoyl]trifluoroacetamide (IVc).** A solution of 0.0643 mol of *p*-nitrophenyl azide in 5 ml of benzene was added to a solution of 0.0643 mol of *N*-(diphenylphosphino)-*N*-methyltrifluoroacetamide (**Ib**) in 10 ml of benzene, and the mixture was left overnight. The solvent was removed in a vacuum, and the oily material that separated crystallized when ground in hexane. Yield 84%, mp 45–47°C. IR spectrum (KBr), ν, cm^{-1}: 1710 (C=O), 1300–1340 (P=N). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.4 d.q (NCH3, $^{3}J_{HP}$ 8.8, $^{5}J_{HF}$ 1.6 Hz), 7.45–8.06 m (H_{arom}). ^{19}F NMR spectrum (benzene), δ_F, ppm: –71.20. ^{31}P NMR spectrum (benzene), δ_P, ppm: 14.25 m. Found, %: N 9.17; P 6.93. $C_{21}H_{17}F_3N_3O_3P$. Calculated, %: N 9.39; P 6.92.

***N*-Methyl-*N*-[*N*-(4-nitrophenyl)diethoxyphosphorimidoyl]trifluoroacetamide (IVd).** A solution of 0.0643 mol of *p*-nitrophenyl azide in 10 ml of benzene was added to a solution of 0.0111 mol of *N*-(diethoxyphosphino)-*N*-methyltrifluoroacetamide (**Ic**) in 5 ml of benzene. The mixture was left overnight, the solvent was removed in a vacuum, and the residue was subjected to a water-jet-pump vacuum. Yield 97%, yellow oil. IR spectrum (CCl_4), ν, cm^{-1}: 1715 (C=O), 1320–1350 (P=N). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.32 t (6H, CH_2CH_3, ^{3}J 7 Hz), 3.41 d.q (3H, NCH_3, $^3J_{HP}$ 9.2, $^5J_{HF}$ 1.6 Hz), 4.04–4.32 m (8H, OCH_2). ^{19}F NMR spectrum (benzene), δ_F, ppm: –71.03. ^{31}P NMR spectrum (benzene), δ_P, ppm: –8.05. Found, %: N 11.18; P 8.01. $C_{13}H_{17}F_3N_3O_5P$. Calculated, %: N 10.96; P 8.08.

***N*,*N*'-Diphenyl-*N*-(diphenylphosphinoyl)trifluoroacetimidamide (Va).** A solution of 0.0037 mol of compound **IVa** in 5 ml of xylene was refluxed for 10 h and then reduced by 2/3 in a vacuum. The residue was diluted with 2 ml of hexane, and the precipitate was filtered off. Yield 79%, mp 139–140°C. IR spectrum (KBr), ν, cm^{-1}: 1590, 1660 (C=C), 1160–1210 (P=O). ^1H NMR spectrum (acetone-d_6), δ, ppm: 6.99, 7.15, 7.3 m (5H, H_{arom}, NPh), 7.43–7.66 m (10H, H_{arom}, Ph2P), 7.84–8.01 m (5H, H_{arom}, P=NPh). ^{19}F NMR spectrum (benzene), δ_F, ppm: –59.71. ^{31}P NMR spectrum (benzene), δ_P, ppm: 30.60. Found, %: N 6.09; P 6.71. $C_{26}H_{20}F_3N_2OP$. Calculated, %: N 6.03; P 6.67.

***N*'-(4-Fluorophenyl)-*N*-(diphenylphosphinoyl)-*N*-phenyltrifluoroacetimidamide (Vb).** A solution of 0.0021 mol of compound **IVb** in 5 ml of xylene was refluxed for 10 h and then reduced in a vacuum by 2/3. The residue was diluted with 2 ml of hexane, and the precipitate was filtered off. Yield 83%, mp 143–144°C. IR spectrum (KBr), ν, cm^{-1}: 1670, 1610 (C=C), 1190–1230 (P=O). ^1H NMR spectrum (acetone-d_6), δ, ppm: 7.01–7.27 m (5H, H_{arom}, NPh), 7.38–7.64 m (10H, H_{arom}, Ph2P), 8.25 d (2H, H_{arom}), 8.30 d (2H, H_{arom}). ^{19}F NMR spectrum (benzene), δ_F, ppm: –58.80 (CF3), –116.07 (F). ^{31}P NMR spectrum (benzene), δ_P, ppm: 29.85. Found, %: N 5.98; P 6.47. $C_{26}H_{19}F_4N_2OP$. Calculated, %: N 5.81; P 6.42.

***N*-(Diphenylphosphinoyl)-*N*-methyl-*N*'-(4-nitrophenyl)trifluoroacetimidamide (Vc).** A solution of 0.0019 mol of compound **IVc** in 5 ml of toluene was refluxed for 6 h. The solvent was removed in a vacuum, and the residue was crystallized from benzene. Yield 90%, mp 100–102°C. IR spectrum (KBr), ν, cm^{-1}: 1180–1250 (P=O), 1620 (C=N). ^1H NMR spectrum (acetone-d_6), δ, ppm: 3.15 d (3H, CH_3, $^3J_{HP}$ 8.5 Hz), 7.08–8.09 m (28H, H_{arom}). ^{19}F NMR spectrum (acetone-d_6), δ_F, ppm: –75.53 d ($^4J_{FP}$ 9.2 Hz). ^{31}P NMR spectrum (acetone-d_6), δ_P, ppm: 30.97. Found, %: N 9.35; P 6.88. $C_{21}H_{17}F_3N_3O_3P$. Calculated, %: N 9.39; P 6.92.

Diethyl *N*-methyl-*N*-[*N*-(4-nitrophenyl)trifluoroacetimidoyl]phosphoramidate (Vd). A solution of 0.0072 mol of compound **IVd** in 5 ml of toluene was refluxed for 4 h. The solvent was removed in a vacuum, and the residue was crystallized from benzene. Yield 75%, mp 113–115°C. IR spectrum (KBr), ν, cm^{-1}: 1610 (C=C), 1670 (C=N), 1200–1230 (P=O). ^1H NMR spectrum ($CDCl_3$), ν, ppm: 2.61 d (3H, NCH_3, $^3J_{HP}$ 12.3 Hz), 1.30 t (3H, OCH_2CH_3, *J* 7 Hz), 4.00–4.30 m (8H, OCH_2CH_3). ^{19}F NMR spectrum (benzene), δ_F, ppm: –71.10. ^{31}P NMR spectrum (benzene), δ_P, ppm: 1.50. Found, %: N 10.93; P 8.10. $C_{13}H_{17}F_3N_3O_5P$. Calculated, %: N 10.96; P 8.08.

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