A Scheme of the Stepwise Reaction of Diphenylchlorophosphine with *N,N*-Dialkylformamides in the Presence of NaI

V. P. Morgalyuk and T. V. Strelkova

Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ul. Vavilova 28, Moscow, 119991 Russia e-mail: morgaliuk@mail.ru

Received November 8, 2010

Abstract—On an example of DMF was proposed and experimentally verified stepwise reaction scheme of the reaction of diphenylchlorophosphine with *N*,*N*-dialkylformamides. The first stage is autocatalytic reaction of the synthesis of (diphenylphosphoryl)(*N*,*N*-dialkylamino)chloromethanes proceeding through the intermediate formation of diphenyldichloro[(*N*,*N*-dialkylamino)chloromethyl]phosphoranes. In the second stage that includes NaI, the (diphenylphosphoryl)(*N*,*N*-dialkylamino)chloromethanes are reduced by diphenyliodo-phosphine (or triphenylphosphine) to form the final *N*,*N*-dialkyl(diphenylphosphinomethylene)iminium iodides. One can assume that the reaction of the synthesis of *N*,*N*-dialkyl(diphenylphosphinomethylene)-iminium iodides proceeds in a similar way, starting with diphenyliodphosphine.

DOI: 10.1134/S1070363211100094

In a previous report [1] was shown that the reaction of diphenylchlorophosphine Ph_2PCl (I) with *N*,*N*dialkylformamides R_2N -CHO (II) in the presence of NaI affords *N*,*N*-dialkyl(diphenylphosphinomethylene)iminium iodides (III):



Therewith, it was evidenced [2] that chlorophosphine I itself does not react with formamide II. In the presence of NaBr reaction also does not occur. The reaction proceeds with the diphenyliodophosphine Ph_2PI (IV) formed in the reaction medium from Ph_2PC1 (I) and NaI, that further reacts with II to form iminium salts III and diphenylphosphinic iodide V [reaction (1)]:





We failed to extend the reaction (1) over other carboxylic acid *N*,*N*-dialkylamides. However, when trying to perform the reaction between Ph₂PCl (I) and *N*,*N*-dimethylacetamide (DMAA, VI) in the presence of NaI, we isolated the adduct of diphenyltriiodophosphorane Ph₂PI₃ (VII) [3] with DMAA of the composition Ph₂PI₃·6 DMAA (VIII) (δ_P 32 ppm) in 29% yield. In the ³¹P NMR spectrum of the reaction mixture there was a second signal, at –16 ppm, corresponding to tetraphenyldiphosphine Ph₂P–PPh₂ (IX) [4].

This allowed us to suggest that, by analogy with the data of [5], the first step of reaction (1) is the disproportion of diphenyliodphosphine IV into Ph_2PI_3 (VII) and Ph_2P-PPh_2 (IX) [stage (1)]:

$$3 \operatorname{Ph}_2\operatorname{PI} \to \operatorname{Ph}_2\operatorname{PI}_3 + \operatorname{Ph}_2\operatorname{P}-\operatorname{PPh}_2.$$
(2)

Next, phosphorane **VII** reacts with formamide **II** [6] affording *N*,*N*-dimethylaminoiodomethyleneiminium

iodide $[R_2N=C(H)I]^+I^-$ (X) and iodphosphinite V [reaction (3)]:



The resulting iminium salt **X** reacts with Ph_2PI (**IV**) forming the corresponding diphenyldiiodo[(*N*,*N*-

dialkylamino)iodmethyl]phosphorane (XI) [reaction (4)]:



Then phosphorane **XI** reacts then with R_2N -CHO (**II**) forming the corresponding (diphenylphospho-

ryl)(*N*,*N*-dialkylamino)iodomethane (**XII**) [reaction (5)]:



Simultaneously is regenerated $[R_2N=C(H)I]^+I^-(X)$ entering to the next cycle of interaction with Ph₂PI (VI). Thus, the sequence of reactions (4) and (5) is an autocatalytic reaction. Perhaps, for the occurrence of these steps enough the presence of $[R_2N=C(H)I]^+I^-(X)$ in a catalytic amount. Accordingly, it is sufficient only a slight (probably no more than by a few mole percents) disproportion of diphenyliodphosphine (IV) in the stage (2).

X

Later on, the formed compound **XII** is reduced by Ph_2PI (**IV**) to the final product, *N*,*N*-dialkyl(diphenyl-phosphinomethylene)iminium iodide (**III**) [reaction (6)]:



In the proposed stepwise reaction scheme (1) the stages 1–2 play the role of a "trigger," generating the key compound $[R_2N=C(H)I]^+T^-(X)$ whose appearance in the reaction medium makes it possible occurrence of the subsequent stages (4)–(6). However, it is obvious that for the implementation of stages (4), (5) the origin

of compound **X** is not essential: it can be synthesized by other methods [7]. Therefore, the stages (2), (3) of the proposed scheme are not required for proceeding the reaction (1). Significant are the stages (4)–(6), and they are identical to the scheme of the synthesis of N,N-dialkyl(diphenylphosphinomethylene)iminium-

(5)

iodides (III) established experimentally [reaction (1)] [2].

Starting from this consideration, we tested the stepwise scheme (1) experimentally using the available *N*,*N*-dimethylformamide (**Ha**, **R** = Me) as a starting material. Instead of highly reactive Ph₂PI (**IV**) we used the more accessible and less reactive Ph₂PCl (**I**). This allowed us to isolate and identify the intermediate reaction products. Instead of the highly reactive iodide $[R_2N=C(H)Cl]^+I^-$ (**X**) was taken its more accessible analog, *N*,*N*-dimethylchloromethyleneiminium chloride $[Me_2N=C(H)Cl]^+Cl^-$ (**XIII**) (Vilsmeier–Haack reagent) [8].

Since the origin of salt XIII (as well as X) is not of principal significance, it can be generated in the



Compound **XVa** was isolated from the reaction mixture as an adduct with one DMF molecule.

The stage (7) is reversible. In DMF at -5° C the equilibrium is shifted toward the formation of **XVa**. On dissolving in CHCl₃ at 20°C, **XVa** is decomposed rapidly to the original Ph₂PCl (**I**) and **XIII**. In 50 min after the start of registration, in the ¹H NMR spectrum of **XVa** in CDCl₃ there are the signals of Ph₂PCl (**I**) and [Me₂N=C(H)Cl]⁺Cl⁻ (**XIII**) only, in 1:1 ratio, and ³¹P NMR spectrum contains a signal of Ph₂PCl (**I**) only, at 82 ppm [10]. Therefore, we could reconstruct



In accordance with reaction scheme (8), simultaneously with the synthesis of **XVIa** proceeds regeneration of **XIII**, which. can react with Ph₂PCl (I) again forming **XVa** [reaction (7)]. Therefore compound **XIII** can be considered as both a reagent and a catalyst. It turned out also that for the occurrence of stages (7) and (8) is sufficient the presence of **XIII** in a reaction medium from DMF (**IIa**) and oxalyl chloride (COCl)₂ (**XIV**) [9]:

$$(\text{COCl})_2 + \text{Me}_2\text{NC}(\text{H})\text{O} \rightarrow [\text{Me}_2\text{N}=\text{C}(\text{H})\text{Cl}]^+\text{Cl}^-$$

XIV IIa XIII

This allowed us to begin experimental verification of the proposed stepwise reaction scheme (1) at the stage (4).

Compound **XIII** synthesized directly in DMF (**IIa**) was introduced at -5° C in the reaction with Ph₂PCl (**I**). This resulted in precipitation with high yield of diphenyldichloro[(*N*,*N*-dimethylamino)chloromethyl]-phosphorane (**XVa**), the first representative of previously unknown diphenyldichloro[(*N*,*N*-dialkyl-amino)chloromethyl]phosphoranes (**XV**) [reaction (7)]:



the structure **XVa** from the data of ¹H and ³¹P NMR spectra: there are the signals of all expected proton groups in the relevant ratio, the spin-spin coupling constant ${}^{2}J_{PH} = 15$ Hz indicates the presence of a P–C(H) fragment, the ³¹P signal at 22 ppm is characteristic of phenyl(halo)-substituted phosphoranes [10].

Reaction of **XVa** with DMF (**IIa**) at 10°C, as expected, resulted in formation of (diphenylphosphoryl)(N,N-dimethylamino)chloromethane (**XVIa**) [reaction (8)]:



catalytic amount (5–10 mol %), as is expected from the proposed scheme of the reaction (4) and (5). Hence the sum of the reactions (7) and (8) can be considered as an independent catalytic reaction of the synthesis of (diphenylphosphoryl)(*N*,*N*-dialkylaminochloro)methanes (**XVI**) [reaction (9)], as has been suggested earlier [11] and confirmed experimentally [11, 12].



The isolated **XVIa** at 20°C is reduced rapidly in DMAA by Ph_2PI (**IV**) or in DMF by Ph_3P (**XVII**) in the presence of one equivalent of NaI. In both





After completion of the reaction of **XVIa** with Ph_2PI (**IV**), in the ³¹P NMR spectrum of the reaction mixture there was two signals in 1:1 ratio: at 29 ppm, corresponding diphenylphosphinic iodide (**V**) (the product of Ph_2PI oxidation) [2, 3], and at -6.5 ppm, corresponding to a solution of **IIIa** in DMAA. Similarly, after the completion of the reaction **XVIa** with Ph_3P (**XVII**), in the ³¹P NMR spectrum of the reaction mixture also there was two signals in 1:1 ratio: at 30 ppm, corresponding to triphenylphosphine oxide Ph_3PO (**XVIII**) (the product of Ph_3P oxidation) [2, 10], and at -4.5 ppm, corresponding to compound **IIIa**. In both the cases, the spectra were similar to the

³¹P NMR spectra of the reaction mixture after the reaction of Ph₂PCl (I) with DMF (IIa) in the presence of NaI [or Ph₂PI (IV) with DMF (IIa)], and after the reaction of Ph₂PCl (I) with DMF (IIa) in the presence of NaI and Ph₃P (XVII) [2].

In the absence of NaI, neither Ph₂PI (**IV**), nor Ph₃P (**XVII**) reduces **XVIa**. Ph₂PCl (**I**) also does does not react with **XVIa**. Obviously, the compound which actually is reduced is (diphenylphosphoryl)-*N*,*N*-dimethyl-aminoiodomethane (**XIX**) formed in the reaction mixture containing **XVIa** and NaI:



However, we failed to isolate individual compound **XIX**, probably because of its high reactivity.

The totality of the experimentally implemented reactions (7), (8), and (10) corresponds to the

previously established [2] reaction scheme: N,Ndialkyl(diphenylphosphinomethylen)iminium iodide (III) is fromed from diphenylchlorophosphine (I) and an N,N-dialkylformamide (IIa) [the same in the presence of triphenylphosphine (XVII)] in the presence of NaI. Therefore we can assume that, by analogy with the reactions (7), (8), and (10), the reaction leading to the synthesis of N,N-dialkyl-(diphenylphosphinomethylen)iminium iodides (III) is a sequence of two reactions:

(1) autocatalytic reaction of the synthesis of a (diphenylphosphoryl)(*N*,*N*-dialkylaminoiodo)methane (**XII**), which consists of two stages: (4) and (5);

(2) the reduction of the (diphenylphosphoryl)-*N*,*N*-dialkylaminoiodmethane (**XII**) in the reaction with diphenyliodphosphine (**IV**) [or triphenylphosphine (**XVII**)] [2] to corresponding *N*,*N*-dialkyl(diphenylphosphinomethylene)iminium iodide (**III**), that proceeds with involvement of NaI [reaction (6)].

EXPERIMENTAL

The ¹H, ³¹P and ³¹P–{¹H} NMR spectra were registered on a Bruker Avance 300 spectrometer at the operating frequencies 300.11 and 121.50 MHz, respectively. The ³¹P and ¹H NMR spectra of individual compounds were taken from solutions in CDCl₃, the ³¹P NMR spectra of reaction mixtures were recorded using solutions in DMF, DMAA and CH₂Cl₂, external referece 85% H₃PO₄. The DMF and DMAA used in the work were distilled twice over CaH₂, the CDCl₃, CH₂Cl₂, benzene, toluene, diethyl ether and dioxane over P₂O₅. The reagents Ph₂PCl (Aldrich) and (COCl)₂ (Acros Organics) were used without preliminary treatment. Diphenyliodphosphin Ph₂PI (**VI**) was synthesized according to previously published method [2].

Synthesis of the diphenyltriiodophosphorane adduct with N,N-dimethylacetamide (VIII). To 4.1 g of NaI (0.025 mol) in 4.2 ml of DMAA (VI) (0.005 mol) while stirring in an atmosphere of inert gas was added 5 g (4.1 ml, 0.023 mol) of Ph₂PCl (I) and 5 ml of CH₂Cl₂. The mixture warmed spontaneously to 50°C, and a white precipitate began to fall down. Stir was continued for another 2 h at 20°C. The precipitate was filtered off, washed twice with 5 ml of benzene and dried in a vacuum. The product was reprecipitated from dioxane to benzene and dried in a vacuum. Compound VIII (2.329 g, 29%) was obtained. Colorless needles, mp 70–72°C (decomp.) The compound is hygroscopic. ${}^{31}P-{}^{1}H$ NMR spectrum, δ , ppm: 32 s. ¹H NMR spectrum, δ , ppm: 7.72 m (4H, o-H, Ph), 7.47 m (2H, p-H, Ph), 7.37 m (4H, m-H, Ph), 3.21 s (18H, NCH₃), 3.10 s (18H, NCH₃), 2.40 s (18H,

CH₃C(O)). Found, %: C 37.93; H 6.32; I 35.80; N 8.00; P 2.78. C₃₆H₆₄I₃N₆O₆P. *M* 1088.02. Calculated, %: C 38.70; H 5.94; I 34.96; N 7.72; P 2.84.

Synthesis of the adduct of diphenyldichloro-[(N,N-dimethylamino)chloromethyl]phosphorane (XVa) with DMF (IIa). To 4 ml of DMF (IIa) at 0°C while vigorous stirring was slowly added dropwise 0.57 g (0.4 ml, 0.0054 mol) of (COCl)₂ (XIV). After the cessation of gas evolution, to the resulting suspension of XIII at -5°C while stirring was added 1.2 g (0.0054 mol) of diphenylchlorophosphine (I). The mixture was left at the same temperature for 18 h. Then the solidified reaction mixture was diluted while stirring with 20 ml of the toluene cooled to -10° C and stirred for 1 min. After formation of precipitate the liquid was decanted, the operation was repeated thriple. After drying in a vacuum was obtained 1.22 g (77%) of **XVa** as colorless needles, decomp. above 50°C. A highly hygroscopic substance, at storage decomposed rapidly. ³¹P NMR spectrum, δ , ppm: 22.0 d (²J_{PH} = 15 Hz), ¹H NMR spectrum, δ , ppm: 8.62 d (¹H, C-H, ${}^{2}J_{PH} = 15$ Hz,), 03.08 s (${}^{1}H$, DMF), 7.98 m (4H, C_6H_5 , o-H), 7.54 m (6H, C_6H_5 , m,p-H), 3.30 s (6H, 2NCH₃), 2.94 s (3H, NCH₃, DMF), 2.84 s (3H, NCH₃, DMF). Found, %: C 50.26, H 5.74, N 6.64, P 7,34. C₁₈H₂₄Cl₃N₂OP. M 421.71. Calculated %: C 51.26, H 5.71, N 6.39; P 7.70

Synthesis of (diphenylphosphoryl)-N,N-dimethylaminochloromethane (XVIa). A suspension of 1 g of the diphenyldichloro [(N, N-dimethylamino)chloromethyl)phosphorane] adduct with DMF (XVa) in 5 ml of DMF in an inert gas atmosphere was stirred for 6 h at 10°C. The precipitate formed was filtered off, washed with the cooled to 5°C of DMF (2×5 ml) and benzene (2×5 ml), and dried in a vacuum. 0.38 g (54%) of XVIa was obtained as a white substance, mp 92-94°C (decomp.). A highly hygroscopic substance. ¹H NMR spectrum, δ, ppm: 7.97 m (4H, *o*-H, Ph), 7.75 d (1 H, CH, ${}^{2}J_{PH} = 11$ Hz), 7.52 m (6H, *m,p*-H, Ph), 3.00 s [6H, N(CH₃)₂]. ³¹P NMR spectrum, δ, ppm: 22.7 d (${}^{2}J_{PH}$ = 11 Hz). Found, %: C 60.63, H 5.64, N 4.69, P 10.49. C₁₅H₁₇ClNPO. M 293.74. Calculated, %: C 61.34, H 5.83, N 4.77, P 10.55.

Catalytic synthesis of (diphenylphosphoryl)-(*N*,*N*-dimethylaminochloro)methane (XVIa). To a mixture of 6 ml of DMF (IIa) and 2 ml of benzene at 0°C while stirring was slowly added dropwise 0.17 g (0.12 ml, 0.0013 mol) of (COCl)₂ (XIV). Then, in an inert gas atmosphere was added 2 g (0.0091 mol) of diphenylchlorophosphine (I). After 1 h the reaction mass became of red-brown color, and deposition of the analytically pure compound **XVIa** started. After 18 h, to the reaction mixture was added 20 ml of benzene, and the mixture was stirred for 5 min. The precipitate was filtered off, washed with benzene (3×10 ml) and dried in a vacuum. 2.42 g (91%) of **XVIa** was obtained as colorless needles, mp 92–94°C (decomp.). The compound is hygroscopic. ³¹P NMR spectrum, δ , ppm: 22.8 g (²*J*_{PH} = 11 Hz). ¹H NMR spectrum, δ , ppm: 7.97 m (4H, *o*-H, Ph), 7.89 d (1H, CH, ²*J*_{PH} = 11 Hz), 7.53 m (6H, *m,p*-H, Ph), 3.08 s [6H, N(CH₃)₂]. Found, %: C 61.44, H 5.79, N 4.68, P 0.40. C₁₅H₁₇CINPO. *M* 293.74. Calculated, %: C 61.34, H 5.83, N 4.77, P 10.55.

Synthesis of N,N-dimethyl(diphenylphosphinomethylene)iminium iodide (IIIa) by reduction of (diphenylphosphoryl)(N,N-dimethylamino)chloromethane (XVIa) with diphenyliodophosphine (IV). To 1.5 g (0.0051 mol) of (diphenylphosphoryl)-N,Ndimethylaminochloromethane (XVIa) in 5 ml of DMAA while stirring in an inert gas atmosphere was added 0.74 g (0.0056 mol) of NaI and 1.75 g (0.0056 mol) of Ph₂PI (IV). The reaction mixture was stirred at 20°C for 3 h, then diluted with 30 ml of CH₂Cl₂. After 2 h the precipitate was filtered off and washed with CH_2Cl_2 (4×5 ml). The filtrate was evaporated under vacuum, and the oily residue was kept in a vacuum desiccator at 0.1 mm Hg. Over P₂O₅ for 18 h (to remove most of solvent). The resulting mixture of oil and crystals was triturated in 30 ml of diethyl ether, the solid residue was reprecipitated from DMF to benzene, and then from CH₂Cl₂ to benzene. After filtration, washing with benzene $(2 \times 5 \text{ ml})$ and drying in a vacuum, was isolated 1.33 g (71%) of IIIa as a palevellow needle-like crystals, mp 140–142°C (decomp.) [1]. ¹H NMR spectrum, δ , ppm: 9.92 d (1H, N=CH, ${}^{2}J_{\text{PH}} = 6$ Hz), 7.82 m (4H, C₆H₅, *o*-H), 7.47 m (6H, C₆H₅, *m*,*p*-H), 3.90 d (3H, CH₃, ${}^{4}J_{PH} = 6$ Hz), 3.22 d (3H, CH₃, ${}^{4}J_{PH} = 3$ Hz). ${}^{31}P-{}^{1}H$ NMR spectrum, δ , ppm: -2.2 s. Found, %: C 48.87, H 4.50, I 34.30, N 3.79, P 8.30. C₁₅H₁₇INP. M 369.09. Calculated, %: C 48.80, H 4.62, I 34.38, N 3.80, P 8.39.

Synthesis of *N*,*N*-dimethyl(diphenylphosphinomethylene)iminium iodide (IIIa) by reduction of (diphenylphosphoryl)-*N*,*N*-dimethylaminochloromethane (XVIa) with triphenylphosphine (XVII). To 1.5 g (0.0051 mol) of (diphenylphosphoryl)-*N*,*N*dimethylaminochloromethane (XVIa) in 5 ml of DMF while stirring under inert gas atmosphere was added

0.74 g (0.0056 mol) of NaI and 1.47 g (0.0056 mol) of Ph₃P (**XVII**). The reaction mixture was stirred at 20°C for 5 h, then diluted with 30 ml of CH₂Cl₂. After 2 h the precipitate formed was filtered off and washed with CH_2Cl_2 (4×5 ml). The filtrate was evaporated under vacuum, and to the oily residue was added 30 ml of benzene, the mixture was stirred for 10 min. The precipitate formed was reperecipitated from a DMFbenzene and then CH₂Cl₂-benzene mixtures. After filtration, washing with benzene $(2 \times 5 \text{ ml})$ and drying in a vacuum was isolated 1.54 g (82%) of IIIa as a pale-yellow needle-like crystals, mp 140-142°C (decomp.) [1]. ¹H NMR spectrum, δ , ppm: 9.92 d (1H, N=CH, ${}^{2}J_{PH} = 6$ Hz), 7.82 m (4H, C₆H₅, *o*-H), 7.47 m (6H, C₆H₅, *m*,*p*-H), 3.90 d (3H, CH₃, ${}^{4}J_{PH} = 6$ Hz), 3.22 d (3H, CH₃, ${}^{4}J_{PH} = 3$ Hz). ${}^{31}P-\{{}^{1}H\}$ NMR spectrum, δ , ppm: -2.2 s. Found, %: C 48.94, H 4.67, I 34.40, N 3.65, P 8.33. C₁₅H₁₇INP. M 369.09. Calculated, %: C 48.80, H 4.62, I 34.38, N 3.80, P 8.39.

REFERENCES

- Nifant'ev, E.E., Morgalyuk, V.P., Petrovskii, P.V., and Lysenko, K.A., *Izv. Ros. Akad. Nauk, Ser. Khim.*, 2007, vol. 56, no. 10, p. 2059.
- Morgalyuk, V.P., Petrovskii, P.V., Lysenko, K.A., and Nifant'ev, E.E., *Zh. Obshch. Khim.*, 2010, vol. 80, no. 1, p. 105.
- Gomelya, N.D., Matyusha, A.G., and Feshchenko, N.G., *Zh. Obshch. Khim.*, 1984, vol. 56, no. 6, p. 1242.
- Foss, V.L., Zh. Obshch. Khim., 1973, vol. 43, no. 6, p. 1000; Al'fonsov, V.A., Pudovik, D.A., Batyeva, E.S., and Pudovik, A.N., Izv. Akad. Nauk SSSR, Ser. Khim., 1982, vol. 4, p. 951.
- Feshchenko, N.G., Kovaleva, T.V., and Mel'nichuk, E.A., *Zh. Obshch. Khim.*, 1976, vol. 46, no. 2, p. 252.
- 6. Gloede, J., Z. Chem., 1982, vol. 22, p. 126.
- March, J., Advanced Organic Chemistry, Moscow: Mir, 1987, vol. 1, p. 176.
- Organicum, Weinheim: Wiley-VCH, GmbH & KGaA, 2004, p. 383.
- Bosschard, H.H., Mory, R., Schmidt, M., and Zollinger, H., *Helv. Chim. Acta*, 1959, vol. 42, p. 1659.
- 10. ³¹P Nuclear Magnetic Resonance, Graison, M. and Griffith, E.J., Eds., New York: Wiley, 1967.
- Morgalyuk, V.P., Abstract of Papers, 13th Int. Conf. on Phosphorus Chemistry (ICCP-XV), St. Petersburg: 2008, R-89.
- Morgalyuk, V.P., Petrovskii, P.V., Lysenko, K.A., and Nifant'ev, E.E., *Izv. Ros. Akad. Nauk, Ser. Khim.*, 2009, vol. 58, no. 1, p. 245.