Letters to the Editor

New synthesis of functionalized tertiary phosphines

E. E. Nifant´ev, V. P. Morgaliuk,* P. V. Petrovskii, and K. A. Lyssenko

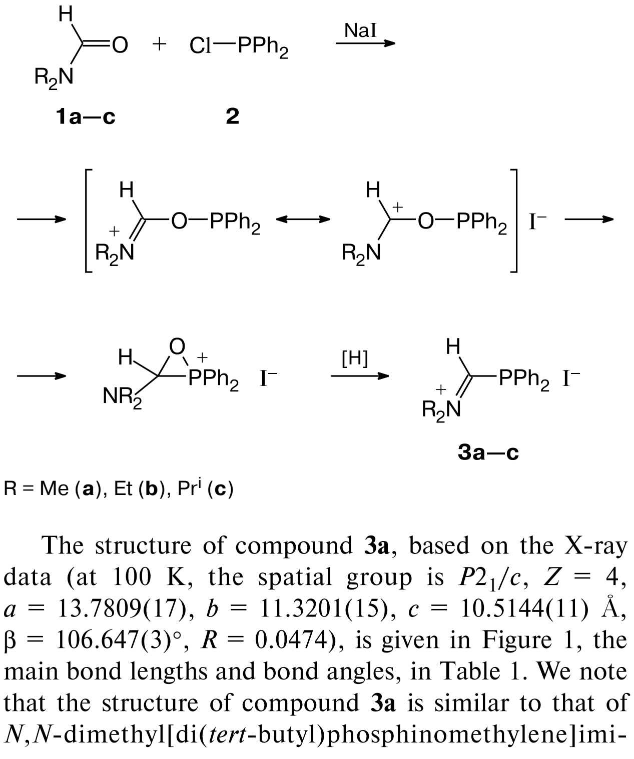
A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 119991 Moscow, Russian Federation.
Fax: +7 (499) 135 6549. E-mail: zaq@ineos.ac.ru

Functionalized phosphines and related phosphamides have been studied occasionally so far. Meanwhile, they are valuable subjects for solution of a number of structural problems[1,2] and development of the organophosphorus synthesis.[3—5] In particular, they are of use in the synthesis of stable aminophosphine carbene ligands for metal complexes with potential catalytic activity.[5]

In the present communication, a new reaction that is promising for the synthesis of complex phosphine compounds is presented. It consists in the interaction of *N*,*N*-dialkylformamides **1a—c** with chlorodiphenylphosphine **2** in the presence of NaI to give *N*,*N*-dialkyl(diphenylphosphinomethylene)iminium iodides **3a—c**. The suggested reaction pathway is given in Scheme 1.

It should be noted that the proposed scheme formally corresponds to the Vilsmeier—Haack reaction,[6] which includes the interaction of *N*,*N*-dimethylformamide with phosphorus oxychloride. The first step of this reaction consists in the formation of a complex phosphate, similar to the structures presented above, which rapidly decomposes to the phosphate anion and iminium cation. Thus, formamides behave differently in the reactions with phosphorus(III) and phosphorus(V) acid chlorides, which reflects the profound distinctions between these types of organophosphorus compounds.

Scheme 1



R = Me (**a**), Et (**b**), Pr^i (**c**)

The structure of compound **3a**, based on the X-ray data (at 100 K, the spatial group is $P2_1/c$, $Z = 4$, $a = 13.7809(17)$, $b = 11.3201(15)$, $c = 10.5144(11)$ Å, $\beta = 106.647(3)°$, $R = 0.0474$), is given in Figure 1, the main bond lengths and bond angles, in Table 1. We note that the structure of compound **3a** is similar to that of *N*,*N*-dimethyl[di(*tert*-butyl)phosphinomethylene]imi-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 2059—2060, October, 2007.

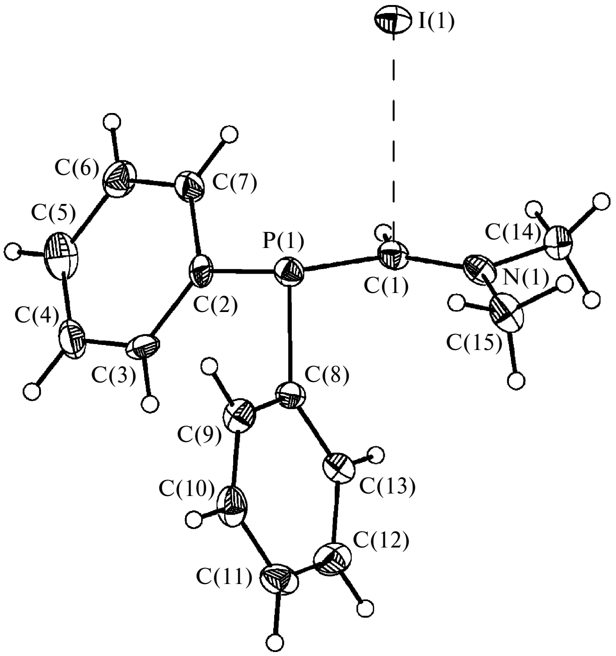


Fig. 1. General view of compound **3a** with atoms represented by thermal ellipsoids of vibrations (p = 50%).

Table 1. The main bond lengths (d) and bond angles (ω) in compound **3a**

Bond	d/Å	Angle	ω/deg
P(1)—C(1)	1.807(6)	C(1)—P(1)—C(8)	106.3(3)
P(1)—C(8)	1.826(6)	C(1)—P(1)—C(2)	98.8(2)
P(1)—C(2)	1.838(6)	C(8)—P(1)—C(2)	103.5(3)
N(1)—C(1)	1.289(7)	C(1)—N(1)—C(15)	123.2(5)
N(1)—C(15)	1.455(7)	C(1)—N(1)—C(14)	121.4(5)
N(1)—C(14)	1.475(7)	C(15)—N(1)—C(14)	115.4(5)
I(1)...—C(1)	3.526(2)	N(1)—C(1)—P(1)	127.8(5)

nium chloride[1] and *N,N*-diisopropyl[bis(diisopropylamino)phosphinomethylene]iminium dichlorophosphate,[3] synthesized earlier by other methods.

***N,N*-Dimethyl(diphenylphosphinomethylene)iminium iodide (3a).** Chlorodiphenylphosphine (**2**) (4.1 mL, 5 g, 0.023 mol) and NaI (3.5 g, 0.023 mol) were added to DMF (**1a**) (7 mL, 6.58 g, 0.09 mol) with stirring and in the atmosphere of an inert gas. The reaction mixture was stirred for 10 h at 20 °C and diluted with CH_2Cl_2 (30 mL). The precipitate that formed after 2 h was filtered off and washed with CH_2Cl_2 (2×5 mL). The combined filtrate was concentrated *in vacuo*, benzene (30 mL) was added to the oily residue, the precipitate that formed was reprecipitated from DMF with benzene, and then from CH_2Cl_2 with benzene, filtered, washed with benzene (2×5 mL), and dried *in vacuo*. Compound **3a** (3.35 g, 41%) was obtained as light yellow needle-like crystals, m.p. 140—141 °C (decomp.). ^{31}P NMR (162 MHz, $CDCl_3$), δ: –3.42. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 9.88 (m, 1 H, N=CH); 7.79 (m, 4 H, C_6H_5, *o*-H); 7.45 (m, 6 H, *m*-H, *p*-H, Ph); 3.89 (d, 3 H, Me, $^4J_{P,H}$ = 12.1 Hz); 3.32 (d, 3 H, Me, $^4J_{P,H}$ = 5.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 190.99 (d, P—C=N, $^1J_{C,P}$ = 39.7 Hz); 134.88 (d, *o*-Ph, $^2J_{C,P}$ = 21.6 Hz); 131.09 (s, *p*-Ph); 129.53 (d, *m*-Ph, $^3J_{C,P}$ = 9.0 Hz); 127.44 (d, P—C_{ipso}, $^1J_{C,P}$ = 1.8 Hz); 54.41 (d, Me, $^3J_{C,P}$ = 2.9 Hz); 46.62 (d, Me, $^3J_{C,P}$ = 10.5 Hz). Found (%): C, 48.29; H, 5.08; N, 3.75; P, 8.53; I, 34.75. $C_{15}H_{17}NPI$. Calculated (%): C, 48.80; H, 4.62; N, 3.80; P, 8.39; I, 34.38.

Compounds **3b** and **3c** were synthesized similarly. In both cases, the reaction time was 48 h.

***N,N*-Diethyl(diphenylphosphinomethylene)iminium iodide (3b)**, the yield was 45%, yellow needles, m.p. 78—80 °C. ^{31}P NMR (162 MHz, $CDCl_3$), δ: –5.80. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 9.90 (m, 1 H, N=CH); 7.82 (m, 4 H, *o*-H); 7.49 (m, 6 H, *m,p*-H); 4.27 (m, 2 H, CH_2); 3.71 (q, 2 H, CH_2, $J_{H,H}$ = 6.8 Hz); 1.48 (d, 3 H, Me, $^3J_{H,H}$ = 7.2 Hz, $J_{P,H}$ = 1.6 Hz); 1.06 (d, 3 H, Me, $^3J_{H,H}$ = 7.2 Hz, $J_{P,H}$ = 2.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 188.87 (d, P—C=N, $J_{C,P}$ = 40.5 Hz); 134.54 (d, *o*-Ph, $J_{C,P}$ = 21.5 Hz); 132.67 (s, *p*-Ph); 129.3 (d, *m*-Ph, $J_{C,P}$ = 11.7 Hz); 128.27 (d, P—C_{ipso}, $J_{C,P}$ = 2.2 Hz); 56.90 (d, CH_2, $J_{C,P}$ = 2.2 Hz); 52.20 (d, CH_2, $J_{C,P}$ = 10.5 Hz); 13.55 (d, Me, $J_{C,P}$ = 1.8 Hz); 10.10 (s, Me). Found (%): C, 51.43; H, 5.26; N, 3.55; P, 7.71; I, 31.99. $C_{17}H_{21}NPI$. Calculated (%): C, 51.40; H, 5.33; N, 3.53; P, 7.80; I, 31.93.

***N,N*-diisopropyl(diphenylphosphinomethylene)iminium iodide (3c)**, the yield was 24%, lemon yellow needles, m.p. 152—154 °C. ^{31}P NMR (162 MHz, $CDCl_3$), δ: –8.60. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 9.55 (m, 1 H, N=CH); 7.68 (m, 4 H, *o*-H); 7.48 (m, 6 H, *m,p*-H); 4.61 (sept.d, 1 H, N—CH, $J_{H,H}$ = 6.6 Hz, $J_{P,H}$ = 1.4 Hz); 4.56 (sept.d, 1 H, N—CH, $J_{H,H}$ = 6.7 Hz, $J_{P,H}$ = 1.8 Hz); 1.62 (dd, 6 H, Me, $J_{H,H}$ = 6.6 Hz, $J_{P,H}$ = 1.7 Hz); 1.21 (d, 6 H, Me, $J_{H,H}$ = 6.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 188.35 (d, P—C=N, $J_{C,P}$ = 42.6 Hz); 133.8 (d, *o*-Ph, $J_{C,P}$ = 20.8 Hz); 130.57 (s, *p*-Ph); 129.11 (d, *m*-Ph, $J_{C,P}$ = 8.4 Hz); 127.45 (d, P—C_{ipso}, $J_{C,P}$ = 13.1 Hz); 62.18 (d, N—CH, $J_{C,P}$ = 16.0 Hz); 56.37 (s, N—CH); 23.40 (s, Me); 17.64 (s, Me). Found (%): C, 53.51; H, 5.86; N, 3.30; P, 7.33; I, 29.96. $C_{19}H_{25}NPI$. Calculated (%): C, 53.66; H, 5.93; N, 3.29; P, 7.28; I, 29.84.

References

1. O. I. Kolodyazhnyi and A. I. Chernega, *Zh. Obshch. Khim.*, 1992, **62**, 2670 [*Russ. J. Gen. Chem.*, 1992, **62** (Engl. Transl)].
2. M. Joleibhavoup, A. Baceiredo, O. Traitler, R. Ahlrichs, M. Nieger, and G. Bertrand, *J. Am. Chem. Soc.*, 1992, **114**, 10559.
3. J. Youmri, Y. Leridu, H. Gornitzka, A. Baceidero, and G. Bertrand, *Eur. J. Inorg. Chem.*, 1998, **10**, 1539.
4. N. Mercerou, A. Baceiredo, and G. Bertrand, *Chem. Commun.*, 2002, **16**, 2250.
5. S. Conejero, Y. Canac, F. S. Than, and G. Bertrand, *Ang. Chem. Int. Ed.*, 2004, **43**, 4088.
6. Sh. A. Samsoniya, *Khim. Geterotsikl. Soedin*, 1982, **2**, 206 [*Chem. Heterocycl. Compd.*, 1982, **2** (Engl. Transl.)].

Received July 19, 2007;
in revised form August 23, 2007