Heteroatom Chemistry
Volume 3, Number 4, 1992

1,1-Dichloroalkylphosphonates: Convenient Starting Materials for Low-Coordinated Trivalent Phosphorus Compounds

Catherine Grandin, Elie About-Jaudet, and Noël Collignon*

Laboratoire des Composés Organophosphorés, INSA-IRCOF, BP O8, 76131 Mont-Saint-Aignan Cedex, France

Jean-Marc Denis

Groupe de Physicochimie Structurale 3, UA CNRS n°704, Université de Rennes I, Campus de Beaulieu, 35042 Rennes Cedex, France

Philippe Savignac

Laboratoire de Chimie du Phosphore et des Métaux de Transition, DCPH-Ecole Polytechnique, 91128 Palaiseau Cedex, France

Received 22 July 1991

ABSTRACT

Diisopropyl 1,1-dichloroalkylphosphonates bearing various groups (alkyl, aryl, allyl, benzyl, phenylthiolate, trimethylsilyl) in the α-position were reduced to the corresponding primary 1,1-dichlorophosphines by the $LiAlH_4$–$AlCl_3$ system in diethyl ether. Subsequent dehydrochlorination with tertiary amines in the presence of trapping dipolar compounds (ethyl diazoacetate or n-hexylazide) led to the expected 1,2,4-diazaphospholes or 3H-1,2,3,4-triazaphospholes.

Since the first report by Gier [1] on the synthesis of phosphaethyne, numerous methods for the preparation of phosphaalkynes and phosphaalkenes have been described and fully reviewed in the literature [2–5]. Unquestionably, the β-elimination strategy appears to be a significant methodology that emerges from the various reaction pathways. Flash vacuum pyrolysis or base-induced dehydrohalogenation are currently used to convert halogenated or silylated phosphine precursors into a wide variety of kinetically stabilized as well as short-lived phosphorus compounds containing P≡C or P=C bonds. In spite of the rapid development of this chemistry, its synthetic impact remains related to problems such as easy access to starting materials, improved experimental techniques, and enlargement of the structural field to include other functional groups.

Recently [6, 7], we demonstrated the utility of diisopropyl 1,1-dichloroalkylphosphonates **1** as starting materials for unstabilized phosphaalkynes **4** through a sequence combining low temperature reduction with high temperature elimination (VGSR). Successive vacuum transfers are needed to assure the purification of 1,1-dichloroalkylphosphine intermediates **2** and subsequent dehydrochlorination. However, the vacuum technique limits the applicability of the method to volatile phosphines **2** (R^1 = H, low alkyl, Me_3Si, Cl).

In the present work, we wish to present new developments of this methodology, especially the extension to heavier R^1 groups. For this purpose, we propose to realize the entire manipulation, re-

*To whom correspondence should be addressed.

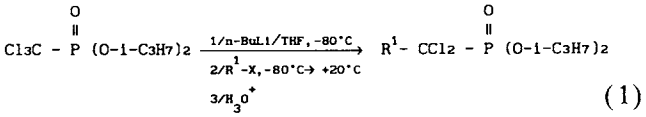
1042-7163/92/$3.50 + .25

duction, and dehydrochlorination in solution and to trap the transient phosphaalkenes with a dipolar molecule.

RESULTS AND DISCUSSION

Synthesis of the 1,1-Dichloroalkylphosphonates **1**

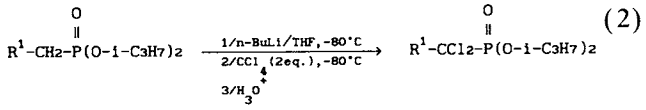
The 1,1-dichloroalkylphosphonates **1** bearing an alkyl, allyl, benzyl, or trimethylsilyl group in the α position were prepared in 60–80% isolated yields from diisopropyl trichloromethylphosphonate and related halogenated reagents by the conventional anionic route [8, 9] (Eq. 1).



(1)

1a : R^1= CH_3
1b : R^1= n-C_3H_7
1c : R^1= n-C_5H_{11}
1d : R^1= CH_2=CH-CH_2
1e : R^1= C_6H_5-CH_2
1i : R^1= $(CH_3)_3Si$

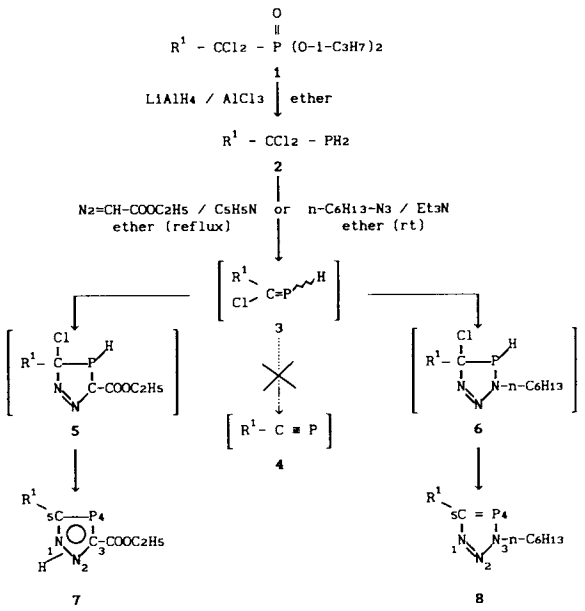
For R^1 = aryl, the corresponding arylmethylphosphonates were used as starting materials. Treatment of the intermediate carbanions with two equivalents of CCl_4 led to the expected 1,1-dichloroalkylphosphonates in good yields [10] (Eq. 2).



(2)

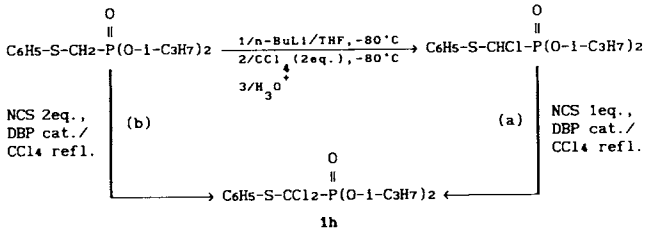
1f : R^1= C_6H_5
1g : R^1= 3-CH_3O-C_6H_4

The same procedure applied to the phenylthiomethylphosphonate gave only the monochlorinated product [11] (in 56% yield after flash chromatography). This last compound was then chlorinated with *N*-chlorosuccinimide (NCS) in refluxing CCl_4, in the presence of a catalytic amount of dibenzoyl peroxide (DBP), to afford the 1,1-dichlorophenylthiomethylphosphonate **1h** in 52% isolated yield (overall yield from phenylthiomethylphosphonate by route (a): 30%). Another more expeditious route (b) consisted of the direct dichlorination of the phenylthiomethylphosphonate with two equivalents of NCS affording **1h** in 50% isolated yield (Eq. 3).



SCHEME 1

(3)



Reduction of the 1,1-Dichloroalkylphosphonates **1**

We studied the course of the overall sequence (reduction, elimination) in a diethyl ether solution under dry nitrogen, and we trapped the phosphaalkene intermediates **3** by ethyl diazoacetate or *n*-hexyl azide, which led to the primary adducts **5** or **6**; these spontaneously aromatized to **7** or **8**, respectively (Scheme 1).

Reduction (**1** → **2**) was performed at −80°C in ether with a stirred mixture of $LiAlH_4$ and $AlCl_3$. The relative amounts of the reagents were adjusted for the generation of the formal $AlHCl_2$ reducing agent [12]. This system proved to be ineffective for $R^1 = C_6H_5—S$, most likely because of the strong complexation between the very electropositive metallic site of the reagent and the sulfur atom of the substrate. In this last case, reduction was achieved by the AlH_3 reducing agent [13] using a strict stoichiometric amount. With an excess of the reagent, we observed a signal at $\delta = -80$ in the ^{31}P-NMR spectrum, which is attributed to the monochlorophosphine $C_6H_5—S—CHCl—PH_2$.

In all the other examples examined, the reduction was quantitative and limited to the phosphonate group as indicated by ^{31}P NMR spectroscopy.

Subsequent hydrolysis was performed at a temperature lower than −10°C by addition of deoxygenated water (6 eq) in order to precipitate the aluminum salts. Separation of the dichloroalkylphosphine **2** from this heterogeneous mixture was easily realized by filtration under a slight pressure of nitrogen, leading to the ether solution of **2**, which was ready for further reactions (Method A). In addition, volatile phosphines **2a–2d** could be purified by trap-to-trap distillation (Method B). The overall yield (^{31} PNMR spectroscopy, with $(C_6H_5)_3P$ as internal reference) was always higher than 65%. All the phosphines had to be used immediately after filtration. Phosphines **2a–2g** and **2i** decomposed slowly at room temperature; by contrast, phosphine **2h** started to decompose spontaneously at −30°C.

Dehydrochlorination of phosphines **2** was effected under dry nitrogen, in an ether solution containing the trapping dipolar molecule and the tertiary amine. Progress of the addition of the dipolar molecule to the phosphaalkene intermediate **3** was monitored by ^{31} P NMR spectroscopy. We never detected the formation of the primary cycloadduct **5** or **6**. The conditions depended on the strength of the base: For the more stable phosphines **2a–2e** and **2i**, the reaction with ethyl diazoacetate was achieved in about 3 hours in refluxing ether in the presence of pyridine; with *n*-hexyl azide the addition was preferably conducted with triethylamine at room temperature and was complete in about 12 hours. The very unstable phosphine **2h** decomposed before it reacted.

The spectroscopic data of the isolated adducts **7** and **8** were consistent with the proposed structures (see Experimental section for ^{1}H and ^{13}C NMR data). As for the examples reported in the literature [14–17], 1,2,4-diazaphospholes **7** are stable products that might be purified by flash chromatography. By contrast, the 3H-1,2,3,4-triazaphospholes were relatively unstable compounds that decomposed on chromatographic columns. Only the adducts **8a–8d** and **8i** could be isolated at room temperature, after removal of the triethylammonium chloride by filtration and elimination of the volatile residues from the filtrate under vacuum. The adducts **8f–8h** were not observed.

CONCLUSION

Starting from readily available 1,1-dichloroalkylphosphonates **1**, we conducted the successive operations using conventional equipment: reduction of **1** to 1,1-dichloroalkylphosphines **2**, subsequent dehydrochlorination, and trapping the transient reactive phosphaalkene intermediates **3**. This method seems particularly well adapted for the study of high-boiling and functional derivatives.

EXPERIMENTAL

General

Reactions and transfers were carried out under dry nitrogen in a well-ventilated hood. In Method A, the reduction, filtration and condensation steps were performed in conventional glassware flamed before use. For Method B, a vacuum apparatus similar to the one previously described was used [12]. Ether and THF were dried by distillation from sodium-benzophenone. ^{1}H NMR spectra were recorded on a Varian T-60 or a Bruker AC-200 spectrometer at 60 or 200 MHz respectively. ^{31}P and ^{13}C NMR spectra (^{1}H-decoupled, FT) were recorded on a Bruker AC-200 spectrometer at 81.00 and 50.32 MHz respectively. Chemical shifts are reported with respect to tetramethylsilane (TMS) as an internal standard for ^{1}H and ^{13}C and to 85% phosphoric acid as an external standard for ^{31}P. Positive shifts are downfield of reference. The coupling constants are given in Hertz. IR spectra were recorded on a Beckmann 4250 spectrophotometer. Gas chromatographic separations (GC) were performed on a Girdel 300 chromatograph. Flash chromatography (FC) was performed with Merck 60 silica gel or active neutral aluminum oxide (50–160 μm). Elemental microanalyses were realized on a Carlo Erba analyzer. Melting points were taken on a Kofler apparatus and are uncorrected.

Preparation of the Diisopropyl 1,1-Dichloroalkylphosphonates **1**

General Procedure for **1a–1e**, **1i** *(Eq. 1) [8, 9].* To a stirred solution of *n*-BuLi (1.1 eq) in anhydrous THF at −80°C was added dropwise a solution in THF of 1 eq of diisopropyl trichloromethylphosphonate (prepared by the Arbuzov reaction between CCl_4 and triisopropyl phosphite [18]), and stirring was continued at −80°C for 15 min. A solution of R^1X (1.5 eq) in THF was then added at −80°C, and the resulting mixture was slowly warmed to room temperature. An aqueous solution of 4 N HCl was then added until the pH was slightly acidic. After separating the resulting two phases, the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried ($MgSO_4$), the solvent was removed under reduced pressure, and the crude product purified (distillation or FC on silica gel). Results are given as follows: R^1X/bp°C, mmHg or eluting

solvent/pure yield %/^{31}P NMR ($CDCl_3$): δ/^{1}H NMR ($CDCl_3$): δ, multiplet (J in Hz), nH, type of H.

1a: CH_3I/63, 0.1/74/10.0/1.3, d(6), 12H, $[(CH_3)_2CH—O]_2$; 2.1, d(12), 3H, $CH_3—CCl_2$; 2.8, m, 2H, $[(CH_3)_2CH—O]_2$.

1b: n-C_3H_7I/85, 0.1/62/10.2/0.92, t(7), 3H, $CH_3—(CH_2)_2$; 1.3, d(6), 12H, $[(CH_3)_2CH—O]_2$; 1.7, m, 2H, $CH_3—CH_2—CH_2$; 2.2, m, 2H, $CH_2—CCl_2$; 4.8, m, 2H, $[(CH_3)_2CH—O]_2$.

1c: n-C_5H_7—I/105, 0.1/60/10.2/0.74, t(7), 3H, $CH_3—(CH_2)_4$; 1.2, d(6), 12H, $[(CH_3)_2CH—O]_2$; 1.6, m, 6H, $CH_3—(CH_2)_3—CH_2$; 2.1, m, 2H, $CH_2—CCl_2$; 4.9, m, 2H, $[(CH_3)_2CH—O]_2$.

1d: $CH_2=CH—CH_2Br$/80, 0.1/70/9.08/1.2, d(6), 12H, $[(CH_3)_2CH—O]_2$; 2.85, t(6), 2H, $CH_2—CCl_2$; 4.8, m, 2H, $[(CH_3)_2CH—O]_2$; 4.6 to 6.0, m, 3H, $CH_2=CH$.

1e: $C_6H_5CH_2Br$/ether, hexane: 70, 30/60/9.3/1.4, d(6), 12H, $[(CH_3)_2CH—O]_2$; 3.4, d(6), 2H, $CH_2—CCl_2$; 4.8, m, 2H, $[(CH_3)_2CH—O]_2$; 7.23, s, 5H, C_6H_5.

1i: $(CH_3)_3SiCl$/85, 0.2/80/12.2/0.3, s, 9H, $(CH_3)_3Si$; 1.3, d(6), 12H, $[(CH_3)_2CH—O]_2$; 4.85, m, 2H, $[(CH_3)_2CH—O]_2$.

General Procedure for **1f** *and* **1g** *(Eq. 2).* To a stirred solution of n-BuLi (1.1 eq) in THF at −80°C was added dropwise a solution in THF of 1 eq of the diisopropyl arylmethylphosphonate (prepared by the Arbuzov reaction between the corresponding arylmethyl bromide and triisopropyl phosphite [15]) with stirring continued at −80°C for 15 minutes. A solution of CCl_4 (2 eq) in THF was then added at −80°C. The resulting black mixture was allowed to warm to 0°C and hydrolyzed at this temperature. After separating the phases, the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried ($MgSO_4$) and the solvents removed in vacuo to give a black oil that was first purified by FC on silica gel (eluent: ether/hexane = 50/50), then distilled. The results are given as follows: bp°C, mmHg/pure yield %/^{31}P NMR ($CDCl_3$): δ/^{1}H NMR ($CDCl_3$): δ, multiplet (J in Hz), nH, type of H.

1f: 135, 0.5/60/7.76/1.26, t(6), 12H, $[(CH_3)_2CH—O]_2$; 4.62, m, 2H, $[(CH_3)_2CH—O]_2$; 7.2 to 7.8, m, 5H, C_6H_5.

1g: 160, 0.5/60/7.62/1.24, t(6), 12H, $[(CH_3)_2CH—O]_2$; 3.8, s, 3H, $CH_3—O$; 4.65, m, 2H, $[(CH_3)_2CH—O]_2$; 6.8 to 7.5, m, 4H, C_6H_4.

General Procedure for Phosphonate **1h** *(Eq. 3, route (b)).* In a two-necked flask equipped with a magnetic stirrer, thermometer, and reflux condenser was refluxed under stirring for 8 hours, a mixture of 10 g (35 mmol) of diisopropyl phenylthiomethylphosphonate (prepared by the Arbuzov reaction between chloromethyl phenyl sulfide and triisopropyl phosphite), 10.3 g (77 mmol) of N-chlorosuccinimide, 200 mL of CCl_4, and a few mg of dibenzoyl peroxide. After cooling, the mixture was filtered, the filtrate was washed with water and dried ($MgSO_4$), and the solvent was removed in vacuo to give a colorless oil (8.1 g). The crude product was purified by FC on silica gel (eluent: ether/hexane = 70/30) to give 6.2 g (50% yield) of pure **1h**: ^{31}P NMR($CDCl_3$) δ = 5.78/^{1}H NMR ($CDCl_3$) δ = 1.3, d(6 Hz), 12H, $[(CH_3)_2CH—O]_2$; 4.86 ppm, m, 2H, $[(CH_3)_2CH—O]_2$; 7.1 to 8.1, m, 5H, C_6H_5.

Preparation of the 1,1-Dichloroalkylphosphines **2**

General Procedure for **2a–2e**, **2i**. $LiAlH_4$ (15 mmol) as 15 mL of a 1 M solution in diethyl ether was introduced into a 50-mL two-necked flask. The flask was cooled to −80°C, and $AlCl_3$ (6.0 g, 45 mmol) was quickly added under magnetic stirring. The resulting suspension was allowed to warm to nearly 10°C until the mixture became homogeneous, then cooled again at −80°C, and freshly distilled diethyl ether (15 mL) was added. The 1,1-dichloroalkylphosphonate (15 mmol) in diethyl ether (5 mL) was dropped into the stirred mixture at a rate to maintain the temperature near −80°C. At the end of the addition, the mixture was allowed to warm to room temperature, then hydrolyzed at −10°C with degased water (1.6 mL, 90 mmol). The resulting heterogeneous mixture was filtered at room temperature, through a porous plate (n°4), under a slight pressure of nitrogen to give a 0.3 M etheral solution of the 1,1-dichloroalkylphosphine.

General Procedure for **2f** *and* **2g**. The reduction was performed under the conditions reported above up to the end of addition of the phosphonate. The mixture was allowed to warm to −50°C, then hydrolyzed and rapidly filtered so that the temperature of the filtrate was maintained lower than −10°C.

Typical Procedure for **2h**. The reduction and subsequent work-up were conducted under similar conditions as above (**2f** and **2g**) except for the respective amounts of reagents: In this case, we used 45 mL of the 1 M etheral solution of $LiAlH_4$ (45 mmol) and 2 g of $AlCl_3$ (15 mmol) to reduce 5.3 g (15 mmol) of the phosphonate **1h**.

Preparation of the 1,2,4-Diazaphospholes **7**

General Procedure for Compounds **7a–7e**, **7i**. An ether solution of the 1,1-dichloroalkylphosphine **2** (12 mmol) was introduced under N_2, at room temperature, into a 50-mL two-necked flask equiped with a septum, reflux condenser, and magnetic stirrer. 2.5 mL of ethyl diazoacetate (24 mmol), then 3.8 mL of pyridine (48 mmol) were injected and

the mixture refluxed for about 5 hours, until the phosphine **2** was fully consumed as confirmed by ^{31}P NMR measurements. The precipitate of pyridinium hydrochloride was separated by filtration and washed with ether, and the filtrate was evaporated under reduced pressure. The oily residue was then purified by flash chromatography on activated alumina; excess of reagents was first removed (eluant:hexane/ether = 30/70, vol/vol), then subsequent elution with methanol gave the pure 1,2,4-diazaphosphole **7**.

General Procedure for Compounds **7f** *and* **7h**. The same amounts of reagents as above were used. The solution of the phosphine **2** was introduced into the flask cooled at −80°C, and the other reagents were successively added at this temperature. The freezing bath was then removed and the mixture was allowed to warm to room temperature with stirring until complete consumption of the phosphine had occurred. Subsequent work-up was the same as described above.

The following data (physical state; IR (in KBr for solids, film for liquids), cm^{-1} (group); ^1H NMR ($CDCl_3$): δ, multiplet (*J* in Hz), nH, type of H; ^{13}C NMR ($CDCl_3$): δ ($^nJ_{CP}$ in Hz), type of C; elemental CHN analysis) refer to the successive entries of Table 1.

7a: white crystals, mp = 130°C (Lit.: 134°C [12]; IR: 3140 (NH), 2985 (CH), 1730 (CO), 1400, 1325, 1285, 1100, 1025; ^1H NMR: 1.4, t(7), 3H, CH_3CH_2O; 2.6, d(10), 3H, $CH_3—C_{(5)}$; 4.4, q(7), 2H, CH_3CH_2O; 10.2, bl, 1H, NH; ^{13}C NMR: 14.05, CH_3CH_2O; 14.9 (^2J = 20.8), $CH_3—C_{(5)}$; 61.4, CH_3CH_2O; 163.5 (^2J = 22.6), C(O); 166.5 (^1J = 59), $C_{(5)}$; 174.8 (^1J = 55), $C_{(3)}$; Anal. Calcd. for $C_6H_9N_2O_2P$: C, 41.86; H, 5.23; N, 16.28. Found: C, 41.4; H, 4.9; N, 16.5.

7b: oil; IR: 3140 (NH), 2980 (CH), 1720 (CO), 1400, 1320, 1290, 1110, 1025; ^1H NMR: 1.1, t(7), 3H, $CH_3CH_2CH_2$; 1.45, t(7), 3H, CH_3CH_2O; 1.7, m, 2H, $CH_3CH_2CH_2$; 3.0, dt (8, 7), 2H, $CH_2—C_{(5)}$; 4.45, q(7), 2H, CH_3CH_2O; 12.0, bl, 1H, NH; ^{13}C NMR: 13.45, $CH_3CH_2CH_2$; 14.0, CH_3CH_2O; 24.2 (^3J = 7), $CH_3CH_2CH_2$; 31.2 (^2J = 16), $CH_2—C_{(5)}$; 61.1, CH_3CH_2O; 163.7 (^2J = 23.2), C(O); 166.5 (^1J = 59), $C_{(5)}$; 180.2 (^1J = 56), $C_{(3)}$; Anal. Calcd. for $C_8H_{13}N_2O_2P$: C, 48.00; H, 6.50; N, 14.00. Found: C, 48.8; H, 6.9; N, 13.5.

7c: oil; IR: 3130 (NH), 2980 (CH), 1750 (CO), 1400, 1320, 1285, 1100, 1025; ^1H NMR: 0.95, m, 3H, $CH_3(CH_2)_4$; 1.4, t(7), 3H, CH_3CH_2O; 1.2 to 1.8, m, 6H, $CH_3(CH_2)_3CH_2$; 2.9, dt (9, 7), 2H, $CH_2—C_{(5)}$; 4.35, q(7), 2H, CH_3CH_2O; 12.0, bl, 1H, NH; ^{13}C NMR: 13.6, $CH_3(CH_2)_4$; 14.0, CH_3CH_2O; 23.2 and 23.3, $CH_3(CH_2)_2CH_2CH_2$; 23.9 (^3J = 7), $CH_2CH_2—C_{(5)}$; 30.7 (^2J = 16), $CH_2—C_{(5)}$; 61.2, CH_3CH_2O; 163.5 (^2J = 23), C(O); 166.5 (^1J = 59), $C_{(5)}$; 180.0 (^1J = 56), $C_{(3)}$; Anal. Calcd. for $C_{10}H_{17}N_2O_2P$: C, 52.63; H, 7.45; N, 12.28. Found: C, 52.9; H, 7.8; N, 12.0.

7d: oil; IR: 3080 (NH), 2980 (CH), 1750 (CO), 1640, 1490, 1370, 1215; ^1H NMR: 1.3, t(7), 3H, CH_3CH_2O; 3.7, dd (8, 7), 2H, $CH_2—C_{(5)}$; 4.3, q(7), 2H, CH_3CH_2O; 5 to 6.2, m, 3H, $CH_2=CH$; 10.3, bl, 1H, NH; ^{13}C NMR: 13.7, CH_3CH_2O; 33.1 (^2J = 17), $CH_2—C_{(5)}$; 60.9, CH_3CH_2O; 127.6, $CH_2=CH$; 146.7, $CH_2=CH$; 163.9 (^2J = 23.5), C(O); 166.5 (^1J = 50), $C_{(5)}$; 177.6 (^1J = 54), $C_{(3)}$; Anal. Calcd. for $C_8H_{11}N_2O_2P$: C, 48.48; H, 5.55; N, 14.14. Found: C, 48.8; H, 5.9; N, 13.9.

TABLE 1 ^{31}P NMR (C_6D_6) Chemical Shifts and Yields of the 1,1-Dichloroalkylposphines **2**, of the 1,2,4-Diazaphospholes **7**, and of the 3H-1,2,3,4-Triazaphospholes **8**

Entry	R^1	δ (Yield %) of **2**	δ (Yield[c] %) of **7**	δ (Yield[d] %) of **8**
a	CH_3	−48[e] (85[a], 80[b])	+99.6[g] (40)	+173.8 (35)
b	*n*-C_3H_7	−56 (83[a], 70[b])	+98.1 (36)	+172.9 (33)
c	*n*-C_5H_{11}	−56 (80[a], 65[b])	+98.2 (34)	+174.5 (35)
d	$CH_2=CH—CH_2$	−61 (85[a], 70[b])	+98.3 (40)	+174.0 (30)
e	$C_6H_5—CH_2$	−60 (87[a])	+96.5 (30)	+175.0 (35)
f	C_6H_5	−32.5 (85[a])	+95.6[h] (25)	[i] —
g	3-$CH_3O—C_6H_4$	−32.7 (85[a])	[i] —	[i] —
h	$C_6H_5—S$	−51.7 (70[a])	+95.8 (20)	[i] —
i	$(CH_3)_3Si$	−83[f] (70[a])	+134.0 (15)	+211.0 (20)

[a] Yields of **2** after filtration (Method A).
[b] Yields of **2** after trap-to-trap distillation [19] (Method B).
[c] Yields of **7** after purification by flash chromatography on neutral Al_2O_3.
[d] Yields of crude **8**, pure in ^{31}P NMR.
[e] Lit.: −46 ($CDCl_3$) [7].
[f] Lit.: −79 ($CDCl_3$) [7].
[g] Lit.: +98.9 ($CDCl_3$) [17].
[h] Lit.: +98.6 (C_6D_6) [20].
[i] Not observed.

7e: oil; IR: 3215 (NH), 2980 (CH), 1685 (CO), 1510, 1405, 1325, 1105, 800, 750, 700; ^{1}H NMR: 1.3, t(7), 3H, $C\underline{H}_3CH_2O$; 3.5, d(7), 2H, $C\underline{H}_2—C_6H_5$; 4.4, q(7), 2H, $CH_3C\underline{H}_2O$; 7.3, s, 5H, $C_6\underline{H}_5$; 10.0, bl, 1H, N$\underline{H}$; ^{13}C NMR: 14.1, $\underline{C}H_3CH_2O$; 35.8 (^2J = 18.6), $\underline{C}H_2—C_{(5)}$; 61.4, $CH_3\underline{C}H_2O$; 126.7, $\underline{C}_{arom(2')}$; 128.6, $\underline{C}_{arom(3',4')}$; 138.7, $\underline{C}_{arom(1')}$; 163.0 (^2J = 22.4), $\underline{C}$(O); 165.2 (^1J = 58.3), $\underline{C}_{(5)}$; 179.6 (^1J = 56.5), $\underline{C}_{(3)}$; Anal. Calcd. for $C_{12}H_{13}N_2O_2P$: C, 58.06; H, 5.24; N, 11.29. Found: C, 58.2; H, 5.6; N, 11.1.

7f: yellow solid, mp = 120°C; IR: 3180 (NH), 2965 (CH), 1710 (CO), 1490, 1470, 1450, 1400, 1385, 1300, 1180, 1140, 1105; ^{1}H NMR: 1.3, t(7), 3H, $C\underline{H}_3CH_2O$; 4.4, q(7), 2H, $CH_3C\underline{H}_2O$; 7.2 to 7.8, 5H, $C_6\underline{H}_5$; 10.0, bl, 1H, N$\underline{H}$; ^{13}C NMR: 13.95, $\underline{C}H_3CH_2O$; 61.5, $CH_3\underline{C}H_2O$; 126.2 (^3J = 9.9), $\underline{C}_{arom(2')}$; 128.8, $\underline{C}_{arom(3')}$; 129.1, $\underline{C}_{arom(4')}$; 133.0 (^2J = 16.8), $\underline{C}_{arom(1')}$; 162.5 (^2J = 22.6), $\underline{C}$(O); 165.0 (^1J = 56), $\underline{C}_{(5)}$; 177.8 (^1J = 55.9), $\underline{C}_{(3)}$; Anal. Calcd. for $C_{11}H_{11}N_2O_2P$: C, 56.41; H, 4.70; N, 11.96. Found: C, 56.5; H, 4.9; N, 11.6.

7g: oil; IR: 3120 (NH), 2980 (CH), 1715 (CO), 1600, 1490, 1465, 1430, 1400, 1300, 1225, 1110; ^{1}H NMR: 1.15, t(7), 3H, $C\underline{H}_3CH_2O$; 3.65, s, 3H, $C\underline{H}_3O$; 4.1, q (7), 2H, $CH_3C\underline{H}_2O$; 7.1 to 7.35, m, 4H, $C_6\underline{H}_4$; 10.5, bl, 1H, N$\underline{H}$; ^{13}C NMR: 13.8, $\underline{C}H_3CH_2O$; 55.0, $\underline{C}H_3O$; 61.15, $CH_3\underline{C}H_2O$; 110.7 (^3J = 9.7), $\underline{C}_{arom(2')}$; 115.4, $\underline{C}_{arom(5')}$; 118.8 (^3J = 10.7), $\underline{C}_{arom(6')}$; 129.9, $\underline{C}_{arom(4')}$; 133.1 (^2J = 16.2), $\underline{C}_{arom(1')}$; 159.8, $\underline{C}_{arom(3')}$; 163.0 (^2J = 23), $\underline{C}$(O); 166.3 (^1J = 57), $\underline{C}_{(5)}$; 176.9 (^1J = 53.4), $\underline{C}_{(3)}$; Anal. Calcd. for $C_{12}H_{13}N_2O_2P$: C, 54.54; H, 4.92; N, 10.60. Found: C, 55.2; H, 5.1; N, 10.2.

7i: oil; IR: 3130 (NH), 2980 (CH), 1720 (CO), 1380, 1305, 1250, 1205, 1100, 1000, 850; ^{1}H NMR: 0.4, s, 9H, $(C\underline{H}_3)_3Si$; 1.35, t(7), 3H, $C\underline{H}_3CH_2O$; 4.4, q(7), 2H, $CH_3C\underline{H}_2O$; 10.0, bl, 1H, N$\underline{H}$; ^{13}C NMR: −0.58 (^3J = 4), $(\underline{C}H_3)_3Si$; 14.1, $\underline{C}H_3CH_2O$; 61.0, $CH_3\underline{C}H_2O$; 164.1 (^2J = 23), $\underline{C}$(O); 168.7 (^1J = 65.6), $\underline{C}_{(5)}$; 178.1 (^1J = 72.6), $\underline{C}_{(3)}$; Anal. Calcd. for $C_8H_{15}N_2O_2PSi$: C, 41.74; H, 6.52; N, 12.17. Found: C, 41.9; H, 6.6; N, 11.9.

Preparation of the 3H-1,2,3,4-Triazaphospholes **8**

General Procedure. An ether solution of the 1,1-dichloroalkylphosphine **2** (12 mmol) was introduced under N_2, at −60°C, into a 50-mL two-necked flask equipped with a septum, reflux condenser, and magnetic stirrer. Three milliliters of *n*-hexyl azide (24 mmol), then 6.7 mL of triethylamine (48 mmol) were added at −60°C, and the resulting mixture was allowed to warm to room temperature, with stirring, until complete consumption of the phosphine had occurred. The precipitate of triethylammonium chloride was separated by filtration and washed with ether, and the filtrate was evaporated under reduced pressure to give the crude 3H-1,2,3,4-triazaphosphole **8** as oil.

The following data (IR (film), cm^{-1}; ^{1}H NMR ($CDCl_3$): δ, multiplet (J in Hz), nH, type of $\underline{H}$; ^{13}C NMR ($CDCl_3$): δ ($^nJ_{CP}$ in Hz), type of $\underline{C}$) refer to the successive entries of Table 1.

8a: IR: 2965, 1460, 1260, 1040, 800; ^{1}H NMR: 0.9, m, 3H, $C\underline{H}_3—(CH_2)_5$; 1.33, m, 8H, $CH_3—(C\underline{H}_2)_4$; 2.7, d(12), 3H, $C\underline{H}_3—C_{(5)}$; 4.5, dt (7, 6), 2H, $C\underline{H}_2—N_{(3)}$; ^{13}CNMR: 13.6, $\underline{C}H_3—(CH_2)_5$; 14.2 ($^2J$ = 24.6), $\underline{C}H_3—C_{(5)}$; 22.1 and 25.8, $CH_3—(\underline{C}H_2)_2$; 30.8, $\underline{C}H_2—(CH_2)_2N_{(3)}$; 32.0 ($^3J$ = 3.6), $\underline{C}H_2—CH_2N_{(3)}$; 52.0 ($^2J$ = 12), $\underline{C}H_2—N_{(3)}$; 178.4 (^1J = 50.7), $\underline{C}_{(5)}$.

8b: IR: 2980, 1460, 1260, 1010, 800; ^{1}H NMR: 0.9, m, 3H, $C\underline{H}_3—(CH_2)_5$; 1.1, t(7), 3H, $C\underline{H}_3—(CH_2)_2$; 1.35, m, 8H, $CH_3—(C\underline{H}_2)_4$; 1.7, m, 2H, $CH_3—C\underline{H}_2—CH_2$; 3.1, dt (8, 7), 2H, $C\underline{H}_2—C_{(5)}$; 4.5, dt(7, 6), 2H, $C\underline{H}_2—N_{(3)}$; ^{13}C NMR: 13.2, $\underline{C}H_3—(CH_2)_2$; 13.6, $\underline{C}H_3—(CH_2)_5$; 24.2 ($^3J$ = 7), $CH_3—\underline{C}H_2—CH_2$; 22.1 and 26.1, $CH_3—(\underline{C}H_2)_2$; 30.8, $\underline{C}H_2—(CH_2)_2N_{(3)}$; 31.2 ($^2J$ = 16), $\underline{C}H_2—C_{(5)}$; 32.0 (^3J = 3.6), $\underline{C}H_2—CH_2N_{(3)}$; 52.2 ($^2J$ = 12), $\underline{C}H_2—N_{(3)}$; 178.5 (^1J = 50), $\underline{C}_{(5)}$.

8c: IR: 2960, 1450, 1260, 1040, 800; ^{1}H NMR: 0.95, m, 6H, $C\underline{H}_3—(CH_2)_5$ and $C\underline{H}_3—(C\underline{H}_2)_4$; 1.0 to 1.8, m, 14H, $CH_3—(C\underline{H}_2)_4$ and $CH_3—(C\underline{H}_2)_3$; 2.9, dt (8, 7), 2H, $C\underline{H}_2—C_{(5)}$; 4.5, dt (7, 6), 2H, $C\underline{H}_2—N_{(3)}$; ^{13}C NMR: 13.6, $\underline{C}H_3—(CH_2)_5$; 22.1, 23.2, 23.3 and 26.1, $CH_3—(\underline{C}H_2)_2—(CH_2)_3$ and $CH_3—(\underline{C}H_2)_2—(CH_2)_2$; 30.8, $\underline{C}H_2—(CH_2)_2N_{(3)}$; 31.5 ($^2J$ = 16), $\underline{C}H_2—C_{(5)}$; 32.0 (^3J = 3.6), $CH_2—CH_2N_{(3)}$; 52.3 (^2J = 12), $\underline{C}H_2—N_{(3)}$; 178.0 (^1J = 50), $\underline{C}_{(5)}$.

8d: IR: 2980, 1490, 1260, 1220, 830; ^{1}H NMR: 0.9, m, 3H, $C\underline{H}_3—CH_2)_5$; 1.3, m, 8H, $CH_3—(C\underline{H}_2)_4$; 2.6, dd (12, 7), 2H, $C\underline{H}_2—C_{(5)}$; 4.5, dt (7, 6), 2H, $C\underline{H}_2—N_{(3)}$; 4.6 to 5.5, m, 3H, $C\underline{H}_2=C\underline{H}$; ^{13}C NMR: 13.6, $\underline{C}H_3—(CH_2)_5$; 22.1, 25.8, and 30.8, $CH_3—(\underline{C}H_2)_3$; 32.0 ($^3J$ = 12), $\underline{C}H_2—CH_2N_{(5)}$; 33.2 ($^2J$ = 18), $\underline{C}H_2—C_{(5)}$; 52.2 (^2J = 12), $\underline{C}H_2—N_{(3)}$; 128.6, $\underline{C}H_2=CH$; 146.8, $CH_2=\underline{C}H$; 178.0 (^1J = 50), $C_{(5)}$.

8e: IR: 3040, 2940, 1600, 1450, 1260, 800, 730, 700; ^{1}H NMR: 0.9, m, 3H, $C\underline{H}_3—(CH_2)_5$; 1.3, m, 8H, $CH_3—(C\underline{H}_2)_4$; 3.4, d (7), 2H, $C\underline{H}_2—C_6H_5$; 4.9, m, 2H, $C\underline{H}_2—N_{(3)}$; 7.3, s, 5H, $C_6\underline{H}_5$; ^{13}C NMR: 13.6, $\underline{C}H_3—(CH_2)_5$; 22.1, 25.8, and 30.8, $CH_3—(\underline{C}H_2)_3$; 32.0 ($^3J$ = 4), $\underline{C}H_2—CH_2N_{(3)}$; 35.6 ($^2J$ = 18.6), $\underline{C}H_2—C_{(5)}$; 52.2 (^2J = 12), $\underline{C}H_2—N_{(3)}$; 126.7, $\underline{C}_{arom(2')}$; 128.6, $\underline{C}_{arom(3',4')}$; 138.7, $\underline{C}_{arom(1')}$; 179.6 (^1J = 55), $\underline{C}_{(5)}$.

8i: IR: 2980, 1450, 1250, 1040, 850; ^{1}H NMR: 0.4, s, 9H, $(C\underline{H}_3)_3Si$; 0.9, m, 3H, $C\underline{H}_3—(CH_2)_5$; 1.3, m, 8H, $CH_3—(C\underline{H}_2)_4$; 4.9, dt(6), 2H, $C\underline{H}_2—N_{(3)}$; ^{13}C NMR: −0.57 (^3J = 4), $(\underline{C}H_3)_3Si$; 13.5, $\underline{C}H_3—(CH_2)_5$; 22.1, 25.8, and 30.8, $CH_3—(\underline{C}H_2)_3$; 32.0 ($^3J$ = 4), $\underline{C}H_2—CH_2N_{(3)}$; 52.2 ($^2J$ = 12), $\underline{C}H_2—N_{(3)}$; 178.5 (^1J = 55), $\underline{C}_{(5)}$.

REFERENCES

[1] T. E. Gier, *J. Am. Chem. Soc., 83*, 1961, 1769.
[2] M. Regitz, P. Binger, *Angew. Chem. Int. Ed. Engl., 27*, 1988, 1484.
[3] L. N. Markowski, V. D. Romanenko, *Tetrahedron, 45*, 1989, 6019.
[4] M. Regitz, *Chem. Rev., 90*, 1990, 191.
[5] M. Regitz, O. J. Scherer, *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, G. Thieme Verlag, Stuttgart, 1990.
[6] J.-M. Denis, J.-C. Guillemin, M. Le Gennec, *Phosphorus, Sulfur, and Silicon, 49/50*, 1990, 317.
[7] J. C. Guillemin, T. Janati, P. Guenot, P. Savignac, J.-M. Denis, *Angew. Chem. Int. Ed. Engl., 30*, 1991, 196.
[8] D. Seyferth, R. S. Marmor, *J. Organometal. Chem., 59*, 1973, 237.
[9] P. Coutrot, C. Laurenço, J.-F. Normant, P. Perriot, P. Savignac, J. Villieras, *Synthesis*, 1977, 615.
[10] J. Petrova, P. Coutrot, M. Dreux, P. Savignac, *Synthesis*, 1975, 658.
[11] P. Coutrot, C. Laurenço, J. Petrova, P. Savignac, *Synthesis*, 1976, 107.
[12] J.-L. Cabioch, J.-M. Denis, *J. Organometal. Chem., 377*, 1989, 227.
[13] J.-L. Cabioch, B. Pellerin, J.-M. Denis, *Phosphorus, Sulfur, and Silicon, 44*, 1989, 27.
[14] W. Rösch, U. Hees, M. Regitz, *Chem. Ber., 120*, 1987, 1645.
[15] W. Rösch, T. Facklam, M. Regitz, *Tetrahedron, 43*, 1987, 3247.
[16] E. P. O. Fuchs, M. Hermesdorf, W. Schnurr, W. Rösch, H. Heydt, M. Regitz, P. Binger, *J. Organometal. Chem., 338*, 1988, 329.
[17] M. Hermesdorf, M. Birkel, H. Heydt, M. Regitz, *Phosphorus Sulfur and Silicon, 46*, 1989, 31.
[18] G. M. Kosolapoff, *J. Am. Chem. Soc., 69*, 1947, 1002.
[19] J.-C. Guillemin, M. Le Gennec, J.-M. Denis, *J. Chem. Soc., Chem. Commun.*, 1989, 988.
[20] G. Märkl, I. Trötsch, *Angew. Chem. Int. Ed. Engl., 23*, 1984, 901.