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1,5-Dimethyl-2,3,3,4-tetrachloro-1,5-diaza-2,4-diphosphorinan-6-one and Some Derivatives

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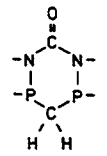
ABSTRACT

A synthesis of C-chlorinated analogues of 1,5-diaza-2,4-diphosphorinan-6-ones is described. The P-chlorophosphine ***3****, a key compound for all reported substitution reactions, reacts in an unusual way with N,N'-dimethyl-N,N'-bis(trimethylsilyl)urea to give the unsymmetrical product* ***5****, the formation of which is accounted for by a silatropy of the intermediate compound* ***4****. Compound* ***5*** *is stable in solution but rearranges quantitatively into isomer* ***6*** *without solvent at room temperature. Compound* ***3****, its fluoro derivative* ***9****, and the alkoxy derivatives* ***10a–d*** *exist as cis- and trans-isomers. Some stereochemical aspects, as well as the possibility of 1,2-chlorotropy, are discussed.*

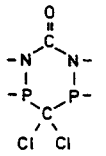
INTRODUCTION

We have previously investigated heterocyclic compounds of type I, containing the structural unit P-CH_2-P. Such compounds possess interesting chemical properties. For example, their oxidation with tetrachloroorthobenzoquinone (TOB) leads to the formation of unusual compounds, containing two phosphorus atoms of opposite formal charge and different coordination number [λ^6P^-, λ^4P^+] [1].

The properties of compounds of type I are determined to a great extent by the presence of two mobile methylene hydrogen atoms between the two phosphorus atoms. Substitution of these hydrogen atoms by other elements, e.g., chlorine, should thus change the chemical properties of compounds of type II containing the structural unit P-CCl_2-P.



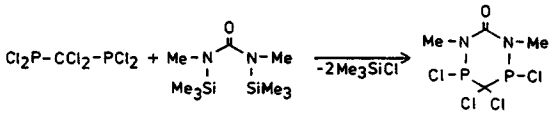
I



II

RESULTS AND DISCUSSION

1,5-Dimethyl-2,3,3,4-tetrachloro-1,5-diaza-2,4-diphosphorinan-6-one **3** was synthesized from dichloromethylenebis(dichlorophosphine) **1** and *N,N'*-dimethyl-*N,N'*-bis(trimethylsilyl)urea **2**. The reaction proceeds readily at room temperature in dichloromethane (Equation 1).



(1)

1 2 3

Because the substituents at the phosphorus atoms can occupy different positions, the heterocyclic compounds of types I and II exist as an equilibrium mixture of cis- and trans-isomers. In the nonchlorinated analogue of compound **3** (with the P-CH_2-P group), the transformation between the two isomers is fast. Its ^{31}P NMR spectrum shows a single

Dedicated to Prof. Jean'ne M. Shreeve on the occasion of her sixtieth birthday.

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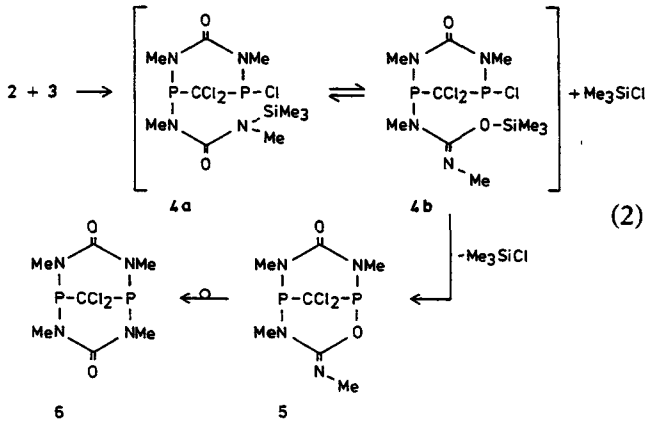
signal at δ = 129.7 [2]. The introduction of two chlorine atoms at the carbon atom reduces the rate of isomerization, and both isomers are seen in the ^{31}P NMR spectrum at δ = 122.5 and 126.5 in the ratio 8:1.

Compound **3** is formed in good yield as a yellow, distillable liquid. The presence of active chlorine atoms at phosphorus in **3** makes this compound an interesting synthon for further substitution reactions, e.g., in its reactions with *N,N'*-dimethyl-*N,N'*-bis(trimethylsilyl)urea **2** (Equation 2). At first, the unsymmetrical product **5** was formed in high yield. The content of the expected symmetrical isomer **6** in the reaction mixture did not significantly depend on the reaction temperature; at 20°C, the ratio of the isomers **5**:**6** was 92:8, with no observable difference at −20°C.

The ^{31}P NMR spectrum showed two intensive, somewhat broadened signals at δ = 103 and 74 (the coupling constant $^{2}J(PP)$ was small and not resolved) and a small singlet due to the symmetrical isomer **6**, at δ = 85. When the reaction was carried out at 60°C in chloroform, the content of **6** amounted to 15%.



(2)

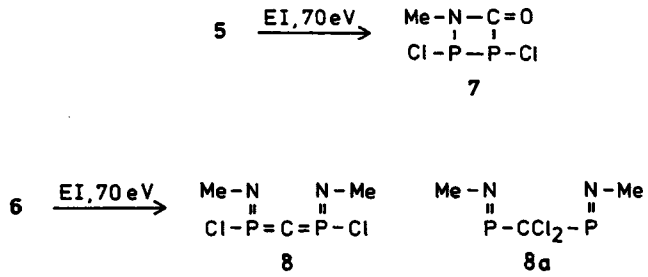
The unsymmetrical structure of **5** was confirmed by its ^{1}H and ^{13}C NMR spectra, showing the nonequivalence of all four methyl groups. For one of these, there is no ^{1}H-^{31}P coupling. The ^{13}C NMR spectrum exhibited two characteristic multiplets due to the presence of two sp^2-hybridized carbon atoms at δ = 149.95 and 137.25.

The same reaction is also known for the nonchlorinated analogue of **3**, but the formation of an analogue of the unsymmetrical product **5** has not been reported [2,3]. We have repeated this reaction in order to compare the results. In contrast to **3**, the (unknown) CH_2 analogue of **5** reacted with **2** very rapidly, even at −20°C. The ^{31}P NMR spectrum showed, immediately after mixing the reagents, an intense singlet at δ = 90.0; caused by the symmetrical product and two small signals of equal intensity at δ = 87.2 and 127.1. These signals, belonging apparently to the CH_2-analogue of **5**, disappeared after 1 minute.

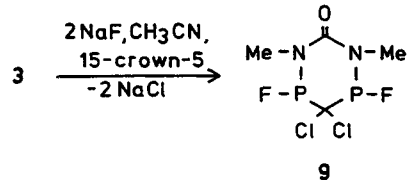
The formation of the unsymmetrical and symmetrical isomers **5** and **6** is, presumably, a consequence of 1,3-silatropy, either of the silyl urea **2** or of the intermediate product **4**, which may exist in two equilibrating forms, **4a** ⇌ **4b**. The position of the equilibrium defines the ratio between the isomers formed.

Compound **5** is stable at −20°C, but at room temperature, it is transformed gradually into the symmetrical isomer **6**. In solution in methylene chloride or chloroform this process continues for about 1 month. In the absence of solvent, **5** is a light-yellow oil which crystallizes completely as the isomeric product **6** over 5–6 days.

The structures of the two isomers were also confirmed by their mass spectra. They show the same peaks for the molecular ions (M = 316) but exhibit different fragmentation patterns. The spectrum of the unsymmetrical product **5** contains an intense signal from fragment **7** (m/z = 189). The mass spectrum of **6** shows another intense signal (m/z = 202), corresponding to fragment **8** or its isomer, **8a**.



The two phosphorus-bonded chlorine atoms of **3** could be substituted by fluorine (Equation 3), using NaF in acetonitrile in the presence of a catalytic amount of crown ether (15-crown-5).

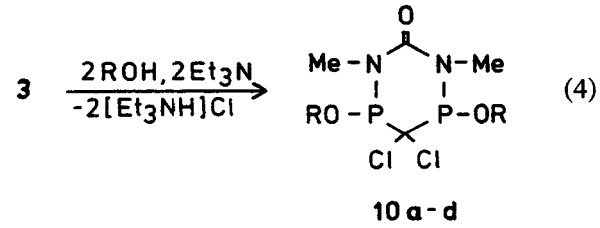


(3)

Compound **9**, like **3**, exists as cis- and trans-isomers. In contrast to **3**, the cis:trans ratio of **9** is 1:3. The analysis of the ^{1}H, ^{31}P, and ^{19}F NMR spectra of **9** reveals the slight magnetic nonequivalence of the methyl groups (NMe) as well as of the phosphorus and fluorine atoms of the thermodynamically more stable isomer. Earlier, when investigating the dialkylamino substituted nonchlorinated analogues of the 1,5-diaza-2,4-diphosphorinan-6-ones, we found that the cis-trans equilibrium is shifted toward the thermodynamically more stable trans form [4]. Apparently, the thermodynamically more stable unsymmetrical isomer of **9** can also be assigned as the trans form.

The reactions of **3** with alcohols or phenol in

the presence of triethylamine led to the substitution of chlorine atoms by alkoxy- or phenoxy substituents (Equation 4).



(4)

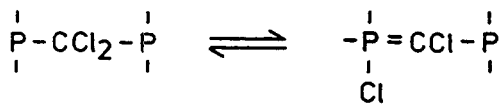
10a-d

The reaction time and the thermal stability of the alkoxy derivatives **10a–c** depend on the size of the substituent R. For R = Me and Et, the reaction proceeds rapidly and without formation of by-products. Compounds **10a** and **10b** are thermally stable and can be isolated in good yield by distillation. With isopropyl alcohol, **3** reacts slowly (24 hours) with formation of **10c**, together with a small amount of by-products. Compound **10c** is thermally not very stable and decomposes partially on distillation in vacuo ($2 \cdot 10^{-5}$ mm). The reaction of **3** with tert-butyl alcohol continues at room temperature for 5–6 days and leads to a mixture of compounds: the expected product can be observed only by ^{31}P NMR spectroscopy.

The interaction of **3** with phenol leads in quantitative yield to the expected product **10d** which is very stable and does not decompose during distillation in vacuo at 250°C.

The alkoxy derivatives **10a–c** also exist as cis- and trans-isomers, the ratio depending on the size of the substituent R. For example, for R = Me, the ratio is 1.3:1. The introduction of bulkier substituents shifts the equilibrium between the isomers. Probably the trans-configuration is also preferred in this case. For R = Et, the cis:trans ratio is 1:4, and for R = *i*–Pr or R = Ph, it is 1:16.

For the phosphines bearing chlorine atoms at the α-carbon, 1,2(C—P)-chlorotropy is conceivable with the formation of an equilibrium ylide structure [5].



A **B**

The position of the equilibrium depends on the substituents at the phosphorus atoms [5]. In compounds **3** and **9**, the phosphorus atoms are connected to the electronegative atoms chlorine or fluorine. The proportion of the ylide structure **B** is apparently very small.

Compound **6** contains the much less electronegative NMe-groups bonded to the phosphorus atoms, and the amount of the ylide form could be appreciable. The $\delta^{31}P$ value 85 for **6** supports this supposition. The $\delta^{31}P$ value for the analogous compound with the P-CH_2-P group is 89 [2,3]. The analysis of $\delta^{31}P$ (e.g., Ref. [6]) shows that the introduction of chlorine atoms at the α-carbon atom of phosphines shifts $\delta^{31}P$ toward the region characteristic of phosphorus ylides.

There is a possibility that an ylidic isomer, involving the structural element **B**, is of some importance in the case of the unsymmetrical product **5**. Its NPN phosphorus atom shows $\delta^{31}P$ = +74, which can be explained by a substantial contribution of the ylide structural element corresponding to **B**. It is interesting that the mass spectrum of this compound shows an intense signal due to fragment **7**, which contains two P-Cl groups and does not involve a CCl_2 unit. This also indirectly supports the P-chloro ylide form **B**.

EXPERIMENTAL

All experiments were conducted with exclusion of moisture in sealed systems in an atmosphere of dried nitrogen (BASF BTS catalyst). Reaction mixtures were stirred magnetically. Solvents were purified and dried according to the usual methods [7,8]. NMR spectra: BRUKER AC 200 (^1H at 200.1 MHz; ^{13}C at 50.3 MHz; ^{19}F at 188.3 MHz; ^{31}P at 81.3 MHz). Reference substances were $SiMe_4$ (TMS) ext. (^1H, ^{13}C) ext. $CFCl_3$ (^{19}F), and 85% H_3PO_4 ext. (^{31}P). High field shifts were given negative signs, and low field shifts were given positive signs. Mass spectrometry: low-resolution electron impact (EI) mass spectra were obtained with the double-focusing instrument Finnigan MAT 8430, (Bremen, Germany) in combination with the data system SSY300. The electron energy was 70 eV. Dichloromethylenebis(dichlorophosphine) **1** [9] and *N,N'*-dimethyl-*N,N'*-bis(trimethylsilyl)urea **2** [10] were synthesized according to the procedures described in the literature.

Synthesis of **3**

A solution of **2** (6.49 g, 27.9 mmol) in 20 mL of ether was added dropwise to a solution of **1** (8.00 g, 27.9 mmol) in 30 mL of ether with stirring. After the reaction mixture had been stirred for 1 hour at room temperature, ether was removed in vacuo (0.5 mm) and the oily residue was distilled in vacuo (0.5 mm); yellow liquid, bp 95°C (0.5 mm), yield 6.3 g (75%). The isomer ratio was 8:1.

^{31}P NMR ($CDCl_3$) δ: 122.23 (s), 126.46 (s). ^+H NMR ($CDCl_3$) δ: 3.11 (d, $^3J(PH)$ = 12.8 Hz, NCH_3), 3.23 (d, $^3J(PH)$ = 13.2 Hz, NCH_3). ^{13}C NMR ($CDCl_3$) δ: 37.11 (d, 3J(PC) = 31.9 Hz, N-CH_3), 39.36 (d, $^3J(PC)$ = 36.5 Hz, N-CH_3), 77.97 (t, $^1J(PC)$ = 59.7 Hz, CCl_2),

152.11 (t, $^2J(PC)$ = 11.3 Hz, *C*=O). Mass spectrum (m/z): 300 (M^+, 0.5%), 243 ($M^+ - CH_3NCO$, 3%), 214 ($M^+ - CH_3NCONCH_3$, 1%), 136 (PCl_3, 30%), 101 (PCl_2, 100%). Anal. calcd for $C_4H_6Cl_4N_2OP_2$ (301.85): C 15.92, H 2.00, N 9.28. Found: C 15.72, H 2.00, N 9.20.

Synthesis of **5**

The silylurea **2** (2.32 g, 10 mmol) was added to a solution of **3** (3.02 g, 10 mmol) in 30 mL of CH_2Cl_2 with stirring, and the reaction mixture was stirred at 20°C for 20 hours. The solvent and the Me_3SiCl formed were removed in vacuo (0.05 mm) with stirring for 10 minutes. Compound **5** remained quantitatively as a colorless oil which contained 6–7% of **6** and showed the following NMR data: ^{31}P NMR ($CDCl_3$), δ: 74.00 (s, *NP*N), 102.94 (s, *NP*O). ^1H NMR ($CDCl_3$), δ: 2.91 (s, NCH_3), 3.10 (d, $^3J(PH)$ = 13.29 Hz, NCH_3), 3.13 (d, $^3J(PH)$ = 12.33, NCH_3), 3.21 (d, $^3J(PH)$ = 12.35, NCH_3). ^{13}C NMR ($CDCl_3$), δ: 33.34 (s, N*C*H_3), 38.37 (d, $^2J(PC)$ = 34.69 Hz, N*C*H_3), 39.19 (d, $^2J(PC)$ = 34.00 Hz, N*C*H_3), 41.63 (d, $^2J(PC)$ = 40.65 Hz, N*C*H_3), 67.35 (dd, $^1J(PC)$ = 16.35 Hz, $^1J(PC)$ = 35.77 Hz, *C*Cl_2), 137.25 (dd, $^2J(PC)$ = 9.30 Hz, $^2J(PC)$ = 15.85 Hz, *C*=N), 149.95 (t, $^2J(PC)$ = 10.58 Hz, *C*=O). Mass spectrum *m/z*: 316 (M^+, 20%), 281 (11%), 189 (44%), 107 (20%), 60 (100%). $C_7H_{12}Cl_2N_4O_2P_2$ (317.05).

Formation of **6**

Compound **5** which was isolated as a colorless oil (see earlier) isomerized quantitatively within 5–6 days at room temperature into the crystalline compound **6**.

^1H NMR ($CDCl_3$) δ: 3.06 (d, $^3J(PH)$ = 12.3 Hz, NCH_3). ^{13}C NMR ($CDCl_3$) δ: 39.02 (d, $^2J(PC)$ = 40.9 Hz, N*C*H_3), 66.77 (t, $^1J(PC)$ = 18.6 Hz, *C*Cl_2), 150.64 (t, $^2J(PC)$ = 10.1 Hz, *C*=O). ^{31}P NMR ($CDCl_3$) δ: 85.29 (s). Mass spectrum *m/z*: 316 (M^+, 65%), 281 (20%), 202 (30%), 167 (50%), 107 (32%), 60 (100%). Anal. calcd. for $C_7H_{12}Cl_2N_4O_2P_2$ (317.05): C, 26.52; H, 3.82; N, 17.02. Found: C, 26.28; H, 3.82; N, 16.74.

Synthesis of **9**

A mixture of **3** (3.02 g, 10 mmol), sodium fluoride (1.68 g, 40 mmol), and the crown ether 15-crown-5 (10 mg) in 20 mL of acetonitrile was stirred at room temperature for 3 days. The reaction mixture was filtered, and the solid material was washed with 20 mL of ether. The combined liquid phase was evaporated in vacuo (0.5 mm), and the residue was distilled in vacuo (0.3 mm). Colorless liquid, bp. 57–59°C (0.3 mm), yield 1.35 g (50%). The isomer ratio was cis:trans = 1:3.

^{31}P NMR ($CDCl_3$), δ: cis-isomer: 133.48 (d, $^1J(FP)$ = 1108.9 Hz); trans-isomer: 138.23 (dd, $^1J(FP)$ = 1144.6 Hz, $^3J(FP)$ = 18.8 Hz), 138.23 (dd, $^1J(FP)$ = 1110.4 Hz, $^3J(FP)$ = 15.6 Hz). ^1H NMR ($CDCl_3$) δ: cis-isomer: 3.17 (dd, $^3J(PH)$ = 13.3 Hz, $^4J(FH)$ = 3.46 Hz, NCH_3); trans-isomer: 3.26 (dd, $^3J(PH)$ = 11.74 Hz, $^4J(FH)$ = 1.2 Hz, NCH_3), 3.27 (dd, $^3J(PH)$ = 11.62 Hz, $^4J(FH)$ = 1.2 Hz, NCH_3). ^{13}C NMR ($CDCl_3$) δ: cis-isomer: 36.67 (dd, $^2J(PC)$ = 35.58 Hz, $^3J(FC)$ = 1.38 Hz, N*C*H_3), 151.79 (t, $^2J(PC)$ = 6.00 Hz, $^3J(FC)$ not resolved, C=O); trans-isomer: 39.69 (d, $^2J(PC)$ = 39.94 Hz, $^3J(FC)$ not resolved, NCH_3), 72.24 (tt, $^1J(PC)$ = 46.5 Hz, $^2J(FC)$ = 13.8 Hz, CCl_2), 148.42 (tt, $^2J(PC)$ = 10.8 Hz, $^3J(FC)$ = 3.8 Hz, C=O). ^{19}F NMR ($CDCl_3$) δ: cis-isomer: −113.29 (dd, $^1J(PF)$ = 1109.6 Hz, $^3J(PF)$ = 3.8 Hz, *F*P), trans-isomer: −115.62 (dd, $^1J(PF)$ = 1146.6 Hz; $^3J(PF)$ = 20.3 Hz, *F*P), −115.64 (dd, $^1J(PF)$ = 1113.3 Hz, $^3J(PF)$ = 14.9 Hz, *F*P). Mass spectrum m/z: 268 (M^+, 10%); 211 (32%), 132 (28%), 43 (100%). Anal. calcd. for $C_4H_6Cl_2F_2N_2OP_2$ (268.94): C, 17.86; H, 2.25; N, 10.42. Found: C, 17.63; H, 2.11; N, 10.54.

Synthesis of **10a**

A solution of MeOH (0.42 g, 13.2 mmol) and Et_3N (1.34 d, 13.2 mmol) in 20 mL of ether was added dropwise at 0°C to a solution of **3** (2 g, 6.6 mmol) in 10 mL of ether with stirring. The mixture was stirred at room temperature for 10 minutes, triethylammonium chloride was removed by filtration, and the solvent was removed by pumping in vacuo (0.5 mm). Distillation of the residue at 90°C in vacuo ($2 \cdot 10^{-5}$ mm) gave 1.68 g (87%) of **10a** as a colorless liquid. The isomer ratio was 1.3:1.

^{31}P NMR ($CDCl_3$) δ: 133.67 (s), 135.29 (s). ^1H NMR ($CDCl_3$) δ: 2.98 (d, $^3J(PH)$ = 10.9 Hz, NCH_3), 3.08 (d, $^3J(PH)$ = 11.2 Hz, NCH_3), 3.66 (d, $^3J(PH)$ = 12.8 Hz, OCH_3), 3.69 (d, $^3J(PH)$ = 12.9 Hz, OCH_3). ^{13}C NMR ($CDCl_3$) δ: 35.56 (d, $^2J(PC)$ = 31.91 Hz, N*C*H_3), 38.15 (d, $^2J(PC)$ = 37.1 Hz, N*C*H_3), 56.50 (d, $^2J(PC)$ = 22.3 Hz, O*C*H_3), 56.55 (d, $^2J(PC)$ = 21.2 Hz, O*C*H_3), 78.37 (t, $^1J(PC)$ = 45.67 Hz, *C*Cl_2), 80.47 (t, $^1J(PC)$ = 47.60 Hz, *C*Cl_2), 151.38 (t, $^2J(PC)$ = 9.9 Hz, *C*=O), 152.74 (t, $^2J(PC)$ = 8.9 Hz, *C*=O). Mass spectrum *m/z*: 292 (M^+, 18%), 257 (12%), 235 (10%); 200 (28%), 93 (100%); 60 (50%); 50 (68%). Anal. calcd. for $C_6H_{12}Cl_2N_2O_3P_2$ (293.02): C, 24.60; H, 4.13; N, 9.56. Found: C, 24.40; H, 4.10; N, 9.59.

Synthesis of **10b**

As described for **10a**, 2.00 g (6.6 mmol) of **3** were allowed to react with EtOH (0.61 g, 13.2 mmol) and Et_3N (1.34 g, 13.2 mmol). The reaction mixture was stirred at room temperature for 2 hours. Yield of **10b** after distillation, 1.44 g (68%); bp. 93°C ($2 \cdot 10^{-5}$ mm). The isomer ratio was 1:4.

^{31}P NMR ($CDCl_3$) δ: 132.30 (s), 132.68 (s). ^1H NMR ($CDCl_3$) δ: 1.28 (t, $^3J(HH)$ = 6.9 Hz, OCH_2CH_3), 3.01 (d, $^3J(PH)$ = 10.7 Hz, NCH_3), 3.12 (d, $^3J(PH)$ = 11.3 Hz, NCH_3), 3.58–4.15 (m, OCH_2CH_3). ^{13}C NMR ($CDCl_3$) δ: 16.78 (d, $^3J(PC)$ = 6.16 Hz, OCH_2CH_3),

16.98 (d, $^3J(PC)$ = 5.80 Hz, OCH_2CH_3), 35.78 (d, $^2J(PC)$ = 31.8 Hz, NCH_3), 38.63 (d, $^2J(PC)$ = 37.9 Hz, NCH_3), 78.35 (t, $^1J(PC)$ = 43.0 Hz, CCl_2), 152.26 (t, $^2J(PC)$ = 10.1 Hz, C=O), 153.55 (t, $^2J(PC)$ = 8.7 Hz, C=O). Mass spectrum *m/z*: 320 (M^+, 24%), 276 (23%), 248 (8%), 199 (22%), 171 (48%), 60 (100%). Anal. calcd. for $C_8H_{16}Cl_2N_2O_3P_2$ (321.07): C, 29.93; H, 5.02; N, 8.73. Found: C, 29.51; H, 5.01; N, 8.60.

Synthesis of **10c**

As described in the preceding experiment, 2.00 g (6.6 mmol) of **3** were allowed to react with *i*-PrOH (0.80 g, 13.2 mmol) and Et_3N (1.34 g, 13.2 mmol). The reaction mixture was stirred at room temperature for 24 hours. After the removal of triethylammonium chloride by filtration and removal of the solvent, **10c** remained as a colorless oil. The purity of the product, according to its NMR data, was about 90%. The distillation of **10c** at 100–120°C in vacuo ($2 \cdot 10^{-5}$ mm) was accompanied by partial decomposition. Yield after distillation, 0.96 g (42%). The isomer ratio was 1:16.

^{31}P NMR ($CDCl_3$) δ: 132.30 (s), 135.89 (s). ^1H NMR ($CDCl_3$) δ: 1.09 (d, $^3J(HH)$ = 6.21 Hz, $OCH(CH_3)_2$), 1.10 (d, $^3J(HH)$ = 6.15 Hz, $OCH(CH_3)_2$), 2.94 (d, $^3J(PH)$ = 11.4 Hz, NCH_3), 4.00–4.25 (m, $OCH(CH_3)_2$). ^{13}C NMR ($CDCl_3$) δ: 23.41 (d, $^3J(PC)$ = 5.8 Hz, $CH(CH_3)_2$), 23.86 (d, $^3J(PC)$ = 3.9 Hz, $CH(CH_3)_2$), 38.13 (d, $^2J(PC)$ = 38.2 Hz, NCH_3), 73.50 (d, $^2J(PC)$ = 24.5 Hz, $CH(CH_3)_2$), 151.75 (t, $^2J(PC)$ = 10.6 Hz, C=O). Mass spectrum *m/z*: 348 (M^+, 12%), 306 (13%), 264 (10%), 207 (18%), 124 (26%), 60 (100%); $C_{10}H_{20}Cl_2N_2O_3P_2$ (394.12).

Synthesis of **10d**

The compound was prepared in a similar fashion as **10a–10c** from **3** (2.00 g, 6.6 mmol), PhOH (1.25 g, 13.2 mmol), and Et_3N (1.34 g, 13.2 mmol). The reaction mixture was stirred at room temperature for 16 hours. Yield of **10d** after distillation 1.54 g (56%); bp 250°C ($2 \cdot 10^{-5}$ mm). The isomer ratio was 1:16.

^{31}P NMR ($CDCl_3$) δ: 126.87 (s), 127.72 (s). ^1H NMR ($CDCl_3$) δ: 3.40 (d, $^3J(PH)$ = 11.6 Hz, NCH_3),7.00–7.60 (m, Ar). ^{13}C NMR ($CDCl_3$) δ: 38.88 (d, $^2J(PC)$ = 37.7 Hz, NCH_3), 76.29 (t, $^2J(PC)$ = 39.65 Hz, CCl_2), 119.16 (d, $^3J(PC)$ = 8.69 Hz, 4C, Ar), 123.81 (s, 2C, Ar), 129.55 (s, 4C, Ar), 150.89 (t, $^2J(PC)$ = 10.4 Hz, C=O), 154.70 (d, $^2J(PC)$ = 11.78 Hz, 2C, Ar). Mass spectrum *m/z*: 416 (M^+, 14%), 359 (8%), 217 (32%), 107 (16%), 60 (100%). Anal. calcd. for $C_{16}H_{16}Cl_2N_2O_3P_2$ (417.16): C, 46.07; H, 3.87; N, 6.72. Found: C, 46.50; H, 4.02; N, 5.83.

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