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Alkylation of [(Diphenylphosphinoyl)cyano]methylenetriphenylphosphorane

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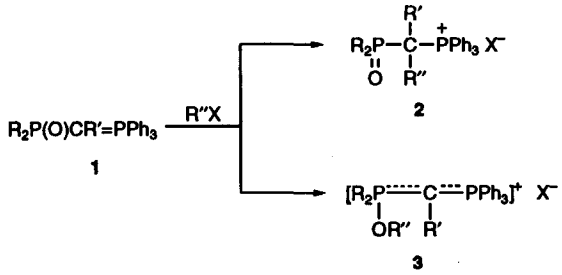
Alkylation of [(diphenylphosphinoyl)cyano]methylenetriphenylphosphorane **6** by 1 mol of triethyloxonium tetrafluoroborate yields {[diphenyl(ethoxy)phosphoranylidene]cyano}methyltriphenylphosphonium tetrafluoroborate **7** and *N*-ethyl[(diphenylphosphinoyl)(triphenylphosphoranylidene)]acetonitrilium tetrafluoroborate **8**, the first example of an organophosphorus compound possessing a nitrilium group.

Alkylidenetriphenylphosphoranes are known to be alkylated at the ylide carbon atom. Phosphinoyl-substituted derivatives **1** (R′ = H) give rise to *C*- as well as *PO*-alkylation products. The introduction of strong electron-withdrawing substitutents [R′ = COOEt, P(O)Ph_2, Ts] results only in *PO*-alkylation products, the stable alkoxyphosphorane–phosphonium salts **3**.[1]



At the same time the reaction of cyanomethylenetriphenylphosphorane Ph_3=CHCN **4** with methyl iodide proceeds at the ylide carbon atom as well as at the CN nitrogen atom; with triethyloxonium tetrafluoroborate only the *N*-ethylation product is formed.[2] The ketenimine structure $Ph_3\overset{+}{P}CH$=C=NEt BF_4^- **5** has been proposed for this compound based on ^{1}H NMR spectroscopy.

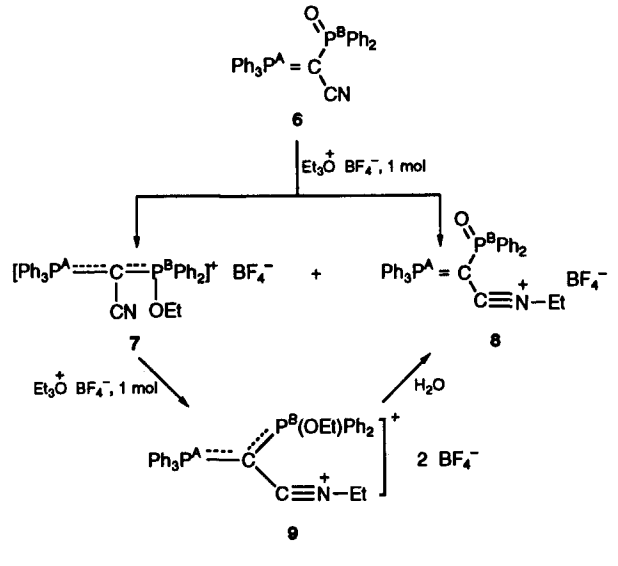


Table 1 M.p., yields and spectral characteristics of compounds **7–9**

Compound[a]	Yield (%)	M.p./°C[b]	IR spectrum (KBr) ν/cm^{-1}	^{31}P NMR–{^{1}H} (CH_2Cl_2) δ(ppm), J/Hz	^{1}H NMR ($CDCl_3$) δ(ppm), J/Hz
7	59.0	176–178 (acetone)	2175 (C≡N)	P^A 23.0 d P^B 60.1 d $J_{P^AP^B}$ 29.0	0.96 t (3H, CH_3CH_2O, $^3J_{HH}$7.0) 3.99 dq (2H, CH_2O, $^3J_{HH}$ = $^3J_{HP^B}$ = 7.0)
8	70.0	191–193 (acetone –ether)	1200 (P=O) 2000–2400 (C≡N–)	P^A 25.9 d P^B 26.9 d $J_{P^AP^B}$ 14.4	0.72 t (3H, CH_3CH_2N, $^3J_{HH}$7.1) 3.42 qt (2H, CH_2N, $^3J_{HH}$ 7.1 $^5J_{HP^A}$ = $^5J_{HP^B}$ = 3.5)
9	76.7	181–182 (acetone) –ether)	2240–2400 (C≡N–)	P^A 24.6 d P^B 61.5 d $J_{P^AP^B}$ 17.0	0.84 t (3H, CH_3CH_2N, $^3J_{HH}$7.2) 1.07 t (3H, CH_3CH_2O, $^3J_{HH}$ 6.9) 3.65 m (2H,CH_2N) 4.38 dq (2H,CH_2O, $^3J_{HH}$ = $^3J_{HP^B}$ = 6.9)

[a] Compounds **7–9** gave satisfactory elemental analyses. [b] All the salts melt with decomposition.

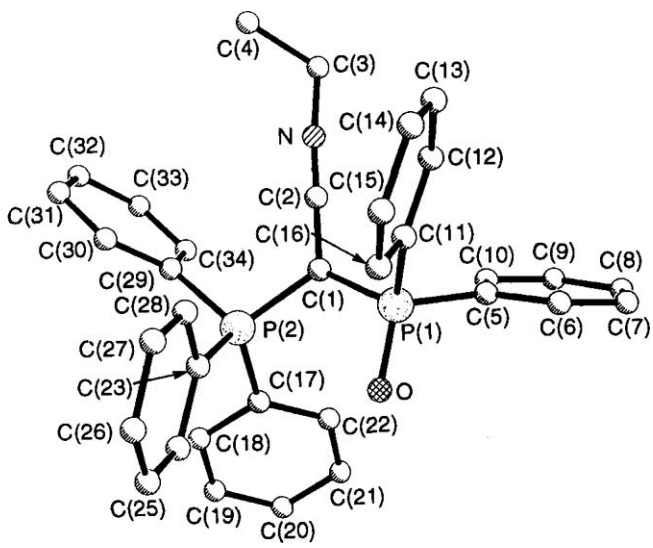


Fig. 1 The general view of the cation **8** and essential bond lengths and bond angles: P(1)–C(1) 1.784(6), P(2)–C(1) 1.766(6), P(1)–O 1.485(4), C(1)–C(2) 1.358(9), C(2)–N 1.123(9), N–C(3) 1.465(8), C(3)–C(4) 1.49(1), P(1)–C(5) 1.791(7), P(1)–C(11) 1.817(6), P(2)–C(17) 1.797(6), P(2)–C(23) 1.790(6), P(2)–C(29) 1.794(6)Å; P(1)C(1)P(2) 118.4(3), P(1)C(1)C(2) 122.0(5), P(2)C(1)C(2) 118.4(5), C(1)C(2)N 176.6(7), C(2)NC(3) 165.0(7), NC(3)C(4) 109.4(6)°.

This study is devoted to the alkylation of [(diphenylphosphinoyl)cyano]methylenetriphenylphosphorane **6**, which has three nucleophilic centres: the ylide carbon atom, the oxygen of the P=O group and the nitrogen of the CN group.

The reaction of phosphorane **6** with methyl iodide was found to fail even upon lengthy refluxing in excess of alkylating agent. With an equimolar amount of triethyloxonium tetrafluoroborate in methylene dichloride at 20 °C, two ethylation products are formed in a 3:1 ratio (^{31}P NMR spectrum data). The major reaction product, characterized by two doublet signals with chemical shifts 60.1 and 23.0 ppm, was isolated in a yield of 59%. A significant downfield shift of the signal of the phosphoryl phosphorus atom compared with the original phosphorane **6** (δ_P 28.7 ppm[3]) pointed to the addition of the ethyl group to the oxygen atom; *i.e.* to the formation of the phosphorane–phosphonium salt **7** (Scheme 1). The structure is in agreement with the coupling constant J_{PP} value [3,4] and parameters of ^{1}H NMR and IR spectra (Table 1).

We failed in isolating the second product, the phosphorane–nitrilium salt **8**, from the reaction mixture. This product, characterized by two doublets in the ^{31}P–{^{1}H}NMR spectrum (δ 25.9 and 26.9 ppm), was obtained in 70% yield upon hydrolysis of the phosphorane–phosphonionitrilium salt **9**, the product of further alkylation of compound **7**.†

The structure of product **8** followed from the spectral data and X-ray analysis. A negligible downfield shift for the phosphoryl phosphorus signal compared with that for the original phosphorane **6** is evidence for a free P=O group. This is also consistent with the IR spectrum ($\nu_{P=O}$ 1200 cm^{-1}). In the ^{1}H NMR spectrum, along with the triplet signal of the methyl protons, a fairly low-field multiplet signal (δ 3.42 ppm, a quadruplet of triplets) is observed. The latter can be assigned to the methylene protons of the ethyl group at the nitrogen atom.‡ The complexity of the signal is due to the additional long-range coupling of the methylene protons to the ^{31}P nuclei. In the IR spectrum of compound **8**, an intense absorbtion in the region 2000–2400 cm^{-1} lies in the frequency region corresponding to the C≡N-group in nitrilium salts.[6] The nitrilium character of the cation counterpart of the molecule (X-ray analysis data§), Fig. 1, is reflected in the shortening of the triple bond C(2)–N to 1.123(9) Å and in nearly linear coordination of the nitrogen and C(2) atoms [corresponding valence angles are 165.0(7)° and 176.6(7)°, respectively].[7] Deviation of the nitrogen atom coordination from linearity (~15°) might partly be associated with the crystal packing effect.[8] Another reason for the observed non-linear coordination of this atom might be due to a certain contribution of the ketenimine resonance form $[Ph_2P(O)](Ph_3\dot{P})C{=}C{=}N{-}Et$ to the electron structure of **8**, which results in the shortened bond length C(1)–C(2), close to the C=C double bond value.[9] Among other characteristics of the cation **8** structure, the almost planar geometry of the central fragment OP(1)C(1)P(2)C(2) should be noted: the mean-square deviation from the plane for the above indicated atoms is 0.030 Å, while the out-of-plane deviation for nitrogen and C(3) atoms

† For the synthesis and structure determination of compound **9** see below.

‡ For the *C*-ethylation product a considerably high-field signal should be observed.[5]

§ *Crystal data for* **8**: $C_{34}H_{30}BF_4NOP_2$, M = 617.432, orthorhombic, space group $P2_12_12_1$, a = 9.071(2), b = 15.028(3), c = 22.313(5) Å, V = 3042(2) Å^3 at 148 K, D_{calc} = 1.348 g cm^{-3}, z = 4, μ(MoKα) = 1.90 cm^{-1}. Data were collected with a Siemens diffractometer P3/PC (λ MoK$_\alpha$, graphite monochromator, θ/2θ scan 2θ≤52°). From 3055 observed independent reflections measured at 148 K, 2088 with $|F| \geq 4\sigma$ were used in further calculations. The structure was solved by direct methods and refined by a least-squares method with anisotropic thermal parameters for all atoms other than hydrogen. Positions of hydrogen atoms defined by the molecular geometry were refined isotropically. Final data: R = 0.056, R_w = 0.042, GOF = 1.62 (the weight scheme $W^{-1} = \sigma^2|F|$). Computing was carried out on a SHELXTL PLUS system using a PC/AT personal computer. Atomic coordinates, bond lengths, valence angles and anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. For details, see Notice to Authors, *Mendeleev Commun.*, 1993, issue 1.

are −0.177 and 0.013 Å, respectively. Corresponding torsional angles in the central fragment are: OP(1)C(1)P(2) 6.5°, OP(1)C(1)C(2) 174.0°, P(1)C(1)C(2)N −45.3°, P(2)C(1)C(2)N 122.2°. Coordination of the central carbon atom C(1) is not strictly planar trigonal: the valence angle sum at the carbon atom is 358.8(5)°, while deviation of the C(1) atom from the nearest environment plane is 0.100 Å. Such coordination distortion is evidently caused by the steric overcrowding of cation **8**. Bond lengths C(1)–P(1) 1.784(6) and C(1)–P(2) 1.766(6) Å have expected values.[9] Other geometric parameters of the structure are conventional. The BF_4 anion has tetrahedral coordination; there are no shortened cation-anion contacts in the crystal.

The dialkylation product **9** was obtained by refluxing phosphorane—phosphonium salt **7** with an equimolar amount of triethyloxonium tetrafluoroborate in methylene dichloride during 8 h. According to the ^{1}H NMR spectrum, there are two different ethyl groups in the molecule. Since the methylene proton signals of both groups are at rather low field (δ 3.65 and 4.38 ppm) one may believe that one ethyl group is at the nitrogen atom and the other at the phosphoryl oxygen atom (Table 1). The latter assumption is confirmed by a signal with a chemical shift of 61.5 ppm in the ^{31}P NMR spectrum. An absorbtion in the 2240–2400 cm^{-1} region of the IR spectrum is characteristic of a compound with the nitrilium structure.[6] In addition, as we mentioned above, this compound is transformed upon hydrolysis into phosphorane–nitrilium salt **8**.

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