xenonate(VIII) obtained by reverse synthesis was identified by its IR spectrum, ν/cm^{-1}: 460, 690.

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A new insertion reaction of phenyl isocyanate

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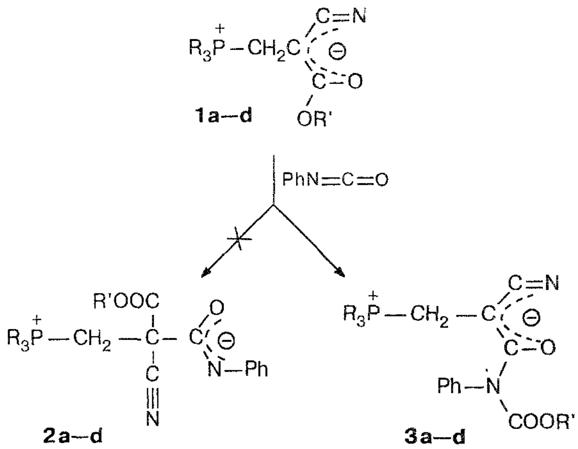
A new reaction of the insertion of phenyl isocyanate into the C—C bond of P-containing zwitterions based on 2-cyanoacrylates was found. A probable mechanism of this reaction has been discussed.

Key words: phenyl isocyanate, zwitterions, insertion reaction.

Reactions involving the insertion of phenyl isocyanate into M—X bonds, where M is C, Si, P, B, or Sn, and X is N, O, S, or Hal, are known.[1,2] We have discovered a new reaction of the insertion of phenyl isocyanate into the C—C bond of zwitterions **1**. We prepared the latter by the reaction of 2-cyanoacrylates with trialkylphosphines and hexaethyltriamide of phosphorous acid.[3] The interaction of phenyl isocyanate with zwitterions **1** resulted in high yields (60—80 %) of crystalline adducts, which turned out to be not the expected zwitterions **2**, but their isomers **3** (Scheme 1), as was unambiguously determined by X-ray diffraction analysis.*

This result may be accounted for by the nucleophilic attack by the N atom in the intermediate zwitterion **2** on the C atom of the carboxyl group, which is favored by the ionic interaction between the positively charged P atom and the carboxyl O atom. Decomposition of the unstable phosphorane **A** involves cleavage of the C—C

Scheme 1



a: R = Pr, R' = Me
b: R = Pr, R' = Et
c: R = Bu, R' = Et
d: R = Et$_2$N, R' = Et

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* The X-ray structural study of compound **3b** was carried out by Yu. T. Struchkov and O. V. Shishkin, and its results will be published separately.

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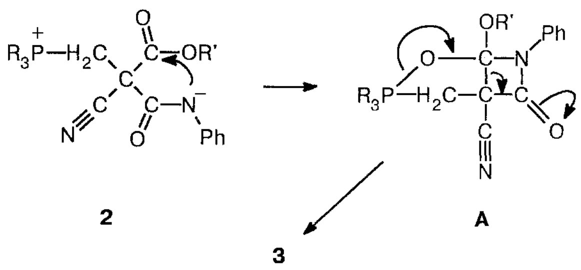
bond and formation of the insertion product **3** (Scheme 2).

Scheme 2



Alternative explanations for the mechanism of this new insertion reaction of phenyl isocyanate may also exist.

The resulting zwitterions **3**, unlike the starting betaines **1**, do not undergo alkylation by alkyl halides.

Experimental

Synthesis of zwitterions 3 (general procedure) exemplified by compound **3b**. All of the operations were carried out in an atmosphere of dry Ar. A solution of phenyl isocyanate (0.46 g, 0.42 mL, 3.85 mmol) in 5 mL of anhydrous toluene was added dropwise to a stirred solution of betaine **1b** (1 g, 3.51 mmol) in 10 mL of anhydrous toluene. The reaction mixture was stirred for 30 min and left overnight. The next day 2/3 of the solvent was evaporated, and hexane was added to the residue. The resulting oil was purified by being reprecipitated five times by hexane from toluene, then it was triturated in ether until it crystallized to give 2.52 g (71.7 %) of finely crystalline **[2-tri-*n*-propylphosphonio-1-cyano-1-(*N*-phenyl-*N*-ethoxycarbonyl)carbamoyl]ethanide (3b).** After recrystallization from toluene, m.p. 141—142.5 °C. Found (%): C, 68.00; H, 8.22; P, 6.88. $C_{22}H_{33}N_2O_3P \cdot 0.5MePh$. Calculated (%): C, 67.60; H, 8.28; P, 6.54. IR (KBr), ν/cm^{-1}: 1715 (NC(O)O); 1615 (C(O)N); 2155 (CN). ^{31}P NMR (CHCl$_3$), δ: 34.0. ^{1}H NMR (CDCl$_3$), δ: 1.01 (t, 9 H, $C\underline{H}_3CH_2CH_2P$); 1.15 (t, 3 H, $C\underline{H}_3CH_2O$); 1.50 (m, 6 H, $C\underline{H}_2CH_2P$); 1.96 (m, 6 H, $CH_2C\underline{H}_2P$); 2.89 (d, 2 H, CH_2P, $J_{H,P}$ = 8.4 Hz); 4.10 (q, 2 H, CH_2O); 7.05—7.39 (m, 5 H, C_6H_5).

Zwitterions **3a**, **3c**, and **3d** were prepared in a similar way.

[2-Tri-*n*-propylphosphonio-1-cyano-1-(*N*-phenyl-*N*-methoxycarbonyl)carbamoyl]ethanide (3a). Yield 68.2 %. M.p. 36.0—37.5 °C. IR (KBr), ν/cm^{-1}: 1720 (NC(O)O); 1610 (C(O)N); 2175 (CN). ^{31}P NMR (CHCl$_3$), δ: 34.1. ^{1}H NMR (CDCl$_3$), δ: 1.07 (t, 9 H, $C\underline{H}_3CH_2CH_2P$); 1.59 (m, 6 H, $C\underline{H}_2CH_2P$); 2.05 (m, 6 H, $CH_2C\underline{H}_2P$); 2.98 (d, 2 H, CH_2P, $J_{H,P}$ = 8.5 Hz); 3.73 (s, 3 H, CH_3O); 7.12—7.41 (m, 5 H, C_6H_5).

[2-Tri-*n*-butylphosphonio-1-cyano-1-(*N*-phenyl-*N*-ethoxycarbonyl)carbamoyl]ethanide (3c). Yield 80.1 %. M.p. 70.5—72.0 °C. Found (%): C, 66.96; H, 8.77; P, 6.87. $C_{25}H_{39}N_2O_3P$. Calculated (%): C, 67.27; H, 8.74; P, 6.94. UV (CHCl$_3$), λ_{max}/nm: 267. IR (KBr), ν/cm^{-1}: 1695 (NC(O)O); 1612 (C(O)N); 2158 (CN). ^{31}P NMR (CHCl$_3$), δ: 35.2. $^{13}C\{^1H\}$ NMR (CHCl$_3$), δ: 13.01 (s, $\underline{C}H_3(CH_2)_3P$); 14.41 (s, $\underline{C}H_3CH_2O$); 25.61 (m, $(\underline{C}H_2)_2CH_2P$); 18.00 (d, $CH_2\underline{C}H_2P$, $J_{C,P}$ = 45.5 Hz); 19.3 (d, $C\underline{C}H_2P$, $J_{C,P}$ = 48.6 Hz); 57.6 (d, $\underline{C}CH_2P$, $J_{C,P}$ = 5.8 Hz); 61.0 (s, CH_2O); 118.4 (s, CN); 153.6 (c, NC(O)O); 127.2 (m, C_6H_5); 167.4 (s, $C\underline{C}(O)N$). ^{1}H NMR (CDCl$_3$), δ: 0.95 (t, 9 H, $C\underline{H}_3(CH_2)_3P$); 1.24 (t, 3 H, $C\underline{H}_3CH_2O$); 1.51 (m, 12 H, $(C\underline{H}_2)_2CH_2P$); 2.10 (m, 6 H, $(CH_2)_2C\underline{H}_2P$); 2.98 (d, 2 H, CH_2P, $J_{H,P}$ = 8.2 Hz); 4.19 (q, 2 H, CH_2O); 7.14—7.49 (m, 5 H, C_6H_5).

[2-Hexaethyltriamidophosphonio-1-cyano-1-(*N*-phenyl-*N*-ethoxycarbonyl)carbamoyl]ethanide (3d). Yield 59.4 %. Thick brown oil. IR (KBr), ν/cm^{-1}: 1715 (NC(O)O); 1610 (NC(O)); 2165 (CN). ^{31}P NMR (CHCl$_3$), δ: 56.1. ^{1}H NMR (CDCl$_3$), δ: 1.09 (t, 18 H, $C\underline{H}_3CH_2N$); 1.21 (t, 3 H, $C\underline{H}_3CH_2O$); 2.91—3.20 (m, 14 H, CH_2N, CH_2P); 4.18 (q, 2 H, CH_2O); 7.12—7.48 (m, 5 H, C_6H_5).

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