A new reaction: insertion of phenyl isothiocyanate into the C—C bond

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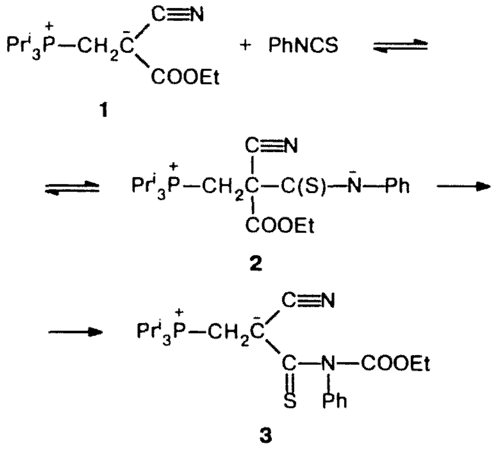
Reactions of the insertion of isothiocyanates into C—C bonds have not yet been described. In a continuation of the study of the reactivity of the P-zwitterions obtained by the interaction of tertiary phosphines with alkyl 2-cyanoacrylates,[1] we introduced P-zwitterion **1** (see Ref. 2) into the reaction with phenyl isothiocyanate. Here we found that when an excess of the latter is present, the reaction yields the product of the insertion of phenyl isothiocyanate into the C—C bond of the initial zwitterion **1**.



Apparently, the reaction occurs *via* normal adduct **2**, which undergoes a rearrangement involving migration of the ethoxycarbonyl group to yield compound **3**. The composition and structure of product **3** were determined by elemental analysis, IR spectra, and the data of ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. The IR spectrum of compound **3** exhibits intense absorption bands corresponding to the conjugated cyano-group (2185 cm^{-1}) and to the non-conjugated C=O group (1740 cm^{-1}). The ^{1}H NMR spectrum contains a doublet typical of a CH_2P group; this is inconsistent with the structure of adduct **2**, since the signals of the protons of the CH_2P group in the latter compound would be manifested as two multiplets, owing to the presence of a chiral center (*cf.* Refs. 1 and 2). The ^{13}C NMR spectrum exhibits signals corresponding to the C atoms of all the fragments of zwitterion **3**.

NMR spectra were recorded on a Bruker AMX-400 instrument in CD_3CN. IR spectra were measured on a Bruker IFS-25 spectrometer with a resolution of 2 cm^{-1}.

A mixture of zwitterion **1** (2.0 g) and phenyl isothiocyanate (7 mL) was heated in an atmosphere of dry argon for 5 h at 90 °C. The reaction mixture was cooled and mixed with 50 mL of anhydrous ether; the red oil thus liberated was reprecipitated from dichloromethane with ether and then kept *in vacuo* to give 2.3 g of compound **3** as a light-yellow powder (yield 80%), m.p. 50—53 °C. IR, ν/cm^{-1}: 1740 (COOEt); 2185 (CN). ^{31}P NMR, δ: 46.3. ^{1}H NMR, δ: 1.36 (t, 3 H, $C\underline{H}_3CH_2$, $J_{H,H}$ = 7.0 Hz); 1.53 (m, 18 H, $C\underline{H}_3CH$); 2.8 (m, 3 H, $C\underline{H}CH_3$); 3.9 (d, 2 H, CH_2P, $J_{H,P}$ = 12.2 Hz); 7.25 (m, 5 H, C_6H_5). ^{13}C NMR, δ: 14.1 (s, $\underline{C}H_3CH_2$); 16.21 (s, $\underline{C}H_3CH$); 20.68 (d, CH_2P, $J_{C,P}$ = 42.0 Hz); 20.5 (d, CHP, $J_{C,P}$ = 31.7 Hz); 61.0 (s, OCH_2); 85.5 (d, $\underline{C}CH_2P$, $J_{H,P}$ = 4.8 Hz); 117.0, 126.3, 126.2 (C_6H_5); 122 (s, CN); 153.0 (s, CO); 180.46 (s, CS). Found (%): N, 6.44 and 6.30. $C_{22}H_{33}N_2O_2PS$. Calculated (%): N, 6.66.

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References

1. T. O. Krylova, O. V. Shishkin, Yu. T. Struchkov, G. D. Kolomnikova, and Yu. G. Gololobov, *Zh. Obshch. Khim.*, 1995, **65**, 1393 [*Russ. J. Gen. Chem.*, 1995, **65** (Engl. Transl.)].
2. Yu. G. Gololobov, V. A. Pinchuk, H. Thonnessen, P. G. Jonts, and R. Schmutzler, *Phosph., Sulf., and Silicon*, 1996, in press.

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