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Unusual Transformations of Ethyl-2-cyanoacrylate in Reactions with Trivalent Phosphorus Compounds

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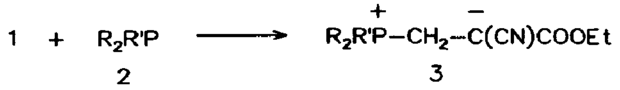
Abstract. Interaction of ethyl-2-cyanoacrylate **1** with trivalent phosphorus compounds can cause not only polymerization of **1**, but under established conditions it affords, depending on the structure of the latter, betaines **3**, spirophosphoranes **5**, i.e. phosphorylated at the carbonyl oxygen esters of 2-cyanopropionic acid or 2-cyano-3-phosphoranylpropionates **9**.

2-Cyanoacrylates e.g. **1** have existed for 40 years[1], but up till now[2] only polymerization processes, effected by various nucleophiles, including trivalent phosphorus compounds[3], have been known.

We have shown that under established conditions ethyl-2-cyanoacrylate $CH_2=C(CN)COOEt$ **1** reacts with trivalent phosphorus compounds not only *via* the anionic polymerization pathway[3], but depending on the structure, it forms stable adducts **3**, **5** or **9**.

Scheme 1



$$1 + \underset{2}{R_2R'P} \longrightarrow \underset{3}{R_2R'\overset{+}{P}-CH_2-\overset{-}{C}(CN)COOEt}$$

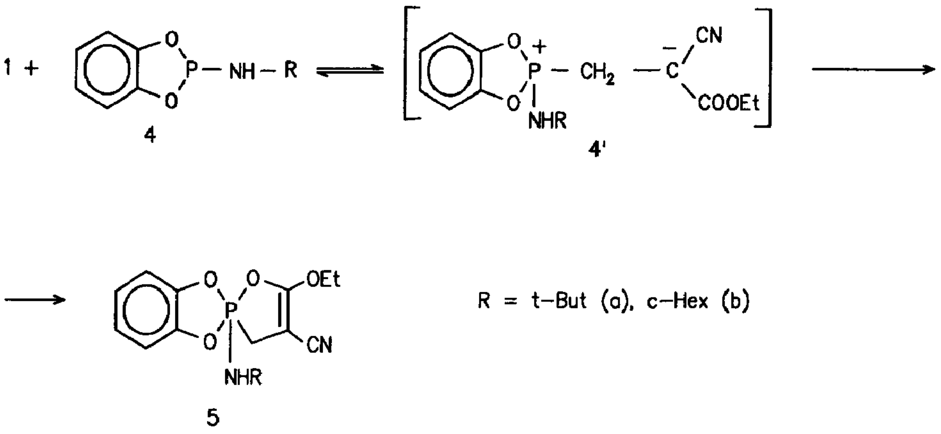
R = R' = Pr (a); R = R' = Bu (b); R = R' = Et_2N (c);

R_2 = $(CH_2)_4$, R' = Et_2N (d); R = Et_2N, R' = NHt-Bu (e).

Only strong nucleophiles react *via* scheme 1 to form stable betaines **3**. Weak nucleophiles (for example Ph_3P) react reversibly with **1**, and the equilibrium is shifted to the left. Therefore, under any conditions of the experiment[4], an excess of **1** is present in the reaction medium, and it instantly polymerizes. In the betaines **3** the anionic charge is significantly delocalized, which is revealed by IR spectra data[5]. The structure of products **3** follows from NMR (^1H, ^{13}C, ^{31}P), IR and UV spectra data and elemental analysis data[8].

The anionic charge in **3** is not stabilized by the shift of a proton to anionic carbon, because its basicity is significantly reduced. The second possibility of the stabilization of the anionic charge in five-membered betaines **4'** is closing into unsaturated ring **5**.

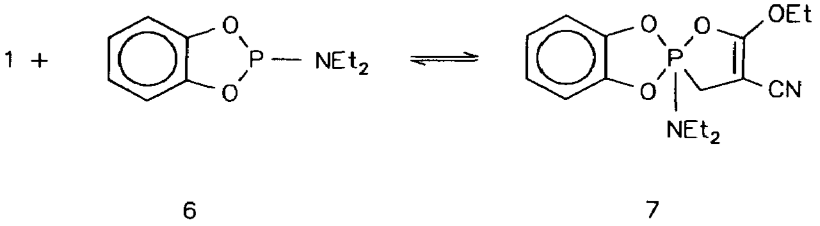
Scheme 2



R = t-But (a), c-Hex (b)

The betaine **4'**, which is formed at the first stage of the reaction, in principal, may be stabilized by the shift of a proton of the group NH to the anionic centre[9]. But this possibility is not realized (the hydrogen atom is not sufficiently mobile[10]), and formation of the favourable spirophosphorane structure **5** takes place. Stereo effects play an important role in its stabilization, because, for example, the analogous derivative **7** with a diethylamino group at phosphorus is rather unstable[11].

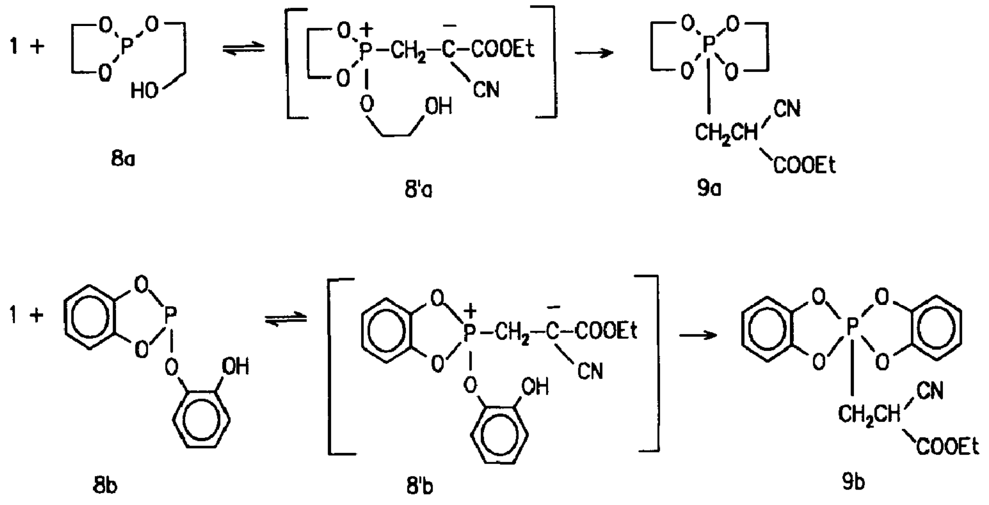
Scheme 3



Carboxylic acid esters with P-C bond, which are intramoleculary phosphorylated at oxygen, were unknown. Moreover, 2-cyanoacrylates were probably the first representatives of acrylic acids esters with an unsubstituted group CH_2, which successfully react with P(III) to afford betaines **3** and spirophosphoranes **5**, **7**.

In the case of the formation of low stable betaines **8'a,b** in reaction between **1** and phosphites, anions **8'a,b** may be trapped by protons of the oxygroups of starting phosphites **8a,b** (scheme 4).

Scheme 4



Probably, scheme 4 depicts the general principle of the preparation of spirophosphoranes which are derivatives of 2-cyanopropionate. The principle includes the creation of the conditions under which selfprotonation of the anion occurs simultaneously with the inclusion of phosphorus into the ring.

Acknowledgement. We are grateful to Dr. P.V.Petrovskyi and Dr. I.A.Garbuzova for recording spectra and discussions thereof.

References and Notes

[1] *Cyanoacrylate Resins - The Instant Adhesives* Ed. H.Lee, Pasadena: Pasadena Thechnol. Press, **1981**, p.241.

[2] Kandror I.I.; Bragina I.O.; Galkina M.A.; Lavruhin B.D.; Gololobov Yu.G. *Izv. Akad.Nauk SSSR, Ser. khim.* **1990**, s.2798.

[3] Cronin J.P.; Pepper D.C., *Makromol. Chem.* **1988**, *189*, s.85

[4] 20% Solution of **1** in pure benzene was added on stirring at 20°C to 10% benzene solution of **2**, **4** or **8**. After 2 - 3 h benzene was evaporated in *vacuo* to 1/3 volume. Pentane was added to the residue, the mixture was stirred and the upper layer was poured off. The operation was repeated 3 - 4 times. The powder residues **3** (quant. yields), **5** and **9b** were dried in *vacuo*, a liquid residue in the case of **9a** was distilled. NMR ^{1}H (200 MHz), ^{13}C (50 MHz) and ^{31}P (81 MHz) spectra (δ ppm, C_6D_6 or C_6H_6, internal reference TMS and 80% H_3PO_4 for ^{1}H, ^{13}C and ^{31}P spectra respectively) entirely consistent with the assigned structures. Selected physical properties as follow: **3a** m.p. 85-86°C; ^{1}H NMR 3.31 (d, $C\underline{H}_2P$, J_{PH} = 7.0 Hz); δ ^{31}P 31.3; m/z 286 $[MH]^+$. **3b** oil, ^{1}H NMR 3.26 (d, $C\underline{H}_2P$, J = 6.8 Hz); δ ^{31}P 32.7. **3c** m.p. 69-70°C; δ ^{31}P 57.5; ^{1}H NMR 3.43 (d, $C\underline{H}_2P$, J_{PH} = 7.4Hz); ^{13}C NMR 26.30 (d, $C\underline{C}H_2P$), 33.36 (s, $\underline{C}CH_2P$); m/z 373 $[MH]^+$. **3d** m.p. 82-

83°C; δ ^{31}P 57.6; ^1H NMR 3.44 (d, CCH_2P, J_{PH} = 7.4 Hz). **3e** m.p. 49-50°C; δ ^{31}P 81.9; ^1H NMR 3.34 (d, CCH_2P, J_{PH} = 7.2 Hz); m/z 285 $[MH]^+$. **5a** yield 91%; m.p. 110-111°C; δ ^{31}P -13.2; ^1H NMR 3.00 - 3.19 (m, CH_AH_BP, J_{PH} = 14.7 Hz); ^{13}C NMR 31.8 (d, $\underline{C}CH_2P$, J_{PC} = 146.7 Hz), 145.9 ($\underline{C}$-CN), 167.5 (C-OEt); IR (cm^{-1} KBr) 1605 (C=C), 2196 (CN), 3330 (NH). **5b** yield 72%; m.p. 98-99°C; ^1H NMR 2.79 - 2.90 (m, CH_AH_BP, J_{PH} = 13.4 Hz); δ ^{31}P -16.8; IR 1625 (C=C), 2195 (C≡N), 3345 (NH). **9a** yield 83%; $b.p._{0.5}$ 172-173°C, m.p. 64-65°C; δ ^{31}P - 12.9; ^1H NMR 2.55 (m, $PC\underline{H}_AH_BCH_X$, $J_{H(A)H(B)}$ = 16.6 Hz,$J_{H(A)H(X)}$ = 7.1 Hz, $J_{H(A)P}$ = 21.3 Hz), 2.64 (m, $PCH_A\underline{H}_BCH_X$, $J_{H(B)H(X)}$ = 7.1 Hz, $J_{H(B)P}$ = 19.5 Hz), 3.72 (m, OCH_2CH_2O, $PCH_2C\underline{H}_X$). **9b** yield 74%; m.p. 107-108°C; δ ^{31}P -5.9; ^1H NMR 2.63 (m, $PC\underline{H}_AH_BCH_X$, $J_{H(A)H(B)}$ = 17.1 Hz, $J_{H(A)P}$ = 23.8 Hz, $J_{H(A)H(X)}$ = 6.7 Hz), 2.74 (m, $PCH_A\underline{H}_BCH_X$, $J_{H(B)P}$ = 22.7 Hz, $J_{H(B)H(X)}$ = 6.7 Hz), 3.34 (m, $PCH_AH_BC\underline{H}_X$, $J_{PH(X)}$ = 14.4 Hz); ^{13}C NMR 32.52 (d, PCH_2, J_{PC} = 177.3 Hz), 33.37 (d, $PCH_2\underline{C}H$, J_{PC} = 4.4 Hz). A reverse mixing of the reagents caused instant polymerization of **1**.

[5] Zwitterion **3** showed an intensive broad at 1611 cm^{-1} and a narrow intensive band at 2148 cm^{-1}, which was characteristic of cyanoacetic ester salts with the anionic moiety $[N{\equiv}C{=}C{=}C{=}O]^-$ [6]. An UV spectrum of **3** contains an absorption band (max 255 nm) characteristic of the anion of cyanoacetic ester[7].

[6] Yuchnovski J.; Nazir A.F.; Sahatchieva M.; Kaneti J.; Binev Y., *Izv. Khim.* (Bulgaria) **1980**, *13*, p.269.

[7] Dale J.; Morgenlie S., *Acta Chem. Scand.* **1970**, *24*, p. 2408.

[8] For all the compounds **3**, **5** and **9** analysis of C, H, N, P was satisfactory.

[9] Pudovick A.N.; Krupnov G.P., *Zh. Obstch. Khim.* **1964**, *34*, s.1157.

[10] According to ^{31}P NMR spectra data, on the introduction of compound **4** into the reaction *via* scheme 2, **5** (R = Ph, δ ^{31}P -12.9) was formed; it was slowly transformed into imine o-$C_6H_4O_2P(=NPh)CH_2CH(CN)COOR$ (δ ^{31}P 20.0) and then into its dimer (δ ^{31}P -53.0).

[11] Addition of **1** to **6** led to instant formation of **7**, the structure of which was confirmed with NMR (^1H, ^{13}C, ^{31}P) and IR data. Selected spectra data as follow: δ ^{31}P -11.27 (C_6H_6); ^1H NMR (C_6D_6) 3.01 (d, $CC\underline{H}_2P$, J_{PH} = 5.2 Hz); ^{13}C NMR (CCl_4) 33.01 (d, CH_2P, J_{PC}= 149.5 Hz), 146.45 (d, $\underline{C}CN$, J_{PC} = 7.9 Hz), 166.0 (d, C-OEt, J_{PC} = 22.4 Hz); IR (cm^{-1} CCl_4) 1634 (C=C), 2203 (CN). After several days an NMR spectrum detected the signal of the starting **6** in a benzene solution. Polymer of **1** was formed also.

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