Contents lists available at ScienceDirect

Comptes Rendus Chimie

www.sciencedirect.com

Account/Revue

1,3-phosphorus zwitterions with cyano-group at anion center

Yuri G. Gololobov [a,*], Mikhail Y. Gololobov [b]

[a] A.N. Nesmeyanov Institute of Organo-Element Compounds, Russian Academy of Science, 11991 M-334, Vavilov Str., 28, Moscow, Russia
[b] Polium Technologies, Inc., 702 Scarborough Circle, Hoffman Estates, IL 60169, IL, USA

ABSTRACT

This review focuses on synthesis and properties of 1,3-phosphorus-containing zwitterions that have at the anionic center cyano-group and either ester (type one) or carbamate (type two) moieties. Zwitterions belonging to type one possess dual nucleophile reactivity, i.e., depending on the properties of the electrophiles they may form either C- or N-derivatives. Zwitterions belonging to type two possess triple nucleophile reactivity. In their reactions with electrophiles, they may form even three types of derivatives, i.e., at the C-, O- or N-atoms. This nucleophile multiplicity is not just interesting from the theoretical standpoint but may also open the ways to the synthesis of new compounds that can be important from the practical standpoint, such as physiologically active compounds, catalysts, analytical reagents, etc.

© 2010 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

1. Introduction

According to IUPAC, zwitterions are neutral compounds having formal unit electrical charges of opposite sign [1]. This review focuses on 1,3-phosphorus-containing zwitterions (1,3-P-zwitterions) with cyano-group at the anion center, i.e., inner salts in which a negative charge formally is localized on the carbon atom bearing cyano-group and a positive charge on a phosphorus atom and in which negatively and positively charged centers are separated just by one carbon atom (cyano-1,3-P-zwitterions).

More than 50 years ago, Horner and Klüpfel [2] discovered formation of 1,3-P-zwitterions upon reaction of tertiary phosphines with vinylidene derivatives. A typical example of reactions between phosphine 1 and alkene 2 that gives 1,3-P-zwitterion 3 is shown in Scheme 1.

Since their first synthesis, 1,3-P-zwitterions have been deserving significant attention from the scientific community [3–8]. General analysis of their properties is beyond

the scope of this publication. Our review focuses on 1,3-P-zwitterions with one cyano-group at the anion center, i.e., cyano-1,3-P-zwitterions. Their general structure is shown in Fig. 1, where R^1, R^2, R^3, are various alkyl- and alkylamino-substituents, R^4 is aryl-group or hydrogen atom and X is either alkoxy- (cyano-1,3-P-zwitterions of type one) or N(Ar)C(O)OAlk-group (cyano-1,3-P-zwitterions of type two).
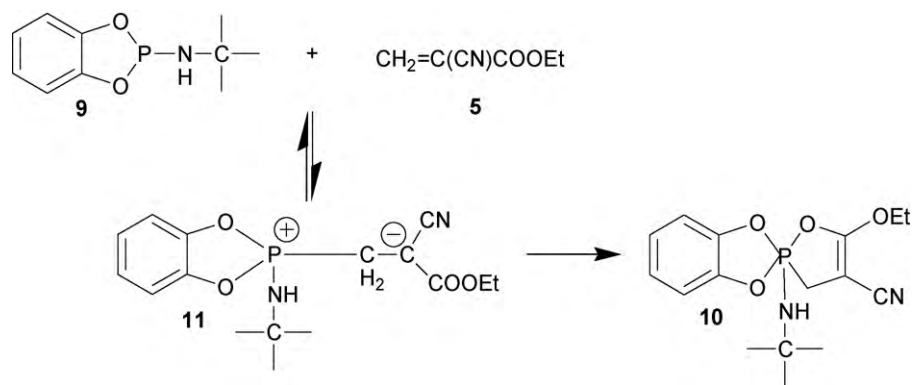
Y.G. Gololobov and his colleagues have been studying these compounds at the A.N. Nesmeyanov Institute of Organo-Element Compounds of the Russian Academy of Sciences since 1995 [9,10]. This review summarizes results they have obtained since that time.

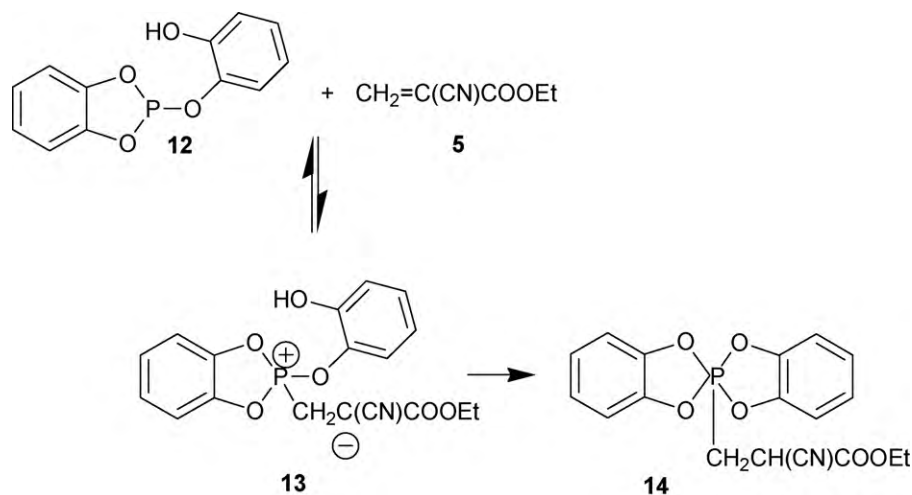## 2. Reactions of P(III) compounds with alkyl-2-cyanoacrylates and synthesis of cyano-1,3-P-zwitterions

Until now, the reaction between tertiary phosphines and substituted alkenes remains the main general method to synthesize 1,3-P-zwitterions. This reaction is usually considered an equilibrium process [3,5,11,12]; its net result depends on both the equilibrium position and the other reactions that might occur to the starting materials and/or the products. The latter depends on properties of

* Corresponding author.
   E-mail addresses: Yugol@ineos.ac.ru (Y.G. Gololobov),
mgololobov0711@gmail.com (M.Y. Gololobov).

Scheme 1.

Fig. 1. 1,3-P-zwitterions of type one.

P(III) compounds and alkenes, which in turn mostly depend on the effect of the substituents on the properties of these compounds. For the formation of stable 1,3-P-zwitterions, substituted alkenes should have strong electron-acceptor groups [13]. In this case, the equilibrium of the reaction is shifted completely to the zwitterion side and stable 1,3-P-zwitterions are the only products.

1,3-P-zwitterions of type one (Fig. 1) are synthesized by reacting P(III) nucleophilic compounds with alkyl-2-cyanoacrylates. Alkyl-2-cyanoacrylates bear strong electron-acceptor groups and therefore one might think they would always reacted smoothly with P(III) compounds with the formation of 1,3-P-zwitterions. However, alkyl-2-cyanoacrylates readily polymerize [14,15] under the action of nucleophiles and, as it is briefly discussed below, the rate of this polymerization strongly depends on the properties of P(III) compounds that react with cyanoacrylates.

Based on reactivity toward alkyl-2-cyanoacrylates, P(III) compounds can be divided into three groups [16]. The first group includes PCl_3 and similarly low nucleophilic phosphorus halides that display no reactivity with respect to 2-cyanoacrylates at room temperature. The second group includes weak nucleophiles such as $(EtO)_3P$, Ph_3P. They do form 1,3-P-zwitterions to some extent by reacting with 2-cyanoacrylates, but since the equilibrium is shifted to the starting materials, concentration of alkyl-2-cyanoacrylates remains high and the major product is the polycyanoacrylate polymer bearing phosphonium group as the head group [15]. A typical example of these reactions is shown in Scheme 2.

While equilibrium of the reaction of alkyl-2-cyanoacrylates with weak P-nucleophiles is shifted to the initial compounds, these reactions may still have interesting implications from the synthetic standpoint. All that is needed to avoid cyanoacrylate polymerization is to turn a newly formed intermediate 1,3-P-zwitterion into another compound [15]. This would shift the equilibrium between a weak nucleophile and alkyl-2-cyanoacrylate to the right side. Protonation of the negatively charged carbon with trifluoroacetic acid is one of the ways to implement this approach (Scheme 3). Protonation turns zwitterion **6** into unstable phosphonium salt **7**. This salt spontaneously gives another P-derivative **8** by eliminating trifluoroacetic acid ester. As a result of all these reactions, the overall equilibrium is completely shifted to new P-derivative **8**.

Rearrangement of newly formed zwiterrions into stable five-membered spirophosphoranes is another way of shifting the equilibrium (Scheme 4) [17]. For example, reaction of cyclic phosphite **9** with ethyl-2-cyanoacrylate **5** gives stable spiro-phospholane **10**, mostly likely, through the formation of intermediate **11**.

Scheme 2.

Scheme 3.

Scheme 4.

Scheme 5.

Reaction between ethyl-2-cyanoacrylate **5** and weak *P*(III) nucleophile **12** can be also driven to the complete consumption of the initial components by "trapping" the anionic charge of zwitterion **13** with the acidic hydrogen as shown in Scheme 5. This pathway can take place only if this proton transfer results in the formation of a stable five-member ring as in product **14**.

The third type of *P*(III) compounds includes strong nucleophiles like trialkylphosphines and hexaethyltriami-dophosphite. These nucleophiles react with cyanoacrylates with the formation of stable cyano-1,3-*P*-zwitterions if certain conditions are obeyed [9,17,18]. High phosphine nucleophilicity is one of these conditions. The order of mixing of the reagents is another mandatory condition. For successful synthesis of target compounds, cyanoacrylate **15** must be added to the solution of phosphine **16** in a non-polar solvent in which the product is not soluble. Under these conditions, during the whole reaction a phosphine is in excess. As a result, an instantaneous formation of crystalline cyano-1,3-*P*-zwitterions **17** with yields of up to 50% takes place (Scheme 6).

3-aryl-2-cyanoacrylates **18** react with tributylpho-sphine **19** in acetonitrile in a similar fashion and afford respective cyano-1,3-*P*-zwitterions **20** with good yields (Scheme 7) [18].

3. Type one cyano-1,3-*P*-zwitterions and their physicochemical characteristics

Table 1 lists spectral properties and melting points of cyano-1,3-*P*-zwitterions of type one that have been synthesized using approaches shown in Schemes 6 and 7.

Delocalization of the negative charge is the key structural characteristic of cyano-1,3-*P*-zwitterions **17** and **20**. While formally this negative charge is assigned to the central carbon atom, in reality electrons are spread from nitrogen of the cyano group to the carbonyl oxygen. Delocalization of the negative charge that is schematically shown in Scheme 8 follows from the experimental data [17]. As is shown in Table 1, because of this delocalization, absorption bands of the *CN*-groups are very intense and shift to the 2144–2160 cm^{-1} range. A similar shift to the region of 1597–1627 cm^{-1} is observed for the $C(O))OR^5$ absorption bands. X-ray diffraction analysis of zwitterions **17** [20] and **20** [18] also support electron conjugation in cyano-1,3-*P*-zwitterions **17**. According to

R^1 and R^2 = Pr, n-Bu, Et_2N, i-Pr, $(CH_2)_4$

R^3 = Pr, n-Bu, Et_2N, i-Pr, NH-t-Bu

R^4 = H

R^5 = Me, Et, Allyl, Propargyl

Scheme 6.

Ar = Ph, p-HO-Ph, p-MeO-Ph, p-Br-Ph

R^5 = Et
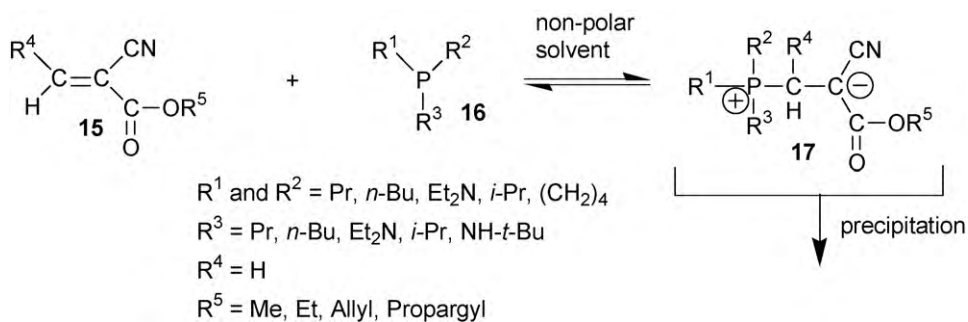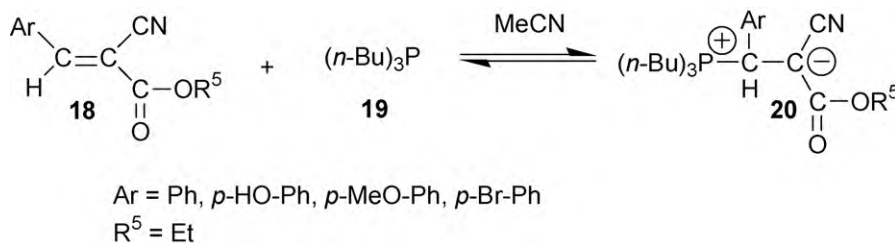
Scheme 7.

Table 1
Spectral properties and melting points of cyano-1,3-P-zwitterions **17** and **20**.

Zwitterion **17** or **20**					M.p. (°C)	IR (ν, cm^{-1})		^{31}P NMR (ppm)	Lit.
R^1	R^2	R^3	R^4	R^5		CN	C(O)OR^5		
Pr	Pr	Pr	H	Et	85–86	2148	1611	N/A	[17,19]
n-Bu	n-Bu	n-Bu	H	Et	Oil	2148	1611	32.7	[17,19]
Et$_2$N	Et$_2$N	Et$_2$N	H	Et	69–70	2148	1611	57.5	[17,19]
Et$_2$N	Et$_2$N	NH-t-Bu	H	Et	82–83	2148	1611	57.6	[17,19]
n-Bu	n-Bu	Et$_2$N	H	Et	49–50	2148	1611	81.9	[19]
i-Pr	i-Pr	i-Pr	H	Me	133–134	2146	1627	38.7	[20]
i-Pr	i-Pr	i-Pr	H	Et	146–147	2136	1602	44.9	[20]
(CH$_2$)$_4$		Et$_2$N	H	Et	82 - 83	–	–	57.6	[17]
i-Pr	i-Pr	i-Pr	H	Allyl	123–124	2143	1619	38.8	[21]
i-Pr	i-Pr	i-Pr	H	Propargyl	122–124	2160	1621	39.18	[21]
n-Bu	n-Bu	n-Bu	p-HOPh	Et	106–107	2138	1598	36.4 (in d-DMSO)	[18]
n-Bu	n-Bu	n-Bu	p-MeOPh	Et	69–70	2140	1608	36.3 (in d-DMSO)	[18]
n-Bu	n-Bu	n-Bu	p-BrPh	Et	99–100	2140	1597	36.1 (in d-DMSO)	[18]
n-Bu	n-Bu	n-Bu	Ph	Et	62–63	2133	1601	36.4 (in d-DMSO)	[18]

these data, bond lengths are distorted from their typical values. This suggests delocalization of the negative charge along the N–C–C–C–O skeleton.

Similar phenomenon for cyano-1,3-P-zwitterions of type two is discussed in Section 5.

4. Chemical properties of type one cyano-1,3-P-zwitterions

4.1. Storage stability of type one cyano-1,3-P-zwitterions 17 and 20

Upon crystallization, zwitterions **17** are relatively stable. At 0–5 °C, they stay intact for several months. In solution, cyano-1,3-P-zwitterions **17** are much less stable

and their stability varies significantly and depends on the solvent. In general, storage of these compounds in solution is not recommended. For example, ^{31}P NMR analysis of the solutions of cyano-1,3-P-zwitterions with isopropyl substituents at the P-atom in methylene chloride, acetonitrile, acetone and THF shows presence in these solutions of several percent of tri-iso-propylphosphine from which these zwitterions were synthesized. Alkyl-2-cyanoacrylate, the second product of the zwitterion decomposition, polymerizes easily and it shifts the equilibrium to the complete decomposition of the zwitterion. Boiling solutions of zwitterions **17** in benzene results in their complete decomposition [19].

Dependence of stability on the type of the solvent is particularly striking for cyano-1,3-P-zwitterions **20** [18]. In
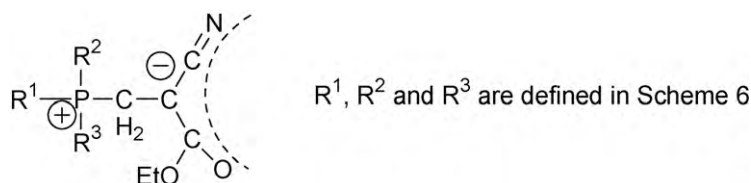
Scheme 8.
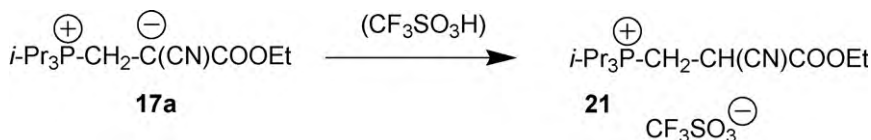
Scheme 9.

polar solvents, such as MeCN, MeNO₂, Me₂SO₂ [22] these zwitterions are relatively stable, whereas in solvents of low polarity tributylphosphine and tributylphosphineoxide (the product of tributylphosphine oxidation) are detected practically immediately after the dissolution of zwitterions **20** in these solvents. After several minutes, composition of the reaction mixture stabilizes and then remains unchanged almost indefinitely because, contrary to 2-substituted cyanoacrylates, 3-substituted cyanoacrylates that are formed in the reaction do not polymerize. The amounts of zwitterions **20** (Scheme 7) that remain intact in the solutions are listed in Table 2.

4.2. Reactivity of type one cyano-1,3-P-zwitterions 17

4.2.1. Protonation of zwitterion 17a

Zwitterions **17** can be easily protonated. For example, reaction of zwitterion **17a** with CF₃SO₃H formed in situ from CF₃SO₂SiMe₃ in wet acetone leads to salt **21** (Scheme 9) [20].

Compounds **17a** and **21** provide a good example of how protonation of the central carbon atom of cyano-1,3-P-zwitterions affects their spectral characteristics. Comparison of ¹H NMR spectrum of compounds **17a** and **21** shows that protonation of the negative charge in **17a** results in the 5–6 ppm upfield shift for all protons.

4.2.2. Alkylation: reaction of zwitterions 17 with alkylhalogens

Zwitterions **17** are nucleophiles that are strong enough to be alkylated by alkyl halides as shown in Scheme 10 [23].

Alkyl halides alkylate cyano-1,3-P-zwitterions **17** at the central atom of the N–C–C–C–O pentade with the formation of salts **22**. In IR spectra of the reaction mixture, characteristic zwitterion band disappears to give way to absorption bands at 1730–1750 cm⁻¹ and 2240 cm⁻¹ caused by oscillations of the ester and nonconjugated nitrile moieties, respectively. In the case of the zwitterion formed by i-Pr₃P, reaction of this zwitterion with 1,3-dichloroacetone links two zwitterions together resulting in molecule **23** bearing two positive charges.

4.2.3. Arylation: reactivity of zwitterion 17a toward 2,4-dinitro- and 2,4,6-trinitrofluorobenzenes

Reactions above occur at the central carbon atom of the N–C–C–C–O skeleton. It would be reasonable to assume that due to electron delocalization other nucleophilic atoms of the N–C–C–C–O skeleton may also serve as nucleophiles. As it is shown below, reaction of zwitterion **17a** with such polynitrofluorobenzenes as 2,4-dinitrofluorobenzene (DNFB) and 2,4,6-trinitrofluorobenzene (TNFB) may result in either C- or N-derivatives depending on the structure of the polynitrofluorobenzene and the temperature for reaction with DNFB.

Depending on the temperature, zwitterion **17a** reacts with DNFB via different pathways (Scheme 11).

At −15 °C, the reaction occurs predominantly according to the traditional pathway ("a") with the formation of new aromatic compound **24**. On the contrary, at room temperature, unexpected pathway "b" takes place that gives compound **25**. Structure of compound **25** was established by IR, NMR (¹H, ¹³C, ³¹P) spectroscopy and

Table 2
Remaining fraction (in %) of zwitterions **20** after their storage in different solvents at room temperature (Unless stated otherwise, R is the substituent at the *para*-position of phenyl-group; E is dielectric permeability [18,22]).

| R/Solvent	H	OH	OCH₃	Br	m-NO₂	NO₂	E
CH₃CN	91.3	98.8	96.9	100	100	100	37.5
Me₂SO₂	87.9	94.3	95.9	97.7	96.8	98.2	48.9
(CH₃)₂CO	40	21.6	30.7	21.4	27.9	29.2	20.70
CHCl₃	1.1	3.1	1.7	2.5	2.8	3.3	4.806
THF	0	3.8	1.3	2.6	2.2	3.1	7.4

Scheme 10.

Scheme 11.
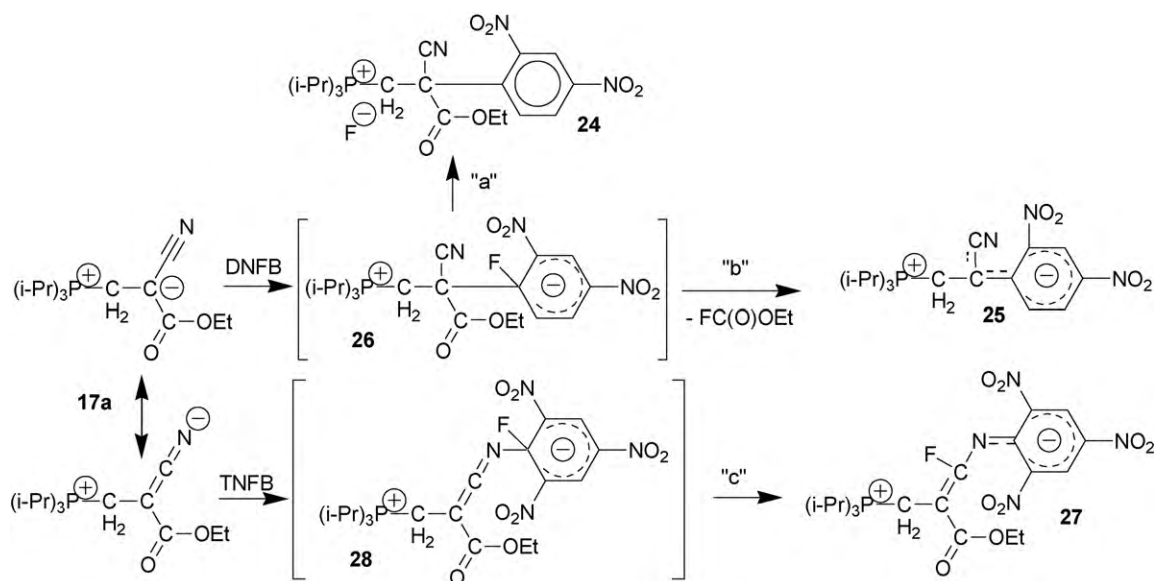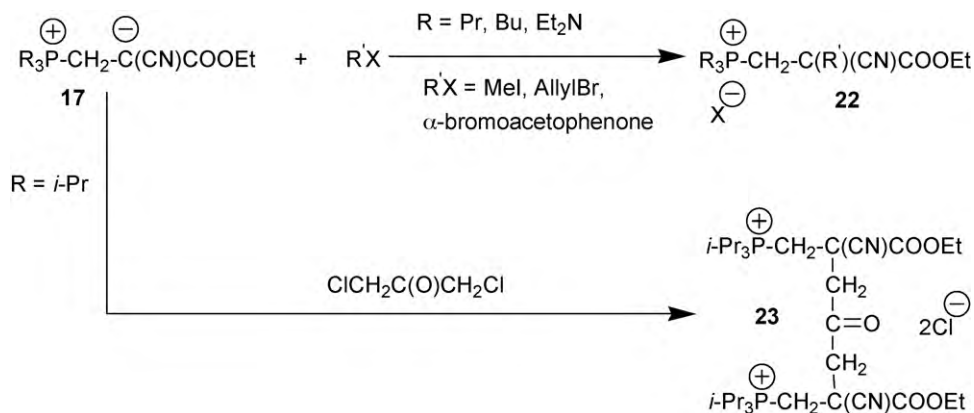
X-ray diffraction analysis [24]. The most feasible mechanism includes the rupture of the weak C–C bond between the α-C atom and the carbonyl group in the α-C–C(O)OEt moiety [25] upon breakdown of σ-complex **26**. It is noteworthy that at room temperature compound **24** does not turn into compound **25**. This suggests formation of **25** directly from σ-complex **26**.

However, contrary to the reaction between zwitterion **17a** and DNFB, the same zwitterion reacts with TNFB with the formation of N-derivative **27** [26] (pathway "c"). At 3 °C, according to the ^{31}P and ^{19}F data, the reaction between zwitterion **17a** and TNFB in methylene chloride quantitatively affords the only product, i.e., crystalline dark-red compound **27**. Structure of this compound was established by a single-crystal X-ray diffraction analysis. In all likelihood, the reaction pathway follows Scheme 11. Zwitterion **17a** may be depicted as a sum of two resonance forms, one with the negative charge at the carbon atom,

and another with the negative charge at the nitrogen atom of the cyano-group. Reaction of TNFB with this nitrogen atom results in the formation of compound **27** most likely directly upon breakdown of σ-complex **28**. Differences between reaction pathways for reaction of zwitterion **17a** with DNFB and that with TNFB can be explained by the steric effect of the second ortho-NO_2-group. Clearly, the approach of the C-anionic center of zwitterion **17a** to the C–F bond should be sterically hindered by the second ortho-NO_2-group. At the same time, the nitrogen atom of the N-resonance form of this zwitterion should lack these steric interferences. This reaction may also include initial formation of unstable dead-end C-σ-complexes.

4.2.4. Formation of carbamate 1,3-P-zwitterions (cyano-1,3-P-zwitterions of type two)

Zwitterions **17** react with unsubstituted phenyl, orto-, meta- and para-substituted phenylisocyanates, 1-naphtyl
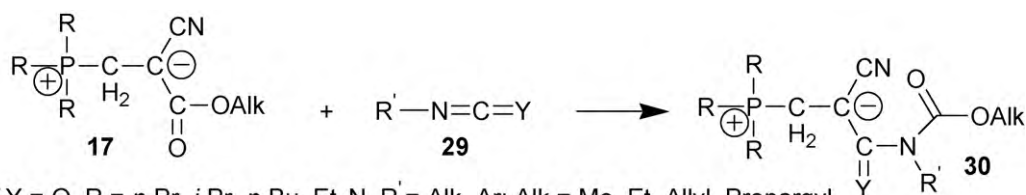
Scheme 12.

isocyanate and phenylisothioisocyanate **29** to give carbamates **30** [9,27,28] (Scheme 12).

Mechanism of this reaction has been studied spectrophotometrically by following its kinetics in a number of solvents at temperatures between 20 °C and 60 °C. It was established that the reaction followed the first order with respect to each reagent; the reaction is second order overall. Most likely, the reaction follows the mechanism shown in Scheme 13 [29].

As shown in Scheme 13, the reaction follows an unusual pathway: a carbanion rather than the ethoxy anion (as in the case of ester aminolysis) acts as the leaving group. Apparently, the unique situation in which breaking a C–C-bond is preferred over breaking a C–O bond is due to the energetic gain from the more effective delocalization of the anionic charge in carbamate **30a** being formed.

The rate of the reaction between zwitterion **17a** and ArNCO strongly depends on the volume of *ortho*-substituent [30]. According to the ^{31}P NMR data, the insertion of the isocyanate moiety into the C–C bond of zwitterion **17a** in the reactions with *ortho*-substituted phenyl isocyanates proceeds slower that the same reactions with phenyl unsubstituted isocyanates. Consequently, bulky *ortho*-substituents create substantial hindrances during the reaction. Most likely, these steric hidrances have particluar effects during nucleophilic substitution at the C-atom of

the ethoxycarbonyl group of **31** [31]. X-ray diffraction studies confirm that in carbamate **30a** *ortho*-substituents and ester group are at a short distances from each other [31]. In its turn, this overcrowding in the vicinity of the carbamate carbonyl group created by the isocyanate *ortho*-substituent at the aromatic ring leads to the hindered rotation around the N–CAr bond and, as a consequence, to the emergence of chirality as ^{1}H NMR data show [31,32] (atropisomerism for **30a** with Ar having bulky *ortho*-substituents).

4.2.5. Reactions of zwitterions 17 with Iso(thio)cyanates not leading to carbamates

Not all iso(thio)cyanates form carbamates upon reaction with zwitterions **17**. Exceptions to Scheme 12 were studied using zwitterion **17a**. As shown below, zwitterion **17a** reacts differently with highly electrophilic tosylisocyanate and extremely sterically hindered arylisothiocyanates.
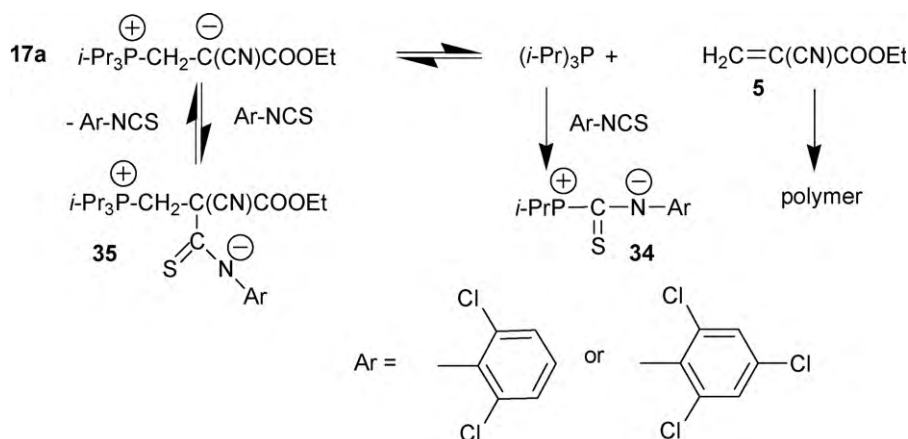
4.2.5.1. Reaction of zwitterion 17a with tosylisocyanate.
Reaction of zwitterion **17a** with highly electrophilic tosyl isocyanate leads to derivative **32** [20] (Scheme 14). ^{1}H and ^{31}P NMR data show that at the first moment tosylisocyanate reacts with zwitterion **17a** with the formation of compound **33**. However, negatively charged nitrogen atom
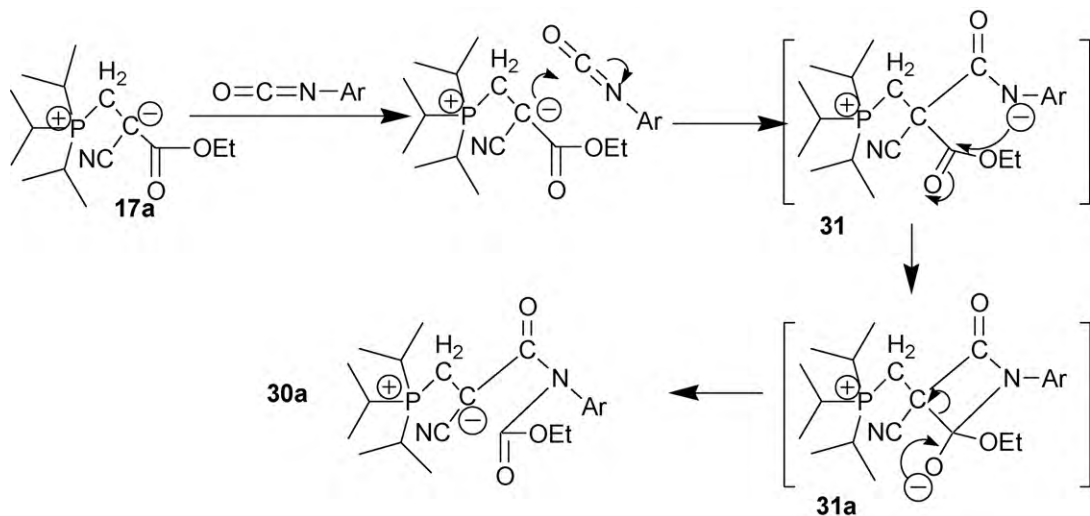
Scheme 13.
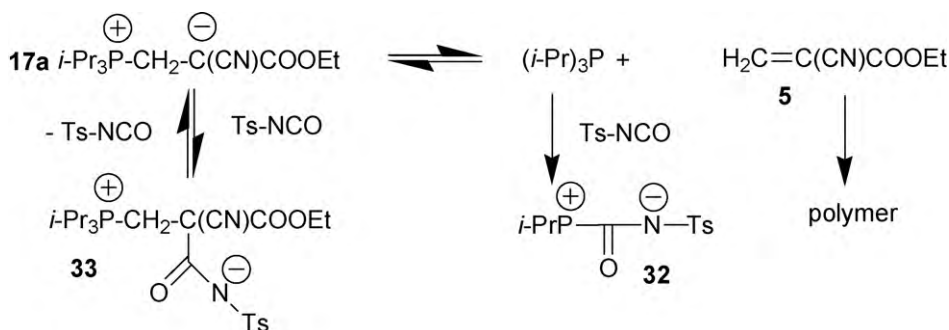
Scheme 14.

Scheme 15.

possesses negligible nucleophilicity due to highly electron withdrawing tosyl-group. Therefore decomposition of adduct **33** cannot proceed according to the mechanism shown in Scheme 13. Since formation of **33** from zwitterion **17a** with tosylisocyanate is a reversible reaction, with time the overall equilibrium completely shifts to compound **32** due to irreversible polymerization of cyanoacrylate **5**.

*4.2.5.2. Reactions of zwitterion **17a** with 2,6-dichloro- and 2,4,6-trichloroisothiocyanates.* Zwitterion **17a** reacts with these isocyanates according to Scheme 15 that also does not lead to carbamates [33]. This reaction gives *P,N*-zwitterion **34** and the cyanoacrylate polymer following the pathway that is similar to that with tosyl isocyanate (Scheme 15). However, contrary to the reaction with tosylisocyanate when electronic factors are the most likely major reasons for such a pathway, in the case of 2,6-dichloro- and 2,4,6-trichloroisothiocyanates steric factors probably play the major role [30]. The electron withdrawing effect of the chlorine atoms in the phenyl ring that should decrease nucleophilicity of the negatively charged nitrogen atom in **35** may also contribute to the overall effect.

*4.2.6. Reaction of zwitterion **17a** with C,N-diphenylnitrilimine*

Reaction of zwitterion **17a** with *C,N*-diphenylnitrilimine **36** in MeCN results in the formation of 2-pyrazoline

37. This is the first known example of a pyrazoline that bears phosphonium group (Scheme 16) [34].

However, the yield of pyrazoline **37** is just about 10%. The reason for such a low yield is that in this case zwitterion **17a** serves not only as latent *i*-Pr₃P but also as latent ethyl-2-cyanoacrylate **5**. Both these compounds react with *C,N*-diphenylnitrilimine **36**. As a result of these side reactions, corresponding phosphonium salt **38** and ethyl-1,3-diphenyl-5-cyano-4,5-dihydro-1*H*-pyrazole-5-carboxylate **39** is formed (Scheme 17).

*4.2.7. Zwitterions **17a** as the source of tri-iso-propylphosphine*

As it was discussed above, formation of cyano-1,3-*P*-zwitterions is a reversible reaction between phosphines and alkyl-2-cyanoacrylates. Therefore, in some cases these zwitterions can serve as latent phosphines. For example, zwitterion **17a** serves as a source of tri-*iso*-propylphosphine in the reactions with HgCl₂ [33], TsN₃ [20], TsNCO and 2.6-Br₂C₆H₃NCO [33]. The products of the reactions are the same as with free *i*-Pr₃P. Reactions are accompanied by the formation of the cyanoacrylate polymer.

5. Type two cyano-1,3-*P*-zwitterions and their physicochemical characteristics

Table 3 lists spectral properties and melting points of type two cyano-1,3-*P*-zwitterions.

PhC(Cl)=N-NHPh   +   Et₃N ⟶ PhC̈=N-N-Ph   +   Et₃NHCl

36
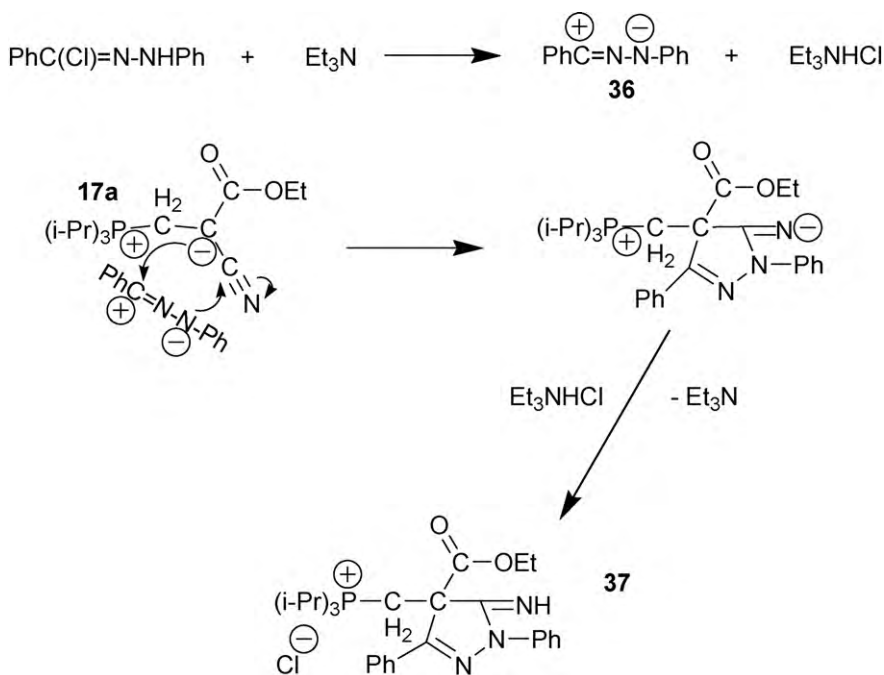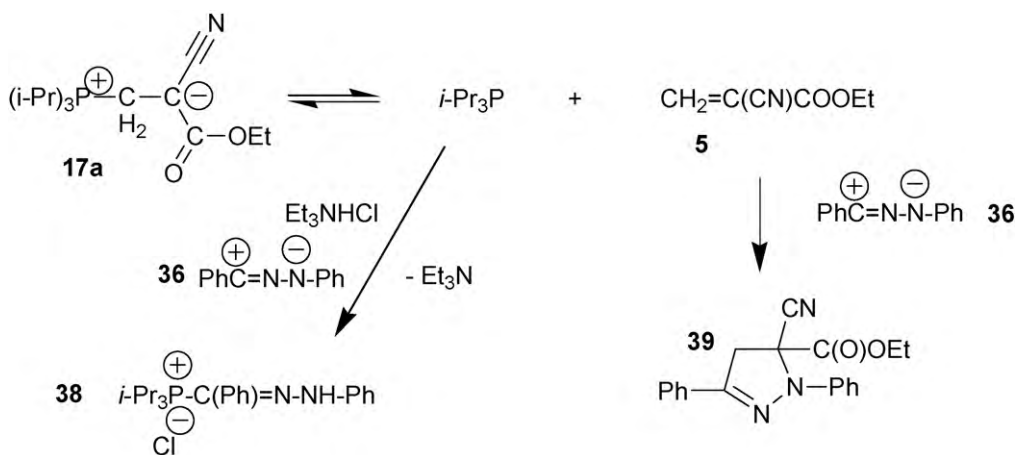
Scheme 16. .

Scheme 17.

In general, zwitterions **17** and **30** share many common features but chemical and physical properties of **30** suggest even higher degree of delocalization of the negative charge in the N–C–C–C–O skeleton than in **17** [20,27]. Higher degree of delocalization of the negative charge result, on one hand, in a weaker overall nucleophile reactivity of zwitterions **30** as compared to zwitterions **17**. This is why zwitterions **30** can serve as nucleophiles with very strong electrophiles only, such as acids [36], methyl triflate [36] and TNFB [37,38]. On the other hand, higher degree of delocalization of the negative charge in the N–C–C–C–O pentade results, as it is evidenced from examples below, in triple nucleophile reactivity of this pentade as illustrated in Scheme 18.

6. Chemical properties of type two cyano-1,3-*P*-zwitterions 30

6.1. Storage stability of type two cyano-1,3-P-zwitterions 30

Cyano-1,3-P-zwitterions of type two are stable compounds. At room temperature, they can be stored in solid form practically indefinitely.

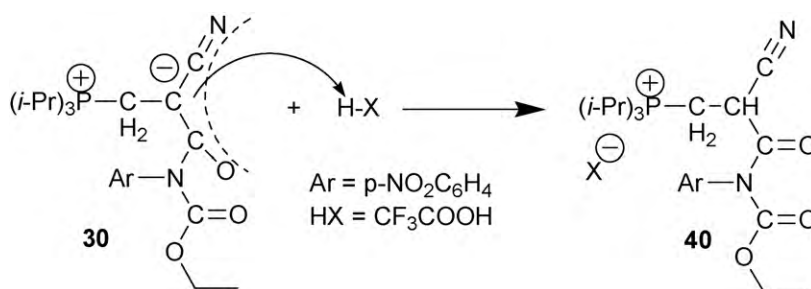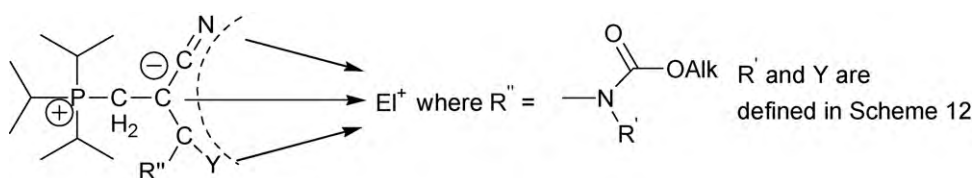### 6.2. Reactivity of type two cyano-1,3-P-zwitterions 30

6.2.1. C-protonation of type two cyano-1,3-P-Zwitterions 30
Reaction of zwitterions **30** with unhydrous acids results in C-protonation [36] (Scheme 19).

Table 3
Spectral properties and melting points of cyano-1,3-P-zwitterions **30** [30].

Zwitterion **30**				M.p. (°C)	IR (υ, cm^{-1})		^{31}P NMR (ppm)	Lit.
R	R'	Alk	X		CN	C(O)OR^5		
Pr	Ph	Me	O	36–37	2172	1718	34.1	[9,28]
Pr	Ph	Et	O	141–142	2155	1715	34.0	[9,28]
Bu	Ph	Et	O	70–72	2158	1695	35.2	[9,28]
Et$_2$N	Ph	Et	O	Dense oil	2165	1715	56.1	[9,28]
i-Pr	Ph	Et	S	146–147	2185	1720	44.38	[27]
i-Pr	Ph	Et	O	171–171.5			41.35	[20]
i-Pr	Me	Me	O	163–164	2158	1690	41.1	[20]
i-Pr	o-FC$_6$H$_4$	Et	O	145–146	2158	1685	40.97	[30]
i-Pr	o-ClC$_6$H$_4$	Et	O	169–170	–	–	41.15	[30]
i-Pr	o-BrC$_6$H$_4$	Et	O	170–171	2143	1619	40.86	[30]
i-Pr	o-IC$_6$H$_4$	Et	O	170–170.5	2160	1621	41.04	[30]
i-Pr	o-MeC$_6$H$_4$	Et	O	177–178	2138	1598	41.33	[30]
i-Pr	o-EtC$_6$H$_4$	Et	O	151–151.5	2140	1608	41.03	[30]
i-Pr	o-i-PrC$_6$H$_4$	Et	O	164–165	2140	1597	41.01	[30]
i-Pr	o-PhC$_6$H$_4$	Et	O	106–107	2133	1601	36.4	[30]
i-Pr	o-CF$_3$C$_6$H$_4$	Et	O	110–111	–	–	40.98 (^{19}F NMR, 60.3)	[30]
i-Pr	o-MeO-C$_6$H$_4$	Et	O	173–174	–	–	40.97	[30]
i-Pr	1-Naphthyl	Et	O	180–181	2170	1715	41.12	[27]
i-Pr	o,p-Me$_2$C$_6$H$_3$	Et	O	171–171.5	2175	1718	41.01	[31]
i-Pr	p-ClC$_6$H$_4$	Et	O	142–143	2170	1720	41.59	[27]
i-Pr	m,p-Cl$_2$C$_6$H$_3$	Et	O	169–170	2175	1730	41.63	[27]
i-Pr	p-NO$_2$C$_6$H$_4$	Et	O	157–158	2180	1725	41.49	[27]
i-Pr	Ph	CH$_2$–C≡CH	O	122–124	2160	1621	39.18	[35]
i-Pr	1-Naphthyl	CH$_2$–CH=CH$_2$	O	123–124	2143	1619	38.81	[35]

Scheme 18.

Scheme 19.

### 6.2.2. O- and S-methylation of type two cyano-1,3-P-zwitterions 30

Methylation of zwitterions **30** requires the use of such a strong methylating reagent as methyl trifluoromethanesulfonate (methyl triflate) (Scheme 20) [36].

6.2.3. N-Arylation of type two cyano-1,3-P-zwitterions 30

Reactions of zwitterions **30** with TNFB lead to N-derivatives (Scheme 21) [37,38].

This is the first known example of N-arylation of cyanocarboanions. Zwitterions **30** react under mild conditions in methylene chloride with the formation of either substituted oxazine-2,4-dione **42** [37] or isomeric barbiturate **43** [38]. The first pathway occurs if aryl substituent at the nitrogen atom of the carbamate moiety has ortho-ethyl group. Most likely, the latter hinders conversion of oxazine into barbiturate. This suggestion is supported by the fact that zwitterions **30** with unsubstituted phenyl group at the
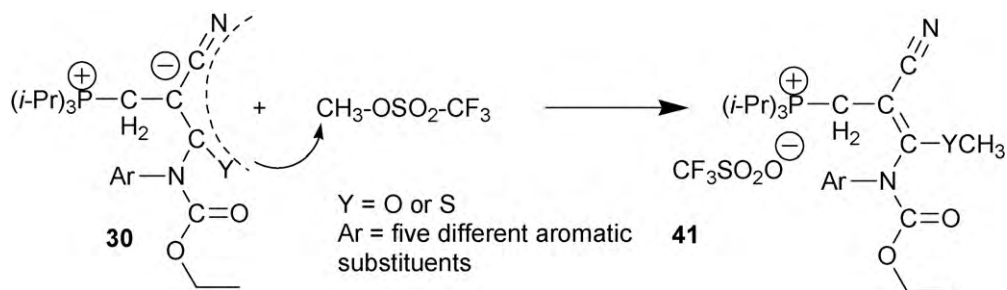
Scheme 20.
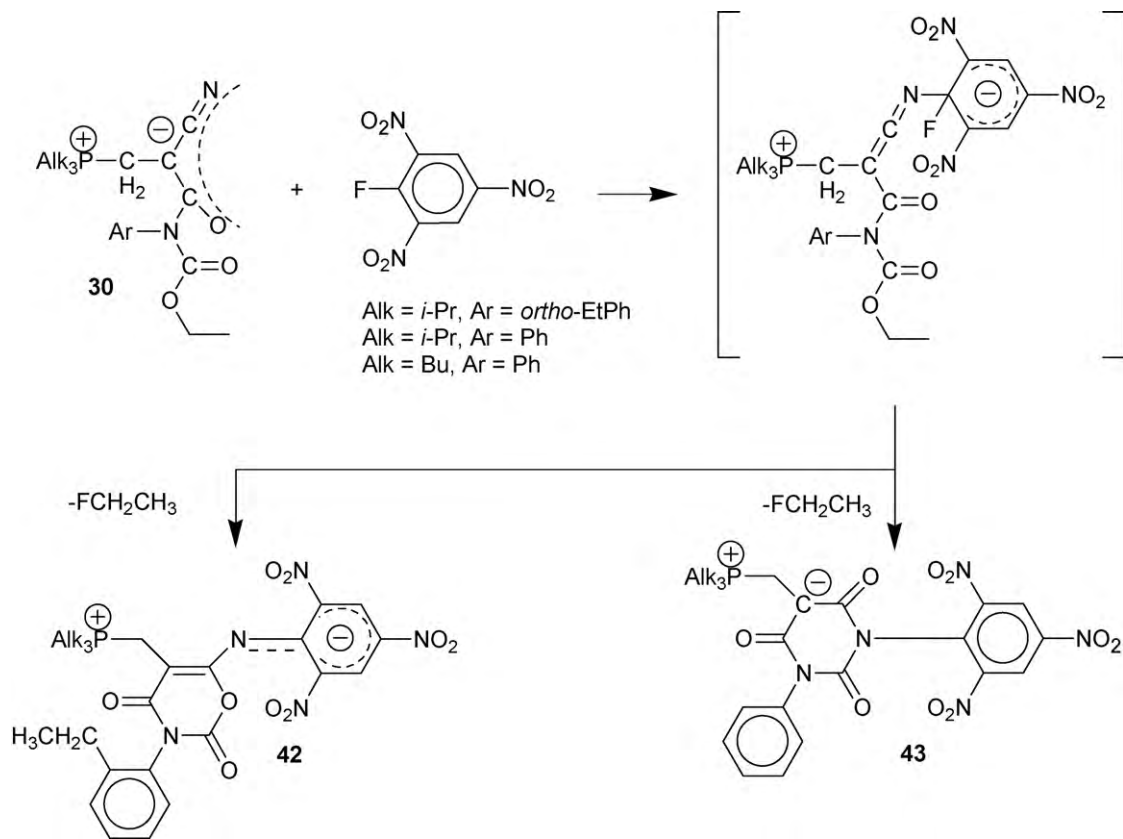
Scheme 21.

nitrogen atom of the carbamate moiety reacts with TNFB with the formation of barbiturate **43**. Structures of the products **42** and **43** were confirmed with X-ray diffraction analysis.

7. Conclusions

The review summarizes results that were obtained in a very interesting field of phosphorus-containing zwitterions of the new types. Reactions that were discovered for these zwitterions are also typical for other non-phosphorus carbanions. For example, carbanion derivatives of cyanoacrylic acid esters [39] also react with isocyanates

with insertion of the isocyanate molecule at the *C-C*-bond with the formation of carbamates. Arylation of carbanions derivative of cyanoacrylic acid esters [24] and cyanoacrylic acid amides [40] with polynitrohalobenzenes gives negatively charged conjugated structures instead of aromatic compounds. Unusual breaking the *C–C*-bond that was observed in the case of formation of **25** according to Scheme 11 occurs also in the reaction of cycloimmonium ylides with TNFB [41]. Therefore, the scope of *P*-zwitterion reactions discussed in this review is beyond of just this specific field of phosphorus chemistry and can be the foundation for expansion of frontiers of organic chemistry in general.

Acknowledgements

References

[1] B. McNaught, A. Wilkinson, IUPAC Compendium of Chemical Terminology, Blackwell Scientific Publications, Oxford, 1997.

[2] L. Horner, K. Klupfel, Justus Liebigs Ann. Chem. 591 (1955) 69.

[3] Z. Rappoport, S. Gertler, J. Chem. Soc (1964) 1360.

[4] H.R. Hudson, Chem. Organophosphor. Comp. 1 (1990) 386.

[5] F. Ramirez, J.F. Pilot, C.P. Smith, Tetrahedron 24 (1968) 3735.

[6] M.Z. Ovakimyan, G.G. Minasyan, P.V. Petrovskii, M.G. Indzhikyan, Russian Chem. Bull. 48 (1999) 1154.

[7] I.V. Borisova, N.N. Zemlyanskii, V.N. Khrustalev, M.S. Nechaev, M.G. Kuznetsova, Y.A. Ustynyuk, Russian Chem. Bull. 51 (2002) 678.

[8] V.I. Galkin, Y.V. Bakhtiyarova, N.A. Polezhaeva, I.V. Galkina, R.A. Cherkasov, D.B. Krivolapov, A.T. Gubaidullin, I.A. Litvinov, Russian J. Gen. Chem. 72 (2002) 384.

[9] Y.G. Gololobov, G.D. Kolomnikova, T.O. Krylova, Russian Chem. Bull. 44 (1995) 181.

[10] Y.G. Gololobov, Chinese J. Chem. 23 (2005) 1103.

[11] F. Ramirez, O.P. Madan, C.P. Smith, J. Am. Chem. Soc. 86 (1964) 5339.

[12] B.A. Arbuzov, N.A. Polezhaeva, Usp. Khim. 43 (1974) 933.

[13] M.A. Shaw, R.S. Ward, Top. Phosphor. Chem. 7 (1970) 1.

[14] H. Lee, Cyanoacrylate Resins: The Instant Adhesives: A Monograph of Their Applications and Technology, Pasadena Technology Press, 1986 .

[15] Y.G. Gololobov, W. Gruber, Russian Chem. Rev. 66 (1997) 953.

[16] Y.G. Gololobov, T.O. Krylova, Heteroatom. Chem. 6 (1995) 271.

[17] Y.G. Gololobov, G.D. Kolomnikova, T.O. Krylova, Tetrahedron Lett. 35 (1994) 1751.

[18] N. V. Slepchenkov, A. S. Peregudov, N. G. Senchenja, P. V. Petrovskii, V. N. Khrustalev, I. A. Garbusova, Y. G. Gololobov, Izvestiia Akademii Nauk SSSR. Seriia Khimicheskaya (2009).

[19] T.O. Krylova, G.D. Kolomnikova, I.A. Garbusova, Y.G. Gololobov, Zhurnal. Obshchei. Khimii. 64 (1994) 409.

[20] Y.G. Gololobov, V.A. Pinchuk, H. Thönessen, P. Jones, G.R. Schmutzler, Phosphorus, Sulfur Silicon Relat. Elem. 115 (1996) 19.

[21] Y.G. Gololobov, N.G. Senchenya, O.A. Linchenko, P.V. Petrovskii, I.A. Garbuzova, Russian J. Gen. Chem. 76 (2006) 1106.

[22] A.J. Gordon, R.A. Ford, The Chemist's Companion, Wiley-Interscience Publications, New York, London, Syndey, Toronto, 1972.

[23] T.O. Krylova, G.D. Kolomnikova, P.V. Petrovskii, Y.G. Gololobov, Russian Chem. Bull. 43 (1994) 1553.

[24] Y.G. Gololobov, O.A. Linchenko, P.V. Petrovskii, Z.A. Starikova, I.A. Garbuzova, Heteroatom. Chem. 18 (2007) 108.

[25] Y.G. Gololobov, O.A. Linchenko, Z.A. Starikova, I.A. Garbusova, P.V. Petrovskii, Russian Chem. Bull. 54 (2005) 2471.

[26] Y.G. Gololobov, O.A. Linchenko, P.V. Petrovskii, I.A. Garbuzova, V.N. Khrustalev, Russian Chem. Bull. 55 (2006) 1309.

[27] Y.G. Gololobov, N.A. Kardanov, V.N. Khroustalyov, P.V. Petrovskii, Tetrahedron Lett. 38 (1997) 7437.

[28] T.O. Krylova, O.V. Shishkin, Y.T. Struchkov, G.D. Kolomnikova, Y.G. Gololobov, Zhurnal Obshchei Khimii 65 (1995) 1393.

[29] V.I. Galkin, Y.V. Bakhtiyarova, Y.G. Gololobov, N.A. Polezhaeva, R.A. Cherkasov, Heteroatom. Chem. 9 (1998) 665.

[30] Y.G. Gololobov, P.V. Petrovskii, E.M. Ivanova, O.A. Linchenko, R. Schmutzler, L. Ernst, P. Jones, G.A. Karacar, M. Freytag, S. Okucu, Russian Chem. Bull. 52 (2003) 427.

[31] Y.G. Gololobov, V.I. Galkin, P.V. Petrovskii, O.A. Linchenko, E.M. Zueva, L.G. Mubarakova, R.A. Cherkasov, R. Schmutzler, L. Ernst, P. Jones, G.M. Freytag, Russian Chem. Bull. 52 (2003) 1920.

[32] Y.G. Gololobov, P.V. Petrovskii, O.V. Dovgan, I.Y. Krasnova, R. Schmutzler, L. Ernst, P. Jones, G.A. Karacar, M. Freytag, S. Okucu, Phosphor. Sulfur Silicon Relt. Elem. 177 (2002) 1677.

[33] Y.G. Gololobov, M.A. Galkina, O.V. Dovgan, I.Y. Krasnova, P.V. Petrovskii, M.Y. Antipin, I.I. Voronzov, K.A. Lyssenko, R. Schmutzler, Russian Chem. Bull. 50 (2001) 279.

[34] Y.G. Gololobov, O.A. Linchenko, Y.G. Trishin, P.V. Petrovskii, S.A. Starikova, Russian Chem. Bull. 53 (2004) 889.

[35] Y.G. Gololobov, M.A. Galkina, O.V. Dovgan, T.I. Guseva, I.Y. Kuzmintseva, N.G. Senchenya, P.V. Petrovskii, Russian Chem. Bull. 48 (1999) 1622.

[36] Y.G. Gololobov, I. Kuzminseva, V.N. Khroustalyov, P.V. Petrovskii, D.V. Griffiths, Heteroatom. Chem. 10 (1999) 644.

[37] Y.G. Gololobov, V.N. Khrustalev, N.V. Slepchenkov, A.S. Peregudov, M.Y. Antipin, Mendeleev Commun. 20 (2010) 39–40.

[38] Y. G. Gololobov, N. V. Slepchenkov, A. S. Peregudov, S.A.Starikova, Mendeleev Commun. 20 (2010), in press.

[39] Y.G. Gololobov, M.A. Galkina, I.Y. Kuz'mintseva, P.V. Petrovskii, Russian Chem. Bull. 47 (1998) 1832.

[40] Y. G. Gololobov, I. R. Golding, F. Terrier, P. V. Petrovskii, K. A. Lisenko, I. A. Garbusova, Russian Chem. Bull. 58 (2009) in press.

[41] Y.G. Gololobov, O.A. Linchenko, P.V. Petrovskii, V.N. Khrustalev, I.A. Garbuzova, Heteroatom. Chem. 18 (2007) 421.