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Experience of σρ-correlations of carbanion reactions with electrophilic reagents

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The problem of the possibility of applying σρ-correlation analysis by the "three sigmas' system" to carbanion reactions with electrophilic reagents was considered. In particular the alkylation as well as Wittig and Horner olefination reactions were discussed. It was shown that the condition for the application of correlation analysis to such reactions is the constancy of the Brönsted's parameter β connected with steric and reorganization factors of the substrates and solvents. Perfect correlations were observed when this condition was met.

Key words: carbanion alkylation, Wittig reaction, Horner reaction, CH-acidity, correlation analysis, "three sigmas' system".

Carbanion reactions with electrophilic reagents represent a broad field of organic chemistry. Among these are such important reactions as syntheses involving organometallic compounds and metallic derivatives of ketoenols, Wittig and Horner reactions, Michael addition, and many others.

For aromatic compounds reaction rate constants of many diverse types of these reactions — S_N2, S_N2', S_NAr, *etc.* — adhere well to Hammett's equation,[1–4] linking σ constants of the substituents in a benzene ring with reaction rate constants of a carbanion center. At the same time numerous reactions of aliphatic and alkylaromatic carbanions of the $XYZC^-$ type, where X, Y, and Z are any substituents in the methane molecule, hitherto are left over and above the correlation analysis giving an annoying lacuna. This paper is an attempt to make up for this deficiency.

The application of σρ-correlation analysis to the dissociation constants of CH-acids and particularly to the rate constants of the carbanion reactions with electrophilic reagents meets a number of difficulties. They are produced by action of many complicating factors and above all by the "saturation effect",[5] when a contribution of a substituent X at a CH-center (*i.e.*, its "acidifying effect", Δp*K*) depends on the substitution extent at this center, *i.e.*, the primary ($X-CH_3$), the secondary ($X-CH_2-Y$) or the tertiary (XYZCH) one. Values of Δp*K* progressively decreases with the successive insertion of the first, the second, and the third substituent to the methane molecule. Undoubtedly, the origin of a saturation effect deals with steric hindrances to *p*—π-conjugation with the lone *p*-pair of a carbanion. In principle this phenomenon is analogous to the well known steric distortion of conjugation in planar aromatic systems. Then a lot of difficulties is connected with reorganization phenomenon of a substrate and solvate layer in the course of reaction and, correspondingly, with changes of macrosolvation of molecules and ions (*i.e.*, molecules of

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CH-acids and carbanions or carbanions and molecules of the reaction products). The Marcus theory[6-8] and its further development[9] are devoted to these phenomena. It seems likely that reorganization factor has to influence on the carbanion reactions with electrophilic reagents stronger than on the ion dissociation of CH-acids due to new C—C bond formation in place of the C—H one. Nevertheless the reversible CH-acids dissociation also is not free from an action of this factor. Sometimes it becomes the main one, for example, at ion dissociation of aliphatic nitro-compounds, especially in hydroxyl-containing media.[10—12]

Finally, in the course of new C—C bond formation a steric factor hindering reagents' attack to a carbanion center, particularly, when a carbanion is strongly flattened (sp^2-hybridization) may play a leading part.

Earlier[13] we have shown that at σρ-correlational analysis of CH-acidity complications caused by saturation effect may be overcome by the application of "three sigmas' system". In this case a constant σ^- for any substituent X is determined in accordance with the substitution degree, namely: $\sigma^-_{CH_3}$ for acid dissociation of monosubstituted methane XCH_3; $\sigma^-_{CH_2}$ for a disubstituted one XCH_2Y; and σ^-_{CH} for a trisubstituted one XYZCH. In this case Hammett type equations are applied:

$$pK = pK^0 - \rho\Sigma\sigma^-_{CH_n}\ (n = 1, 2, \text{ or } 3).$$

Good results, obtained under the application of "three sigmas' system" to a lot of different correlation $\sigma^-_{CH_n}$ series of CH-acids dissociation in various media,[14] show that the influence of saturation effect becomes dominating at the dissociation. It reduces the action of another complicating factors to the limits of standard errors at the correlation.

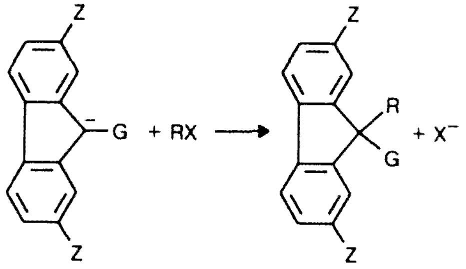
It seems rather tempting to extend the "three sigmas' system" on the carbanion reactions with electrophilic reagents. Therewith the effect of another complicating factors would be expected to be more significant. Their contribution to the kinetics of the carbanion reactions may be defined by the β parameter of the Brönsted's equation[15] in its extended version:

$$\log k = \alpha + \beta \log K,$$

where k is the reaction rate constant of a carbanion, and K is the dissociation constant of the corresponding CH-acid. It is known that steric hindrances to a new covalent bond formation and reorganization factors influence on parameter β. Varying from 0 to 1 it demonstrates the degree of reagents movement according the reaction coordinate to the transition state formation. It is assumed that in the case of carbanion reactions only the substrates with the same β value have to be inserted in the reaction series under the correlation according "three sigmas' system". Then $\sigma^-_{CH_n}$ constants will define the electronic effects of the substituents at the constant steric conditions and the constant reorganization factor.

Alkylation reactions

Bordwell and co-workers[16—18] have studied β coefficients in alkylation reactions of substituted fluorenide anions. The kinetics of the reaction in a dimethyl sulfoxide medium was studied:



where G and Z are any substituents in the fluorene moiety, and RX is diversified alkyl halides, substituted alkyl halides, or onium alkylating salts of the type $XC_6H_4CH_2N^+Me_2C_6H_4Y \cdot X^-$ ($Me_2NC_6H_4Y$ is the neutral leaving group). Unfortunately, in these papers the majority of reaction series contain only two-three fluorenide ions, which prevents their treatment using the "three sigmas' system". The results of series treatment at $n > 3$ are presented in Table 1. From an inspection of these data it appears that at constant β values excellent correlations by the following equation are observed:

$$\log k = \log k^0 + \rho\Sigma\sigma^-_{CH}.$$

In this case the invariability of β and the applicability of the "three sigmas' system" are observed when the G substituent in position 9 of the fluorenide ion is of the constant type (Me, Ar, ArS). It should be noted, that other reaction series ($n \leq 3$) give an excellent linear dependence in the coordinates $\Sigma\sigma^-_{CH}$ and log$k$.

On the contrary, if the β value is not constant in the reaction series, the "three sigmas' system" applies poorly. So for substituted fluorenide ions with different G and Z substituents the alkylation series with $NCCH_2Cl$ as reagent was reported in the paper.[17] At $n = 12$, but when β values are variable, the dependence of pK of CH-acids on $\Sigma\sigma^-_{CH}$ still remains satisfactory (correlation coefficient 0.979), but the correlation of the rate constants with $\Sigma\sigma^-_{CH}$ becomes dissatisfied (correlation coefficient 0.927). Steric and reorganization factors are likely to affect the ion dissociation of the CH-acids to a lesser extent then to influence the rate of the carbanion reaction with alkylating agents.

The kinetics of the alkylation of mesomeric carbanions of β-dicarbonyl compounds (acylacetic esters) with ethyl tosylate was investigated by A. L. Kurts, P. L. Dem'yanov, A. Macias, I. P. Beletskaya and O. A. Reutov.[19,20] Since the anions of the acylacetic esters under study are partially in a free state and partially form nondissociated molecules or ion pairs with cations (K^+ or Cs^+) in HMPA medium, so in these papers the rate constants of free carbanions were calculated from ob-

Table 1. Correlations by the "three sigmas' system" of alkylation reactions of substituted fluorenide anions with various alkylating agents according to the data of F. Bordwell and co-workers[16–18]

Substituents in the fluorene ring	Alkylating agents	n	$\log k^0$	$-\rho$	β	r	s	s_ρ
2,7-Z_2-9-Me 2-Br-9-PhS	m-$NCC_6H_4CH_2N^+Me_2C_6H_5 \cdot Br^-$	4	13.22	10.212	0.40	0.999(7)	0.15	0.19
The same	$[m$-$NCC_6H_4CH_2N^+Me_2C_6H_4Cl$-$m]Br^-$	4	13.50	9.798	0.38	0.998	0.11	0.41
9-Ar*	$NCCH_2Cl$	4	14.73	10.632	0.53	0.996	0.08	0.67
2,7-Z_2-9-ArS	$NCCH_2Cl$	5	18.95	13.214	0.53	0.993	0.13	0.88
9-Ar*	$PhCH_2Cl$	4	9.30	7.335	0.36	0.997	0.05	0.42
2,7-Z_2-9-ArS	$PhCH_2Cl$	4	9.08	6.845	0.31	0.993	0.07	0.55
2,7-Z_2-9-ArS	$Me_2C{=}CH{-}CH_2Cl$	4	10.58	6.910	0.27	0.994	0.07	0.55
2,7-Z_2-9-Ar	$Me_2C{=}CY{-}CH_2Cl$, 20 °C	4	9.56	6.517	0.28	0.993	0.03	0.18
2,7-Z_2-9-Ar	$Me_2C{=}CH{-}CH_2Cl$, 47 °C	4	10.15	6.556	0.28	0.999(8)	0.02	0.12
9-Ar*	$CH_2{=}CH{-}CH_2Cl$**	4	11.77	9.443	0.43	0.982	0.15	1.26
2,7-Z_2-9-Ar*	$MeCH{=}CH{-}CH_2Cl$**	4	11.55	8.289	0.32	0.994	0.08	0.20
2,7-Z_2-9-Ar*	$CH_2{=}CH{-}CHCl{-}CH_3$**	4	9.56	8.038	0.39	0.997	0.05	0.42
9-Ar*	p-$NO_2C_6H_4F$	4	14.94	12.522	0.62	0.996	0.10	0.84

* σ^-_{CH} for m-ClC_6H_4 0.32 (unpublished data). ** A mixture of mechanisms S_N2 and S_N2'.

served reaction rates according to the simple equation:

$$k_2 = \alpha k_i + k_m(1 - \alpha),$$

where k_2 is the observed second order rate constant, and k_i and k_m are the reaction rate constants of the free anions and ion pairs (molecules); in their turn these constants were divided into k_C and k_O, the rate constants of C- and O-alkylated derivatives formation.

Data treatment[19,20] by the "three sigmas system" (when $\sigma^-_{CH_2}$ for the CF_3CO group is equal to 1.41, unpublished data) gave the following results:

1) for overall reaction rate constants of enolate anions ($k_i = k_{O_i} + k_{C_i}$):

$$\log k_i = 4.30 - 3.775\Sigma\sigma^-_{CH_2}$$
$$(n = 4,\ r = 0.997,\ s = 0.11,\ s_\rho = 0.21);$$

2) for O-alkylation rate constants k_{O_i}:

$$\log k_{O_i} = 4.11 - 4.507\Sigma\sigma^-_{CH_2}$$
$$(n = 4,\ r = 0.996,\ s = 0.12,\ s_\rho = 0.22);$$

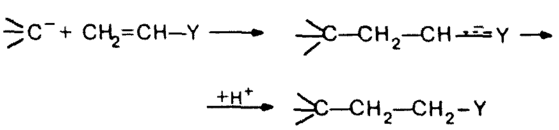
3) for C-alkylation rate constants k_{C_i}:

$$\log k_{C_i} = 4.50 - 4.507\Sigma\sigma^-_{CH_2}$$
$$(n = 3,\ r = 0.967,\ s = 0.14,\ s_\rho = 1.21).$$

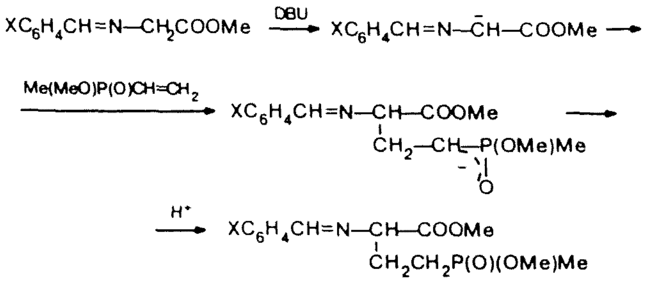
Unfortunately, in the third reaction series correlations were performed only for three substrates, because C-alkylation was not found for CF_3COCH_2COOEt (according to calculations by the correlation equation (3) the ratio $k_C/k_O = 0.045$, so it was difficult to identify it experimentally). The high value of $s_\rho = 1.21$ in this correlation is natural for three points correlation (generally speaking, it is illegal). The low correlation coefficient (0.967) is most likely to be related with an action of steric and reorganization factors at C—C new bond formation.

In the same investigation pK values of acylacetic esters were measured but, unfortunately, in a DMF medium and not in HMPA one. That prevents from proper application of Brönsted's equation. Still parameter β is doubtless constant and this fact explains the successful application of the correlations on "three sigmas' system". For pK values (DMF) both steric and reorganization factors are inconsiderable. It is shown from the excellent correlation: pK = 28.02 − $9.627S\sigma^-_{CH_2}$ with a correlation coefficient equal to 0.993.

On the first stage the carbanion addition to the double bond can be considered as alkylation of the carbanion with a terminal methylene group of an unsaturated compound.:



(Y is a π-acceptor). In our laboratory[21] vinylphosphinate addition to substituted benzylideneglycine esters was studied with DBU catalysis (DBU, 5 mol.%) in DMSO medium at 20°C. The CH-acidity of these benzylideneglycine esters was studied in the same medium.



The second order reaction proceeds at a constant β value (0.57). Inspite of only three constants were measured (X = Me_2N, H, Br) a good linear correlation between log*k* and $\Sigma\sigma^-_{CH_2}$ at positive ρ value is obsereved.

$$\log k = -19.77 + 13.077\Sigma\sigma^-_{CH_2}$$

$$(n = 3,\ r = 0.988,\ s = 0.10,\ s_\rho = 2.03)$$

In going to the related alanine derivatives (steric hindrances) the reaction order changes for the first one. The constancy of β keeps worse (β = 0.43) and correlation quality of log*k* on $\Sigma\sigma^-_{CH2}$ is considerably deteriorated:

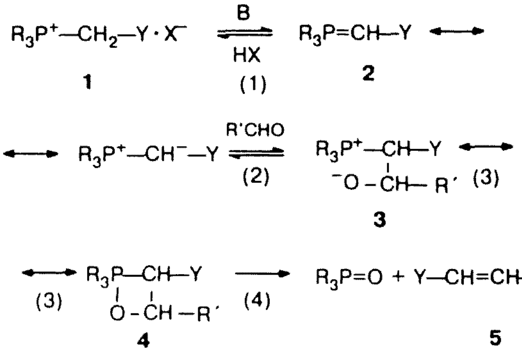
$$\log k = -13.37 + 7.983\Sigma\sigma^-_{CH}$$

$$(n = 3,\ r = 0.964,\ s = 0.21,\ s_\rho = 2.03).$$

Of course, a calculation of correlation parameters from three points is invalid, and its results may be used only for qualitative estimation.

Wittig reaction

As is well-known, this reaction begins from alkylation of a phosphorus ylide by an aldehyde (or sometimes by ketone) and leads finally to an olefin and a phosphine oxide. Its commonly accepted mechanism is expressed by the following scheme[22,23]:



If Y is an effective π-acceptor group, ylide **2** resulting from phosphonium salt **1** on the stage (1) is stable. Alkylation stage (2) is reversible and leads to two stereoisomeric betaines **3**, and stage (3) results in the phosphetanes **4**. There are many arguments in favor of the identity of **3** and **4**, *i.e.*, stage (3) connects a phosphonium alkoxide **3** and a cyclophosphorane **4** as resonance forms. At stage (4) this resonance hybrid turns at once into a phosphine oxide and an olefin.

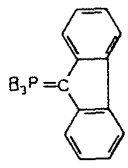
In the reactions of unstabilized ylides stage (1) is inseparable experimentally (synthetically) from others, but this stage, the reaction of a phosphonium salt with a base, influences on the overall kinetics of the process.

S. Fliszar, R. F. Hudson, and G. Salvadory[24] were the first to study the kinetics of the reaction of the stable ylides of the type $Ph_3P{=}CH{-}COR$ with benzaldehyde in $CHCl_3$ at 40°C. They found that the second order rate constant k_2 increases with the increase of ylides basicity. The linear dependence between logk_2 and p*K* of the ylide (true, the rate constants were measured in chloroform, but the p*K* values were measured in 80% ethanol) defines the constancy of the β parameter and thus the ability to apply correlation analysis on the "three sigmas' system".

The excellent correlation coefficient (*r* = 0.992, Table 2) confirms the applicability of the "three sigmas' system" to the Wittig reaction. Other examples of the correlations of the reactions of stabilized ylides with benzaldehydes are given in Table 2. In all cases the correlations are excellent. The ρ-values are negative. It testifyes that a reaction fastens with the ylide basicity and stage 2 is the rate determining one (this conclusion was drawn by the authors themselfs).[24]

However, if strong steric hindrances exist the correlation on the "three sigmas' system" of the Wittig reaction becomes disrupted dramatically. So, A. J. Speziale and co-workers[28,29] studied the kinetics of the Wittig reaction of sterically hindered ylides of the type $Ph_3P{=}CH(X)COMe$ with benzaldehyde in benzene at 25°C and in parallel investigated the basicity of these ylides in methanol. As this take place halosubstituted

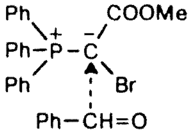
Table 2. Correlations by the "three sigmas' system" of the rate constants of the Wittig reaction of stable ylides with benzaldehydes

No.	Substrate*	Medium	*T*/°C	*n*	logk^0	−ρ	*r*	*s*	s_ρ	Ref.
1	$Ph_3P{=}CH{-}\underline{R}$	$CHCl_3$	40	6	14.11	8.189	0.992	0.24	0.69	24
2		C_6H_6	25	5	49.34	24.200	0.999(8)	0.04	0.34	25
3		C_6H_6	35	4	47.91	23.431	1.000	0.01	0.03	25
4		C_6H_6	45	4	46.34	22.579	0.999	0.06	0.54	25
5	$\underline{R}_3P{=}CH{-}COOEt$	MeCN	20	3	4.89	3.827	0.992	0.07	0.49	26,27

* Variable substituents are underlined.

Note. For Ph_2EtP^+ σ^-_{CH} = 1.00; for $PhEt_2P^+$ σ^-_{CH} = 0.95; and for Et_3P^+ σ^-_{CH} = 0.94 (unpublished data).

ylides ($X = Cl$ or Br) interact slower than unsubstituted ones ($X = H$) clearly due to their lesser basicity (nucleophilicity). At the same time the bromosubstituted derivative having higher basicity than the chlorine derivative (pK equal to 6.7 opposite to 6.3) reacts with benzaldehyde three times slower. To be sure that fact is associated with larger volume of the bromine atom. The Brönsted rule is not obeyed here (β parameter is not constant) Correspondingly, the "three sigmas' system" does not work. The reason has undoubtedly to do with a difficulty of an access of the reagent to the carbanion center.



Steric hindrances are also observed upon an attack by a proton donor. A. J. Speziale and co-workers[29] studied more thoroughly the basicity of ylides of the type $Ph_3P=C(X)-COR$, where $X = H$, Cl, Br, I and $R = Ph_2N$, OEt, Ph, CN (instead of COR). Although correlation on the "three sigmas' system" is exhibited here, $pK = 31.67 - 11.733\Sigma\sigma^-_{CH}$ ($n = 9$, $r = 0.978$, $s = 0.34$, and $s_\rho = 0.94$), but with a lower correlation coefficient (0.978). Undoubtedly, it is connected with steric hindrances of the ylides.

A somewhat different there is the case of unstable ylides. Kinetics of their reaction with aldehydes was investigated by chinese authors.[30] They studied the reaction of substituted benzylphosphonium salts with substituted benzaldehydes in methanol under treatment with lithium methyloxide in the presence of lithium bromide:

$$XC_6H_4CH_2\overset{+}{P}Ph_3\cdot Br^- + YC_6H_4CHO \longrightarrow$$
$$\xrightarrow{MeOLi} Ph_3PO + XC_6H_4CH=CHC_6H_4Y$$

It merits attention and the authors emphasize the fact, that π-acceptor substituents in both the phosphonium salts and benzaldehyde increase the Wittig reaction rate. Evidently the overall reaction rate is not determined by any one stage, but it is determined by a whole complex of three stages, namely: the rate of ylide formation in equilibrium reaction (1) with equlibrium constant K_e, the rate of betaine↔phosphetane formation (with k_2 and k_{-2}) and the rate of reaction product formation (k_4). The kinetics of such type reactions was examined by R. O. Larsen and G. Aksnes[31] while studying the Horner reaction, in which carbanion forms *in situ* and immediately reacts with aldehydes. In this case the rate of the reaction is:

$$\upsilon = \frac{k_2k_4}{k_{-2} + k_4}K_e\,[\text{substrate}]\,[\text{aldehyde}]\,[\text{alcoholate anion}]$$

Naturally K_e increases under the action of π-acceptor substituents in a phosphonium salt, and k_2 increases under the effect of acceptor substituents in an aldehyde molecule but must decrease from acceptor substituents in an ylide. As a whole it was found that π-acceptor substituents increase the reaction rate υ. Because all the substituents both in ylides and in aldehydes are situated in benzene rings the authors applied the usual Hammett equation and obtained good correlations. Even better quality of the correlation achives with the use of "three sigmas' system"; so for the reaction of substituted phosphonium salts with benzaldehyde:

$$\log k = -17.28 + 10.32\Sigma\sigma^-_{CH_2}$$

$$(n = 4,\ r = 0.995,\ s = 0.08,\ s_\rho = 0.70);$$

For the reaction of phosphonium salts with p-methoxybenzaldehyde:

$$\log k = -16.875 + 9.642\Sigma\sigma^-_{CH_2}$$

$$(n = 3,\ r = 0.999,\ s = 0.01,\ s_\rho = 0.11).$$

Nevertheless both methods of σρ-correlations are known to be in a linear relationship for the series of benzene derivatives.[14]

It should be noted, that ρ constant is positive in the case of unstabilized ylides in contrast to the correlation of the Wittig reaction of the stable ylides. The influence of the substituents at a carbanion center on the Wittig reaction rate is seen to be more complex for unstable ylides (phosphonium salts) than in the case of stabilized ones.

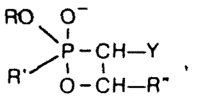
As a whole the "three sigmas' system" can be used to advantage for the purpose of σρ-correlations of the reactions both of stable and unstable ylides taking into account the above-mentioned limitations mainly of steric character.

Horner Reaction

The kinetics of the "PO-activated olefination", according to Horner,

$$(RO)R'P(O)-CH_2-Y + R''CHO \xrightarrow{B}$$
$$\longrightarrow (RO)R'POO^- + Y-CH=CH-R''$$

and the CH-acidity of the relevant phosphonates were studied by R. O. Larsen and G. Aksnes.[31] It should be noted that the β parameter is not constant and the "three sigmas' system" is not applicable. The authors explain the discrepancy between the reaction rate and the CH-acidity of phosphonates by the difference in formation energies of the pentacovalent phosphorus intermediate (transition state):



which bears a negative charge in contrast to the Wittig phosphetane. That seems reasonable. Hence a substrate reorganization effect plays an important role in the kinetics of the Horner reaction.

In conclusion it must be admitted that the "three sigmas' system" of σρ-correlation analysis of carbanion reactions with electrophilic reagents proves its value and may be used at experimental data analysis. Deviations from linear correlations are observed when Brønsted's parameter β is not constant as connected with steric hindrances and an action of reorganization factors.

References

1. A. I. Shatenstein, *Tetrahedron*, 1962, **18**, 95.
2. A. Streitwieser, Jr. and M. F. Koch, *J. Am. Chem. Soc.*, 1964, **86**, 404.
3. A. Streitwieser, Jr. and J. Hammons, *Prog. Phys. Org. Chem.*, 1965, **3**, 7.
4. F. G. Bordwell, *Acc. Chem. Res.*, 1988, **21**, 156.
5. A. G. Pearson and R. L. Dillon, *J. Am. Chem. Soc.*, 1953, **75**, 2439.
6. R. A. Marcus, *J. Phys. Chem.*, 1968, **72**, 891.
7. M. M. Cohen, O. M. Cohen, and O. A. Marcus, *J. Phys. Chem.*, 1968, **72**, 4249.
8. R. A. Marcus, *J. Am. Chem. Soc.*, 1969, **91**, 7224.
9. R. R. Dogonadze, A. M. Kuznetsov, *Itogi Nauki i Tekh., Fiz. Khimia. Kinet.*, VINITI, Moscow, 1973, Ch. 5.
10. V. M. Belikov, A. L. Tal'vik, and Ts. B. Korchemnaya, *Reakts. sposobn. org. soedin.*, 1965, **2**, 10 (in Russian).
11. A. I. Tal'vik, V. G. Timotkheus, and Kh. P. Timotkheus, *Reakts. sposobn. org. soedin.*, 1967, **4**, 478 (in Russian).
12. A. I. Tal'vik, *Reakts. sposobn. org. soedin.*, 1972, **9**, 233 (in Russian).
13. M. I. Kabachnik and T. A. Mastryukova, *Dokl. Akad. Nauk SSSR*, 1984, **260**, 893. [*Dokl. Chem.*, 1984, **260**, 891 (Engl. Transl.)].
14. M. I. Kabachnik and T. A. Mastryukova, *Sov. Sci. Rev., Chem. Rev.*, Ed. M. E. Vol'pin, 1994, **18**, Part 5, 45.
15. J. N. Brønsted and K. Pedersen, *Z. Phys. Chem.*, 1924, **108**, 185.
16. F. G. Bordwell and D. L. Hughes, *J. Am. Chem. Soc.*, 1986, **108**, 5991.
17. F. G. Bordwell and D. L. Hughes, *J. Am. Chem. Soc.*, 1986, **108**, 7300.
18. F. G. Bordwell, A. H. Clemmens, and Jin-Pei Cheng, *J. Am. Chem. Soc.*, 1987, **109**, 1773
19. A. L. Kurts, A. Macias, I. P. Beletskaya, and O. A. Reutov, *Tetrahedron*, 1971, **27**, 4759.
20. A. L. Kurts, P. J. Dem'yanov, A. Macias, I. P. Beletskaya, and O. A. Reutov, *Tetrahedron*, 1971, **27**, 4769.
21. I. L. Odinets, N. V. Mashchenko, P. V. Petrovsky, T. A. Mastryukova, and M. I. Kabachnik, *Zh. Obshch. Khim.*, 1991, **61**, 1947 [*J. Gen. Chem. USSR*, 1991, **61**, 1951 (Engl. Transl.)].
22. E. Vedejs, C. F. Marth, and R. Ruggeri, *J. Am. Chem. Soc.*, 1988, **110**, 3940.
23. E. Vedejs and C. F. Marth, *J. Am. Chem. Soc.*, 1988, **110**, 3948.
24. S. Fliszar, R. F. Hudson, and G. Salvadori, *Helv. Chim. Acta*, 1963, **46**, 1580.
25. P. Floyen, *Acta Chem. Scand.*, 1972, **26**, 2163.
26. C. Richard, P. Panse, and S. Eichler, *Chem. Ber.*, 1967, **100**, 1144.
27. B. Giese, J. Schoch, and C. Richard, *Chem. Ber.*, 1978, **111**, 1395.
28. A. J. Speziale and K. W. Ratts, *J. Am. Chem. Soc.*, 1963, **85**, 2790.
29. A. J. Speziale and D. E. Bissing, *J. Am. Chem. Soc*,. 1963, **85**, 3878.
30. Li Donxia, Wu Dexian, Li Yaozhong, and Zhao Huaming, *Tetrahedron*, 1986, **42**, 4161.
31. R. O. Larsen and G. Aksnes, *Phosphorus Sulfur*, 1983, **15**, 219.

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