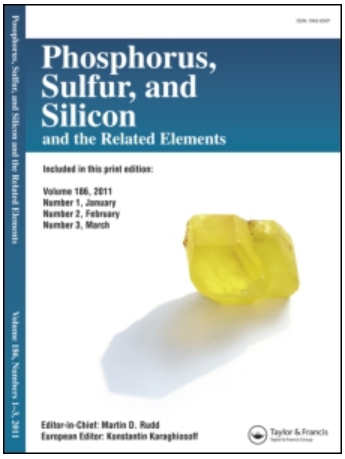

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SYNTHESIS AND CH-ACIDITY OF N,N-DISUBSTITUTED AMINOTRIPHENYL-PHOSPHONIUM SALTS

M. I. Kabachnik[ab]; D. I. Lobanov[ab]; A. G. Matveeva[ab]; O. E. Kovsheva[ab]; M. I. Terekhova[ab]; E. S. Petrov[ab]; P. V. Petrovskii[ab]; E. I. Matrosov[ab]
[a] A. N. Nesmeyanov Institute of Organo-Element Compounds, USSR Academy of Sciences, Moscow, USSR [b] L. Ya. Karpov Physico-Chemical Institute, Moscow, USSR

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SYNTHESIS AND CH-ACIDITY OF N,N-DISUBSTITUTED AMINOTRIPHENYL-PHOSPHONIUM SALTS

M. I. KABACHNIK, D. I. LOBANOV, A. G. MATVEEVA, O. E. KOVSHEVA, M. I. TEREKHOVA, E. S. PETROV, P. V. PETROVSKII and E. I. MATROSOV

A. N. Nesmeyanov Institute of Organo-Element Compounds, USSR Academy of Sciences, Vavilov Str., 28, Moscow II7334, USSR. L. Ya. Karpov Physico-Chemical Institute, Obuch Str., IO, Moscow 103062, USSR

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A number of (substituted-methylamino)triphenylphosphonium salts (APS) with the general formula $[Ph_3\overset{+}{P}N(R)CH_2R']\ X^-$ has been synthesized. CH-Acidity of some of the APS obtained has been measured (pK 14.7–24.8) by an indicator method in DMSO/counterion-K^+, standard-9-phenyl fluorene (pK 18.5)/. Acidification effect of the $Ph_3\overset{+}{P}N(Ph)$ group ($\sigma_{\bar{C}H_2}$ = 0.70) and of the $Ph_3\overset{+}{P}N(Bu)$ group ($\sigma_{\bar{C}H_2}$ = 0.68) has been estimated. The data obtained testify to the presence of an effective positive charge on the nitrogen atom in the APS under study and also to a somewhat increased multiplicity of the nitrogen-phosphorus bond as compared to a single one.

Key words: Triphenylphosphine-N-phenylimine; alkylation; (substituted-methylamino) phosphonium salts; CH-acidity; $\sigma\rho$-analysis.

The (substituted-methylamino) phosphonium salts (APS) have been recently in the focus of attention due to their application in preparative organic chemistry.[1–5] Reactions of APS with various nucleophiles served as a basis for elaborating the methods of synthesis. In these reactions a nucleophile was found to attack the positive charged phosphorus atom. But the problem remains on the feasibility of deprotonation of a CH_2-group bound to a nitrogen atom under the action of a nucleophile, i.e., on the CH-acidity of APS.

The methods of the synthesis of APS have been studied in detail. However, the choice of substituents for phosphorus and nitrogen atoms is limited to phenyl and alkyl groups.[6–10]

Reactions of APS with the bases of various strength were also studied. In the interaction with sodium alkoxides in aprotic solvent, an alkoxide anion attacks a positively charged phosphorus atom with breaking of a P—N bond, giving alkoxy-phosphonium salts as intermediate products which may be further used for the alkylation of alkylmercaptans[1] and primary or secondary amines.[2] The reaction of (N-methyl-N-benzylamino)triphenylphosphonium bromide, $[Ph_3\overset{+}{P}N(Me)\text{-}CH_2\text{-}Ph]Br^-$, with sodium methylate in methanol proceeds in a similar way. As a result, triphenylphosphine oxide and methylbenzylamine were isolated.[10] However in the interaction of the same APS with equimolecular quantity of butyl lithium in aprotic solvent or with NaH in acetonitrile, triphenylphosphine and benzylidenemethylamine were isolated as major products.[10] These compounds are believed to be formed as a result of the decomposition of the unstable zwitterion, $Ph_3\overset{+}{P}N(Me)\bar{C}HPh$.

Therefore, the difference in direction of reactions of APS under study with the bases is determined by both the CH-acidity of APS and the basicity of nucleophiles. So it was also of interest to study CH-acidity of the above mentioned APS and related structures.

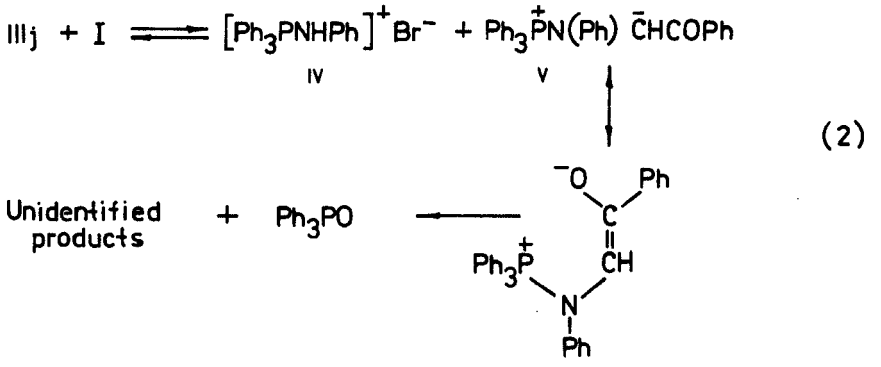
RESULTS AND DISCUSSION

(Substituted-methylamino)phosphonium salts (III) were obtained by alkylation of triphenylphosphine-N-phenylimine (I) with the corresponding substituted alkyl bromides (II) under reflux in acetonitrile for 6–10 hr.

$$\underset{\text{I}}{Ph_3P{=}NR} + \underset{\text{IIa-i}}{XCH_2R'} \longrightarrow \underset{\text{IIIa-i}}{[Ph_3\overset{+}{P}N(R)CH_2R']X^-} \qquad (1)$$

N°	R	R′	X	N°	R	R′	X
a	Ph	COOEt	Br	g	Ph	Ph	I
b	Ph	CH=CH$_2$	Br	h	Ph	CONEt$_2$	I
c	Ph	C≡CH	Br	i	Ph	CN	I
d	Ph	*n*-O$_2$NC$_6$H$_4$	Br	j	Ph	COPh	Br
e	Ph	*n*-BrC$_6$H$_4$	Br	k	Bu	Ph	Br
f	Ph	*n*-MeOC$_6$H$_4$	Br				

Alkylation of imine **(I)** with alkylchlorides **(II)** was not successful even under prolonged reflux; therefore the reaction was carried out in the presence of equimolar quantity of NaI relating to **(II)**. Reaction of **I** with bromoacetophenone **(IIj)** proceeded with formation of triphenylphosphine oxide and the hydrobromide of the initial phosphine imine **(IV)** as reaction products in the ratio ~1:1. In the $^{31}P\{^1H\}$ NMR spectrum of a reaction mixture there was observed besides two basic signals, a weak one (~2–3%) at 40.3 ppm that can be ascribed to the corresponding APS **(IIIj)**. In this case the CH-acidity of APS **(IIIj)** is obviously so high that it reacts with the initial imine **(I)** forming its hydrobromide **(IV)** and zwitterion **(V)** which decomposes to form triphenylphosphine oxide.†



† Presumably a fragment of the molecule not containing phosphorus can easily polymerize, and the monomer product, PhN̄—CH=C̄Ph, cannot be observed. The mixture of oligomers formed consists mainly of substances, the molecular weight of which corresponds to trimer and hexamer.

Decomposition of zwitterion (**V**) is believed to be due to intermolecular reaction of the Wittig type, that is most likely stimulated by high enolization. It should be noted that when obtaining APS (**IIIa**) and (**IIIi**) with electron-acceptor substituents R′(COOEt, CN), the hydrobromide (**IV**) was detected in the reaction mixture in the quantity of 7% and 29%, respectively (according to the data of ^{31}P $\{^1H\}$ NMR spectrum). It somewhat decreases the yield of the end product. The NMR signal of the hydrobromide (**IV**) (δ_p = 33.9 ppm) in the reaction mixture can be observed only if all the initial phosphine imine (**I**) participates in the reaction. If (**I**) and (**IV**) are available in the reaction mixture, then, instead of the two singlets, there is one signal with intermediate value of δ_P present at 30° in the NMR spectrum. This is due to a rapid proton exchange. Special experiments showed that at 30° the ^{31}P $\{^1H\}$ NMR spectra of solutions of the mixtures of (**I**) and (**IV**) in acetonitrile in molar rations of 3:1, 1:1, and 1:3 showed singlet signals at 10.0 ppm 17.8 ppm, and 25.8 ppm respectively. Under the same conditions the signals (**I**) and (**IV**) have chemical shifts of 2.2 ppm and 33.9 ppm. These results are in agreement with a good additive dependence between δ_P and molar fraction of (**IV**), (n), in the mixture with (**I**): $\delta_P = 2.18 + 31.52\,n$. When obtaining APS (**IIIb–h**) hydrobromide (hydroiodide) (**IV**) was not observed in the reaction mixture.

Alkyl bromides (**II**) containing strong electron-acceptor substituents /R′ = $\overset{+}{N}Et_3$, $\overset{+}{P}(Ph)_3$, $CH_3C_6H_4SO_2$, $(EtO)_2P(O)$/, as well as 9-bromofluorene, do not react with phosphine imine (**I**) even at many-hour reflux in acetonitrile and also in the presence of NaI.

(N-butyl-N-benzylamino)triphenylphosphonium bromide (**IIIk**) was obtained by the technique described earlier[10] from triphenyl-dibromophosphorane and N-butyl-N-benzylamine in the presence of triethylamine.

Constants, yields, data of elemental analysis, IR and ^{31}P and ^1H NMR spectra (**III**) are given in Tables I and II.

Equilibrium CH-acidity (see Table III) was determined by the earlier described technique[11] by an indicator method in DMSO (counterion-K^+, standard-9-phenylfluorene (pK 18.5)). Ionic association in the solutions under study was neglected since potassium halides and the salts with large organic cations are as a rule completely dissociated in DMSO. It should be noted that the zwitterions formed under the action of a base are unstable. Having reached the equilibrium quickly, the concentration of an indicator base continues to drop though slower. By-processes lower the accuracy of measurements, but do not hamper the determination of equilibrium position of remetallization reaction with APS participation.

CH-Acidity vary within a wide range (~10 pK units) according to the acidification effect of the substituents, $Ph_3\overset{+}{P}N(R)$ and R′. The constants, $\sigma^-_{CH_2}$ were used to characterize the acidification effects of substituents.[12,13] The values of these constants for the $Ph_3\overset{+}{P}N(R)$ groups were found in the following way.

At first, with the pK data of the indicator CH-acids used a calibrating equation was found.

$$pK = 49.43 - 23.613 \sum \sigma^-_{CH_m} (m = 1; 2)$$

Then for all the APS studied the constants $\sigma^-_{CH_2}$ of the $Ph_3\overset{+}{P}N(R)$ groups were calculated. For R=Ph $\sigma^-_{CH_2}$ = 0.70 ± 0.02 and for R=Bu $\sigma^-_{CH_2}$ = 0.68 were found. To verify these values a correlation equation was used that had been earlier

TABLE I
Constants, yields, and analysis data of APS (III)

Substance	Yield, (%)	Melting point, °C (solvent of recryst.)	Found/Calculated, % C	H	Hal	P	Formula
IIIa	60.0	192–3 ($CHCl_3$-EtOAc)	64.9 / 64.6	5.8 / 5.2	16.0 / 15.4	5.8 / 6.0	$C_{28}H_{27}BrNO_2P$
IIIb	54.0	214–6 ($CHCl_3$-EtOAc)	68.6 / 68.4	5.4 / 5.3	17.0 / 16.8	6.7 / 6.5	$C_{27}H_{25}BrNP$
IIIc	63.5	221–3 (MeCN-C_6N_6)	68.8 / 68.7	5.4 / 4.9	16.7 / 16.9	6.6 / 6.6	$C_{27}H_{23}BrNP$
IIId	82.5	186–7 (MeCN-C_6H_6)	65.2 / 65.4	5.2 / 4.6	14.0 / 14.0	5.4 / 5.4	$C_{31}H_{26}BrN_2O_2P$
IIIe	58.0	233–5 (MeCN-C_6H_6-hexane)	61.4 / 61.7	3.9 / 4.3	26.6 / 26.5	5.2 / 5.1	$C_{31}H_{26}Br_2NP$
IIIf[a]	86.5	189–91 ($CHCl_3$-EtOAc)	67.4 / 67.1	5.4 / 5.5	14.1 / 14.0	5.6 / 5.4	$C_{32}H_{31}BrNO_2P$
IIIg	88.8	248–9 (MeCN)	65.2 / 65.2	4.9 / 4.8	22.7 / 22.2	5.4 / 5.4	$C_{31}H_{27}INP$
IIIh	54.0	214–6 (MeCN-C_6H_6-hexane)	60.7 / 60.6	5.4 / 5.4	21.5 / 21.4	5.0 / 5.2	$C_{30}H_{32}IN_2OP$
IIIi	36.2	217–9 (MeCN-C_6H_6)	60.0 / 60.0	4.4 / 4.3	24.7 / 24.4	5.9 / 6.0	$C_{26}H_{22}IN_2P$
IIIj	55.0	204–5 (MeCN-C_6H_6)	69.1 / 69.0	6.1 / 6.2	[b]	6.2 / 6.1	$C_{29}H_{31}BrNP$

[a] Crystallohydrate **IIIf**·H_2O.
[b] N obtained: 2.9%, calculated: 2.8%.

derived[13] from Shatenshtein's data on CH-acids in DMSO with counterion K^+ by the technique[11] used in the present work.

$$pK = 48.77 - 22.83 \sum \sigma^-_{CH_m}$$

For the $Ph_3\overset{+}{P}N(Ph)$ group $\sigma^-_{CH_2} = 0.71$ and for the $Ph_3\overset{+}{P}N(Bu)$ group $\sigma^-_{CH_2} = 0.68$ were found. The agreement with the above given data is good.

Thus the $Ph_3\overset{+}{P}N(Ph)$ and $Ph_3\overset{+}{P}N(Bu)$ groups have a lower acidification effect than the COOEt group but a higher one than the $CONEt_2$ group.

COOEt	>	$Ph_3\overset{+}{P}N(Ph)$	>	$Ph_3\overset{+}{P}N(Bu)$	>	$CONEt_2$
$\sigma^-_{CH_2}$: 0.725		0.70		0.68		0.58

It is interesting to note that the acidification effect of the $Ph_3\overset{+}{P}N(Ph)$ and $Ph_3\overset{+}{P}N(Bu)$ groups is slightly lower than that of the groups with ammonium nitrogen, for which $\sigma^-_{CH_2} = 0.79$ ($Me_3\overset{+}{N}$) and 0.88 (Me_2PhN), but exceed considerably the groups with trivalent nitrogen, $\sigma^-_{CH_2} = 0.1$ (Me_2N) and 0.25‡ (Ph_2N) (estimations). The conclusion can be easily drawn that the nitrogen valence state

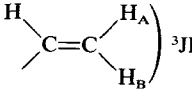
‡ Calculated from the value of pK = 20.3 for $PhCOCH_2NPh_2$[15] by the Equation pK(DMSO) = 49.13–23.35 $\Sigma\sigma^-_{CH_m}$ derived earlier[12] from the data of the same author.

TABLE II

The data on IR and NMR spectra of APS (III)

Substance	IR spectrum (pellets KBr) ν, cm^{-1} P—N	IR spectrum (pellets KBr) ν, cm^{-1} Others[a]	^{31}P NMR (MeCN) δ, ppm	PMR spectrum ($CDCl_3$), δ ppm, J Hz H_{Ar}	2H (NCH_2)	$^3J_{HP}$	Others
IIIa	1085	1750 (C=O)	47.7	7.15–7.90m	4.70d	9.8	4.03q (2H, CH_2)^3 J_{HH} 7.1; 1.10t (3H, CH_3)^3 J_{HH} 7.1
IIIb	1085		46.7	7.18–7.84m	4.45d	6.8	[b]
IIIc	1095	2128 (C≡C)	48.3	7.18–7.84m	4.68d	9.2	2.53t (1H, ≡CH)^4 J_{HH} 2.3
IIId	1072	1525 1325 (NO_2)	47.0	7.09–7.98m	5.86d	5.7	
IIIe	1060		46.2	6.83–7.87m	5.15d	6.7	
IIIf	1052	1028 (C—O—C)	45.5[c]	6.64–7.87m	4.93d	7.2	
IIIg	1050		46.1	6.87–7.83m	5.03d	6.6	
IIIh	1035	1750 (N—C=O)	45.5	7.08–8.02m	4.92d	11.1	(NEtEt') 3.32q (2H, CH_2) 0.90t (3H, CH_3); 3.19q (2H, $\acute{C}H_2$); 0.89t (3H, $\acute{C}H_3$)^3 J_{HH} 7.1
IIIi	1100		50.5	7.24–7.85m	5.12d	8.9	
IIIj	1020		47.2	7.12–7.89m	4.53d	10.7	3.10–3.25m (2H, CH_2); 1.44–1.53m (2H, CH_2); 0.93–1.05m (2H, CH_2); 0.62t (3H, CH_3)^3 J_{HH} 7.1

[a] In the spectra of all compounds there is a band at 1118 cm^{-1} ($Ph_3\overset{+}{P}$).

[b] 5.79 dd (1H, CH=)^3 J_{HH} 6.8 $^3JHH_A$ 10.2 $^3J_{HH}$ 16.8; δ_A 5.13 δ_B 5.02 (IH_A, IH_B, ) ^3JH_AH 10.2 ^3JH_BH 16.8 $^2JH_AH_B$ 1.2.

[c] Solvent-MeCN-alcohol.

TABLE III
Equilibrium CH-acidity of APS $[Ph_3\overset{+}{P}N(R)CH_2R']X^-$ in DMSO, counterion K^+, 298°K

N	R	R'	pK	Indicator (pK)	K_{equil}[a]
1	Ph	Ph	23.9	9-t-Bu-fluorene (25.6)[11]	5.0 ± 0.20
2	Ph	$CONEt_2$	19.7	9-phenyl fluorene (18.5)[11]	0.065 ± 0.02
3	Ph	COOEt	15.2	n-$O_2NC_6H_4CH_2COOEt$ (15.1)[14]	0.78 ± 0.02
4	Ph	n-$O_2NC_6H_4$	15.6	— —	0.34 ± 0.14
5	Ph	CN	14.7	— —	2.96 ± 0.85
6	Bu	Ph	24.8	9-t-Bu-fluorene (24.6)[11]	0.67 ± 0.20

[a] Average over 3–4 measurements.

in these groups is most likely close to that of ammonium due to the effect

$$Ph_3\overset{+}{P}—N—R \leftrightarrow Ph_3P=\overset{+}{N}—R.$$

This result is confirmed by the data of the IR spectra of the APS under study. (See Table II).

Very characteristic changes of the PN band in the IR spectra of triphenylphosphine-N-phenylimine occur upon protonation.

$$Ph_3P = NPh + H^+ \rightarrow Ph_3\overset{+}{P}NHPh$$

The intensive broad band of 1350 cm^{-1} disappears and a new one emerges at 975 cm^{-1}. Vibrational frequency for a single bond P—N should be expected in the range of 750–870 cm^{-1}.[17,18] Therefore, a new band of 975 cm^{-1} can be ascribed to the vibration of the P=N band of a lowered multiplicity. Then the structure of the protonated imine (**IV**) can be assumed to be intermediate between two forms:

$$Ph_3\overset{+}{P}—NHPh \leftrightarrow Ph_3P = \overset{+}{N}HPh,$$

the first one being predominant. In the APS (**III**) spectra the PN frequencies are in the range 1100–1050 cm^{-1} (Table II). Hence, the bond P—N has an intermediate multiplicity in these compounds that testifies to a considerable contribution of ammonium structure.

EXPERIMENTAL

The ^1H and ^{31}P NMR spectra were recorded at 200.13 and 81.01 MHz respectively on a Bruker WP-200SY spectrometer. Internal standard for the PMR spectra is HMDS, external one for the ^{31}P NMR is 85% H_3PO_4. The IR spectra were obtained on the UR-20 spectrometer (pellets with KBr). In CH-acidity determination the spectral measurements were made in a quartz cell on spectrophotometer SF-26. All reactions were carried out in dried purified solvents under argon.

[N-phenyl-N-carbetoxymethylamino]triphenylphosphonium bromide (**IIIa**). A solution of 4.9 g (13.8 mmol) (**I**) and 3.5 g (20.7 mmol) (**IIa**) in 40 ml of MeCN was refluxed for 6 hr with stirring. The solvent was removed in vacuum, the residue was crystallized from a $CHCl_3$-EtOAc mixture. 4.3 g (60.0%) of (**IIIa**) were obtained, m.p. 192–3°. (**IIIb–f**) were obtained in the similar way. Yields, melting points, data of elemental analysis, IR and ^{31}P and ^1H NMR spectra are given in Tables I and II.

[N-phenyl-N-benzylamino]triphenylphosphonium iodide (**IIIg**). A solution of 4.9 g (13.8 mmol) (**I**), 2.7 g (20.7 mmol) (**IIg**) and 3.1 g (20.7 mmol) of NaI in 50 ml of MeCN was refluxed for 8 hr. The solvent was removed in vacuum, the residue was dissolved in 50 ml of $CHCl_3$, the solution was washed with water (2 × 15 ml) and dried over Na_2SO_4, the solvent was removed in vacuum. 7.0 (88.8%) (**IIIg**) were obtained from MeCN by crystallization; m.p. 248–9°. (**IIIh**) and (**IIIi**) were obtained in the similar way.

[N-butyl-N-benzylamino]triphenylphosphonium bromide (**IIIk**). A solution of 2.1 g (13 mmol) of bromine in 15 ml of MeCN was added dropwise within 20 min (20°) under stirring to the solution of 3.4 g (13 mmol) of triphenylphosphine in 50 ml of MeCN, stirring for 20 min (20°) was followed by a dropwise addition of a solution of 2.1 g (13 mmol) of N-benzyl-N-butylamine and 1.3 g (13 mmol) of triethylamine in 20 ml of MeCN. The reaction mixture was stirred at room temperature for 6 hr. 48 hr later (20°), the reaction mixture was evaporated in vacuum, the residue was dissolved in 40 ml of $CHCl_3$, washed with water (2 × 15 ml), and the solution dried over Na_2SO_4. After the removal of the solvent in vacuum, 4.3 g (55%) of (**IIIk**) were obtained by crystallization from MeCN-benzene, m.p. 204–5°.

Interaction of (**I**) *with bromoacetophenone* (**IIj**). A solution of 4.8 g (13.6 mmol) of (**I**) and 2.8 g (13 mmol) of (**IIj**) in 40 ml of MeCN was refluxed for 6 hr. The solvent was removed in vacuum, the residue was crystallized from MeCN-benzene. 2.2 g (74.5%) of (**IV**) were obtained, m.p. 195–7°. The mother solution was evaporated in vacuum and the residue crystallized from THF. 1.3 g (68.7%) of Ph_3PO were obtained, m.p. 155–6°.

Determination of equilibrium CH-acidity. The APS were dried in vacuum before the experiments, DMSO was purified by the known technique.[13] Remetallization reactions were carried out in the diluted DMSO solutions (concentration $\leq 10^{-3}$ mol/l) and freshly prepared solution of $K^+CH_3SOCH_2^-$. The pK values were calculated from spectrophotometric data on concentration constants of equilibrium (K_{equil}) of the remetallization reactions between the CH-acids and K-salts of CH-indicators by the technique.[11] The pK values were calculated using 3–4 values of equilibrium constants (K_{equil}). Carbanions of the CH-acids under study do not absorb light in the visible spectrum. Therefore to determine the value of K_{equil}, a decrease in optical density (D) in the absorption band maximum of the indicator carbanion was determined after the sample of CH-acid had been added to the solution and the equilibrium reached. Further decrease in D is linked with the by-processed and occurs slowly. However in some cases the equilibrium did not shift to the opposite direction when another sample of indicator was added to the solution. In these cases additional experiments were carried out, and an indicator sample was added to the solutions of the K-salt of the CH-acid under study obtained by action of potassium 9-phenylxanthenyl (pK = 28.3) on CH-acid. Coincidence of the pK values in the range of 0.2–0.3 pK units served as correctness criterion (accuracy of the described method is usually 0.1 pK units).[11]

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