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SYNTHESIS AND CH-ACIDITY OF N,N-DISUBSTITUTED AMINOTRIPHENYLPHOSPHONIUM SALTS

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Several substituted methylaminotriphenylphosphonium salts (APS) of general formula [Ph₃PN(R)CH₂R']X⁻ have been synthesized. The CH-acidities of some of the prepared APS have been measured by the indicator method in DMSO, with K⁺ counterion and 9-phenylfluorene (pK 18.5) as standard, showing a pK range of 14.7-24.8. The acidification effect of Ph₃PN(Ph) (σ_{CH_2} = 0.70) and Ph₃PN(Bu) (σ_{CH_2} = 0.68) groups has been evaluated. The results obtained suggest that there is an effective charge on the nitrogen atom in the APS studied and an increased multiplicity of the N-P bond.

Substituted methylaminophosphonium salts (APS) are used in preparative organic chemistry [1-5]. In the development of synthetic procedures, the reaction of APS with different nucleophiles has been fundamental. It has been concluded that in these reactions the nucleophile attacks the positively charged phosphorus atom of the APS. The possibility of deprotonation of the CH_2 group attached to the nitrogen by the action of the nucleophile (i.e., the CH-acidity of the APS) has not been examined.

Methods for the preparation of APS have been fairly thoroughly studied although the selection of substituents on the phosphorus and nitrogen atoms has been restricted to phenyl and alkyl groups [6-10]. The reactions of APS with bases of different strengths have also been studied. In reactions with Na alkoxides in aprotic solvents, the alkoxide anion attacks the positively charged P atom; the P-N bond is thus broken forming alkoxyphosphonium salts as intermediate products which are alkylated by mercaptans [1] and primary and secondary amines [2]. By using mixed cuprates of allyl or α -allene alcohols in analogous reactions one can develop regio- and stereospecific preparative methods for olefins and 1,3-dienes [3-5]. N-Methyl-N-benzylaminotriphenylphosphonium bromide [Ph₃PN(Me)CH₂Ph]Br⁻ reacts in a similar manner with sodium methoxide in methanol and triphenylphosphine oxide and methyl-benzylamine can be isolated from the reaction product [10]. However, when the same APS reacts with butyllithium in an aprotic solvent, or with NaOH in MeCN, the main products are triphenyl phosphine and benzylidenemethylamine [10]. The authors suggest that these compounds are formed by the decomposition of an unstable zwitterion Ph₃PN(Me)CHPh.

Thus, the difference in the direction of reaction of the type of APS under discussion with bases depends on both the CH-acidity of the APS and the basicity of the nucleophile. In this connection we have studied the CH-acidity of the APS referred to above and of related structures.

RESULTS AND DISCUSSION

Substituted methylaminophosphonium salts (III) are prepared by the alkylation of N-phenyltriphenylphosphinimine (I) by the appropriate substituted alkyl bromide (II) for 6-10 h in MeCN at boiling point.

$$Ph_{3}P = NR + XCH_{2}R' \longrightarrow [Ph_{3}PN(R)CH_{2}R']X^{-}$$

$$(1) \qquad (IIa - j) \qquad (IIIa - j)$$

$$R = Ph (a - j); X = Br (a - f, j), I(g, h, i); R' = COOEt (a). CH = CH_{2}(b), C \equiv$$

$$CH (c), p-NO_{2}C_{6}H_{4}(d), p-BrC_{6}H_{4}(e), p-MeOC_{6}H_{4}(f), Ph(g), CONEt_{2}(h), CN(i),$$

$$COPh (j).$$

$$(1)$$

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Com- pound	Yield, %	Mp, °C (solvent)	Found Calculated, %				Empirical
			с	п	Hal	þ	formula
(III a)	60.0	192 - 193	64.9	5.8	16.0	5,8	C28H27BrNO2P
(IIIb)	54.0	214-216 (CH($ch = E(OAc)$)	68.6 68.6	5.2 <u>5.4</u>	15.4 17.0	6.0 <u>6.7</u>	C27H25BrNP
(111c)	63,5	$\frac{221-223}{(Me(N - C_{\rm e}H_{\rm c}))}$	$\frac{68.8}{68.7}$	$\frac{5.3}{-5.4}$	16,8 <u>16,7</u> <u>46,0</u>	6,5 <u>6,6</u>	C ₂₇ H ₂₃ BrNP
(111d)	82,5	$\frac{186-187}{(MeCN - C_6H_6)}$	<u>55.2</u>	5.2	10.9 <u>14.0</u> <u>14.0</u>	5,4 5,4	$C_{31}H_{23}BrN_2O_2I$
(lile)	58,0	233-235 (MeCN - Call, hexane)	$\frac{-51.4}{-01.7}$	$\left \frac{3,0}{4,3} \right $	26.6	$\frac{5.1}{5.1}$	$\mathrm{C}_{34}\mathrm{H}_{26}\mathrm{Br}_2\mathrm{NP}$
(111f) *	86,5	189 -19 1 (CHCia - EtO Ve)	<u> </u>	5.4	<u>14.1</u> <u>14.0</u>	5.0	$C_{32}H_{31}BrNO_2P$
(IIIg)	88,8	248249 (M+CN)	<u>(5,2</u>)	$\frac{4,9}{4,8}$	$\frac{14,0}{22.7}$	5.4	Ca1H27INP
(]][h)	54.0	214-218 (M-CN - Calle - hexane)	60.7	5.4	21.5	5.0	C30H32IN2OP
(1111)	35,2	$\frac{247 \cdot 21}{(\mathrm{MeCN} + \mathrm{C}_{6}\mathrm{H}_{*})}$		4.4	24.7	5,9 <u>6,0</u>	$C_{26}H_{22}IN_2P$
(III k.)	55,0	204-205 (MeCN CeHa)	<u>-69,1</u> -69,0	<u>6.1</u> - 6,2	+	<u>6,2</u> 6,1	C2:JI:31BrNP

TABLE 1. Constants, Yields, and Elemental Compositions of APS (III)

*Crystal hydrate (IIIf) · H₂O. +Found/calculated: N 2.9/2.8%.

Alkyl chlorides (II) fail to effect alkylation of (I) even on boiling for 15-20 h; in these cases the reaction was carried out in the presence of an equimolar quantity [relative to (II)] of NaI. Reaction with bromoacetophenone (IIj) (R' = COPh, X = Br) takes place in 6 h but the reaction product is a ~1:1 mixture of triphenylphosphine oxide and the hydrobromide of the initial phosphinimine (IV). The ${}^{31}P-\{{}^{1}H\}$ NMR spectrum shows, apart from the two main signals, only a weak signal (~2-3%) at 40.3 ppm which could be assigned to the corresponding APS (IIIj). Probably in this case the CH-acidity of (IIIj) is so high that it reacts with the initial (I) forming the hydrobromide of the latter (IV) and the zwitterion (V) which decomposes forming triphenylphosphine oxide. It would seem that the part of the molecule which splits off here and contains no phosphorus polymerizes readily and it is not possible to isolate the monomeric product with the composition PhN-CH=CPh. The mixture of oligomers which is formed consists in the main of compounds with molecular weights corresponding to trimer and hexamer.

Preparation of the hydrobromide (IV) in the reaction of (IIj) with the phosphinimine (I) is also possible via the formation of the carbene $CH-COPh \leftrightarrow \dot{C}H=C(0^{-})Ph$ which, reacting with the initial (I), can form Ph_3PO and the same monomeric fragment $Ph\bar{N}-\bar{C}H=\dot{C}Ph$ or Ph_3P and PhCOCH=NPh which ultimately leads to the same result.



Com- pound	IR spectra (KBr disk) v, cm ⁻¹		³¹ PNMR spectra	PMR spectra (CDC1 ₃) δ, (J, Hz)				
	P-N	others*	(MeCN) δ, ppm	Har	2H, NCH ₂	ъ	others	
(HIa)	1085	1750 (C=O)	47,7	7,15-7,90 m	4.70 d	9,8	$ \begin{array}{c} 4.03 \text{ q} & (2\text{H}, \text{ CH}_2, \\ \mathbf{J}_{HII} = 7, 1); 1.10 \text{ t} \\ (3\text{H}, \text{ CH}_3, \mathbf{J}_{HH} = -7, 1) \end{array} $	
(1111)	1085		46.7	7,18-7,84 m	4.45 d.d	6.8	+	
(IIIc)	1095	2128 (C≡C)	48 ,3	7,18–7,84 m	4,68 d.,d	9,2	$2.53 t (1H. = CH, 4J_{HH} = 2,3)$	
(111d)	1072	1525, 1325 (NO ₂)	47,0	7,09-7,98 m	5,86 d	5,7		
(IIIe)	1060		46,2	6,83-7,87 m	5,15 d	6,7		
(111f)	1052	1028 (C-O-C)	45,5 🕈	6,64-7,87 m	4,93 d	7,2		
(Ilig)	1050		46,f 🕈	6,87–7,83 m	5,03 d	6,6		
(111)	1035	1750 (N-C=O)	45,5	7,08-8,02 m	4,92 đ	11,1	(NEtEt') 3.32 q (2H. CH_2); 0.90 t (3H. CH_3); 3.19 q (2H. $C'H_2$); 0.89 t (3H. $C'H_3$), ${}^{3}J_{HII} =$ =7,1)	
(IIIi)	1100		50,5	7.24-7,85 т	5,12 d	8,9		
(1116)	1020		47.2	7,12-7,89 m	4.53 đ	10,7	$\begin{array}{c} 3.10-3.25 \text{ m } (2\text{H},\\ \text{CH}_2); \ 1.44-1,53 \text{ m} \\ (2\text{H}, \text{CH}_2): \ 0.93-\\ 1.05 \text{ m } (2\text{H}, \text{CH}_2): \\ 0.62 \text{ t } (3\text{H}, \text{CH}_2); \\ 0.62 \text{ t } (3\text{H}, \text{CH}_3,\\ ^3J_{\text{HH}}=7,1) \end{array}$	
*A band +5.79 d	l at l.d.t	1118 cm ⁻¹ (1H, CH=	(Ph ₃ P) , ³ J _{HH}	was pres = 6.8; ³ J	ent in HHA =]	all s .0.2;	 spectra. ³ J _{HHB} = 16.8)	

TABLE 2. IR and NMR Spectra of APS (III)

*A band at 1118 cm⁻¹ (Ph₃Ṗ) was present in all spectra. +5.79 d.d.t (1H, CH=, ${}^{3}J_{HH} = 6.8$; ${}^{3}J_{HHA} = 10.2$; ${}^{3}J_{HHB} = 16.8$); $\delta_{A} = 5.13$; $\delta_{B} = 5.02$ (1H_A1H_B, $\sum_{H_{B}}^{H_{A}} {}^{3}J_{HAH} = 10.2$; ${}^{3}J_{HBH} = 16.8$; ${}^{2}J_{HAHB} = 1.2$).

#Solvent: MeCN/alcohol.

It could be suggested that the decomposition of the zwitterion (V) proceeds via a Wittig type intramolecular reaction, facilitated by the readiness with which (V) assumes the enol form. It should be noted that in the preparation of APS (IIIa) and (IIIi) which contain electmon-acceptor substituents (R' = COOEt, CN) the hydrobromide (IV) was also observed in the reaction mixture in quantities of 7 and 29%, respectively (from their $^{31}P-{^{1}H}$ NMR spectra) and this markedly reduced the yield of the desired products. The signal for the hydrobromide (IV) (&P 33.9 ppm) can be observed in the NMR spectrum of the reaction mixture only when the initial phosphinimine (I) has completely reacted. When both (I) and (IV) are present in the reaction mixture the ${}^{31}P-{}^{1}H$ NMR spectrum at 30°C shows one signal of intermediate op value in place of the two singlets; this is associated with rapid proton exchange. It was shown in separate experiments that at 30°C the ${}^{31}P-{}^{1}H$ NMR spectra of solutions of a mixture of (I) and (IV) in MeCN in molar ratio 3:1, 1:1, and 1:3 consisted of singlets at 10.0, 17.8, and 25.8 ppm, respectively, while under the same conditions the signals of (I)and (IV) had chemical shifts of 2.2 and 33.9 ppm. These results are in good agreement with an additive relationship between δP and the mole fraction of (IV) (n) in mixture with (I): $\delta P = 2.18 + 31.52n$. In the preparation of APS (IIIb-h) no hydrobromide (or hydriodide) was detected in the reaction mixture.

Alkyl bromides (II) having strong electron-acceptor substituents [$R = NEt_3$, P(Ph₃), CH₃C₆H₄SO₂, (EtO)₂P(O)], together with 9-bromofluorene, did not react with the phosphinimine (I) even on boiling for 15-20 h in MeCN, and in the presence of NaI.

N-Butyl-N-benzylaminotriphenylphosphonium bromide (IIIk) (R = Bu, R' = Ph, X = Br) was prepared by the method of [10] from triphenyldibromophosphorane and N-butyl-N-benzylamine in the presence of triethylamine.

TABLE 3. Equilibrium CH-Acidity of APS $[Ph_3PN(R)CH_2R']X^-$ in DMSO (counterion K⁺, 298 K)

R	R'	p <i>K</i>	Indicator (pK)	^K equi	Σσ _{CH2}
Ph Ph Ph Ph Bu 9-t-Bu 9-Ph-1 p-O ₂ N(Ph CONE12 COOEt p-O2NC6H4 CN Ph 1-Fluorene Fluorene 6H4CH2COOEt	$\left \begin{array}{c}23.9\\19.7\\15.2\\15.6\\14.7\\24.8\\24.6\\18.5\\15.1\end{array}\right $	9-t-Bu-Fluorene (24.6) [11] 9-Ph-Fluorene (18,5) [11] p-O ₂ NC ₆ H ₄ CH ₂ COOEt (15,1) [14] * (15,1) 9-t-Bu-Fluorene (24.6) [11] - - -	$ \begin{vmatrix} 5.0 \pm 0.20 \\ 0.065 \pm 0.02 \\ 0.78 \pm 0.02 \\ 0.34 \pm 0.14 \\ 2.96 \pm 0.85 \\ 0.67 \pm 0.20 \\ - \\ - \\ - \\ - \\ - \end{vmatrix} $	1,06 1,28 1,42 1,44 1,50 1,04 1,06 1,29 1,46

*Average of 3-4 measurements.

The physical constants, yields, results of elemental analyses, and IR, and ³¹P and ¹H NMR spectra of compounds (III) are set out in Tables 1 and 2.

Equilibrium CH-acidities (pK values are given in Table 3) were determined by the indicator method of [11] in DMSO with K^+ counterion and 9-phenylflourene (pK 18.5) as standard. Ionic association in the solutions under study was disregarded since K halides and salts with large organic cations are as a rule fully dissociated in DMSO. It should be noted that the zwitterions (V) formed by the action of base are unstable. Once the equilibrium concentration of the indicator base had been attained, it continued to fall, although very slowly. Secondary processes reduce the accuracy of the measurements but nevertheless do not prevent the determination of the position of equilibrium of the transmetallation reaction in which the APS participates.

It can be seen from Table 3 that the CH-acidity of APS (III) varies over a wide range (~10 pK units) in proportion to the acidifying effect of the substituents $Ph_3PN(R)$ and R'. To characterize the acidifying action of the substituents, σ_{CH_2} constants [12, 13] were used; the values of these for the $Ph_3PN(R)$ group were found in the following way. A Hammet calibration curve was first constructed from the points corresponding to the CH-acidity indicator used:

 $pK = 49,43 - 23,613 \Sigma \tau_{CH_m}$ (m = 1,2).

The σ_{CH_2} constants of the Ph₃PN(R) groups were then calculated for all the APS studied: for R = Ph, σ_{CH_2} = 0.70 ± 0.03 and for R = Bu, σ_{CH_2} = 0.68. These values were verified using the correlation equation previously derived [13] from the results of Shatenshtein for CH-acids in DMSO with K⁺ counterion [11], used also in the present work

$$pK = 48,77 - 22,83 \Sigma \sigma_{\text{CH}_m}^{-},$$

$$n = 35; r = 0,995; s = 0,62; \bar{s}_{\rho} = 0,41.$$

In this case, for the group $Ph_3\dot{P}N(Ph)$, σ_{CH_2} = 0.71 ± 0.02 and for $Ph_3\dot{P}N(Bu)$, σ_{CH_2} = 0.68. These results are in good agreement with those given above. Using the values obtained for σ_{CH_2} (0.70 and 0.68) and the results of Table 3 an overall σ_{ρ} -correlation was performed leading to the equation:

$$pK = 48.72 - 23.025 \Sigma \sigma_{CH_m}^{-1},$$

 $n = 9, r = 0.995, s = 0.45 \text{ and } s_0 = 0.85,$

which, within the limits of the values found for s, agrees with the general correlations. Thus, in their acidifying action, the groups $Ph_3\dot{P}N(Ph)$ and $Ph_3\dot{P}N(Bu)$ are only slightly inferior to COOEt and superior to CONEt₂ groups:

$$\begin{array}{rl} \text{COOEt} > \text{Ph}_3\text{PN}(\text{Ph}) > \text{Ph}_3\text{PN}(\text{Bu}) > \text{CONEt}_2\\ \\ \bar{\sigma_{\text{CH}}}: & 0.725 & 0.70 & 0.68 & 0.58 \end{array}$$

It is interesting to note that the acidifying effects of $Ph_3\dot{P}N(Ph)$ and $Ph_3\dot{P}N(Bu)$ are only slightly inferior to groups with ammonium nitrogen for which σ_{CH_2} are known: 0.79

for Ne₃N and 0.88 for Me₂PhN, and are superior to groups with trivalent nitrogen (σ_{CH_2} = 0.1 for Ne₂N and 0.25 for Ph₂N). (Calculated from the value of pK 20.3 for PhCOCH₂NPh₂ [15] by the equation pK(DMSO) = 49.133 - 23.35 $\Sigma\sigma_{CH_m}$, derived previously [12] from the results of the same author.) From this one can readily conclude that the valency state of the nitrogen in these groups is close to ammonium, evidently on account of the effect $Ph_3\dot{P} - \dot{N} - R - Ph_3P = \dot{N} - R$.

This result is confirmed by the IR spectra of the APS studied (Table 2). Assignment of the vibrational frequencies was carried out on the basis of results obtained for the hydrobromide (IV) [16]. The structure of (IV) and of the APS studied can be presented as phosphonium (A) or ammonium (B) resonance structures



The IR spectrum of the phosphinimine (I) shows a broad intense band at 1350 cm⁻¹, characteristic for the P=N bond. As the hydrobromide (IV) is formed this band disappears and a new band is found at 975 cm⁻¹ which is assigned to vibrations of a P=N bond of reduced multiplicity. For a single P-N bond one would expect a vibrational frequency of 750-870 cm⁻¹ [17, 18]. In the IR spectra of APS (III) the vibrational frequency of the P-N bond is found in the 1100-1050 cm⁻¹ region (Table 2). Hence, the P-N bond in these compounds has an intermediate multiplicity which demonstrates the marked contribution of the ammonium structure (B).

EXPERIMENTAL

A Bruker WP 200 SY spectrometer was used to record ¹H and ³¹P NMR spectra at 200.13 and 81.01 MHz, respectively. HMDS was used as internal standard for PMR spectra, and 85% H_3PO_4 as external standard for ³¹P NMR spectra. IR spectra were run on a UR 20 instrument with KBr disks. Spectroscopic measurements for the determination of CH-acidity were carried out in fully sealed quartz cuvettes on an SF 26 spectrophotometer. All the reactions were carried out in anhydrous purified solvents under argon.

<u>N-Phenyl-N-carbethoxymethylaminotriphenylphosphonium Bromide (IIIa)</u>. A solution of 4.9 g (13.8 mmoles) (I) and 3.5 g (20.7 mmoles) (IIa) in 40 ml MeCN was stirred at bp for 6 h. The solvent was distilled off in vacuum and the residue crystallized from a mxture of $CHCl_3$ and EtOAc. The yield was 4.3 g (60.0%) (IIIa), mp 192-193°C. Compounds (IIIb-f) were prepared in a similar way. Yields, melting points, elemental analyses and IR and NMR spectra are set out in Tables 1 and 2.

<u>N-Phenyl-N-benzylaminotriphenylphosphonium Iodide (IIIg)</u>. A solution of 4.9 g (13.8 mmoles) (1), 2.7 g (20.7 mmoles) (IIg), and 3.1 g (20.7 mmoles) NaI in 50 ml MeCN was heated at br for 8 h. The solvent was distilled off in vacuum and the residue dissolved in 50 ml CHCl₃ and the solution washed with water (2 × 15 ml), dried over Na₂SO₄, and the solvent removed in vacuum. Crystallization from MeCN yielded 7.0 g (88.8%) (IIIg), mp 248-249°C. Compcunds (IIIh) and (IIIi) were prepared in a similar way (Tables 1 and 2).

<u>N-Butyl-N-benzylaminotriphenylphosphonium Bromide (IIIk)</u>. To a solution of 3.4 g (13 mmoles) triphenylphosphine in 50 ml MeCN was added, dropwise with stirring over 20 min at 20°C, a solution of 2.1 g (13 mmoles) bromine in 15 ml MeCN and the solution stirred 20 min at 20°C. A solution of 2.1 g (13 mmoles) N-benzyl-N-butylamine and 1.3 g (13 mmoles) triethylamine in 20 ml MeCN was then added dropwise with stirring and the mixture stirred 6 h at ~20°C. After 48 h (20°C) the reaction mixture was evaporated in vacuum and the residue dissolved in 40 ml CHCl₃, washed with water (2 × 15 ml), and dried over Na₂SO₄. Removal of the solvent in vacuum and crystallization from MeCN-benzene yielded 4.3 g (55%) (IIIk), mp 204-205°C.

Reaction of (I) with Bromoacetophenone (IIj). A solution of 4.8 g (13.6 moles) (I) and 2.8 g (13 mmoles) (IIj) in 40 ml MeCN was heated at bp for 6 h. The solvent was removed in vacuum and the residue crystallized from MeCN-benzene to yield 2.2 g (74.5%) (IV), mp 195-

197°C. The mother liquor was evaporated in vacuum and the residue crystallized from THF, yielding 1.3 g (68.7%) Ph_3PO , mp 155-156°C.

Determination of Equilibrium CH-Acidity. The APS under examination was dried in vacuum before use and the DMSO purified by the method of [13]. The transmetallation reaction was carried out in dilute solution in DMSO ($\leq 10^{-3}$ mole/liter) using apparatus evacuated up to $1\cdot10^{-4}$ mm Hg and a freshly prepared solution of K dimsyl. The pK were calculated on the basis of spectrophotometric determination of the equilibrium concentration constant (K_{equi}) for the transmetallation reaction of the CH-acid under study with the K salt of the CH-indicator using the technique of [11]. The pK values were based on three to four determinations of the equilibrium constant (K_{equi}).

The carbanions of the CH-acids examined did not absorb light in the visible region and hence for the determination of K_{equi} the reduction in optical density (D) at the maximum of the absorption band of the indicator carbanion was recorded after introducing a weighed amount of the CH-acid into the solution and (rapidly) reaching equilibrium. The subsequent fall in the value of D associated with side reactions took place slowly. Nevertheless, in some cases the equilibrium did not shift back on introducing a further weighed portion of indicator. In these cases a supplementary experiment was carried out in which a weighed amount of the indicator was added to a solution of the K salt of the studied CH-acid under test, obtained by the action of K 9-phenylxanthenyl (pK 28.3) on the CH-acid. The criterion for the test was that the pK values should agree within 0.2-0.3 pK units (the usual accuracy of the method used is 0.1 pK units [11]).

LITERATURE CITED

- 1. Y. Tanigawa, H. Kanamaru, and Sh.-I. Murahashi, Tetrahedron Lett., No. 25, 4655 (1975).
- 2. Y. Tanigawa, Sh.-I. Murahashi, and I. Moritani, Tetrahedron Lett., No. 7, 471 (1975).
- 3. Y. Tanigawa, H. Kanamaru, A. Sonoda, and Sh.-I. Murahashi, J. Am. Chem. Soc., <u>99</u>, No. 7, 2361 (1977).
- 4. Y. Tanigawa, H. Ohta, A. Sonoda, and Sh.-I. Murahashi, J. Am. Chem. Soc., <u>100</u>, No. 14, 4610 (1978).
- 5. Ch. Fan and B. Cazes, Tetrahedron Lett., 29, No. 14, 1701 (1988).
- 6. H. Staudinger and F. Hauser, Helv. Chim. Acta, 4, 861 (1921).
- 7. H. Zimmer and G. Singh, J. Org. Chem., 28, No. 2, 483 (1963).
- 8. L. Horner and H. Hoffman, Angew. Chem., <u>68</u>, No. 15, 473 (1956).
- 9. L. Horner and H. Oediger, Liebigs Ann. Chem., <u>627</u>, 142 (1959).
- 10. K. Fukui and R. Sudo, Bull. Chem. Soc. Jpn., <u>43</u>, No. 4, 1160 (1970).
- 11. M. I. Terekhova, E. S. Petrov, S. P. Mesyats, and A. I. Shatenshtein, Zh. Obshch. Khim., 45, No. 7, 1529 (1975).
- 12. M. I. Kabachnik and T. A. Mastryukova, Dokl. Akad. Nauk SSSR, 260, No. 4, 893 (1981).
- 13. M. I. Kabachnik and T. A. Mastryukova, Zh. Obshch. Khim., <u>54</u>, No. 10, 2161 (1984).
- E. S. Petrov, E. N. Tsvetkov, S. P. Mesyats, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 4, 782 (1976).
- 15. F. G. Bordwell, Acc. Chem. Res., 21, No. 12, 456 (1988).
- 16. E. I. Matrosov, V. A. Gilyarov, V. Yu. Kovtun, and M. I. Kabachnik, Izv. Akad. Nauk SSSR, Ser. Khim., No. 6, 1162 (1971).
- 17. E. I. Matrosov, Zh. Struktur. Khim., 7, No. 5, 708 (1966).
- 18. H. Sisler and N. Smith, J. Org. Chem., <u>26</u>, No. 2, 611 (1961).