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Some Aminophosphinocarboxylic Acids and Their Derivatives

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ABSTRACT

The addition of Schiff bases of α-aminoacid esters to vinylphosphoryl compounds was studied as a method for the synthesis of phosphinothricin and its analogues. The reaction was found to proceed smoothly in DMSO in the presence of strong nitrogen bases and under the conditions of phase transfer catalysis. The Claisen condensation of β-phosphorylated propionitrile with diethyl oxalate was studied; phosphorylated derivatives of hydroxycitraconic acid nitrile were prepared on hydrolysis; transformation of such a derivative into a cyclic imide as well as into trimethylsilyl esters of these acids and their Z → E transformation were investigated. Cyclization reactions between α,ω-dibromoalkanes and phosphoryl compounds containing an active methylene group affording cyclopropane and other cyclic derivatives were studied. The cyclopropane ring is cleaved by amines to give aminophosphinocarboxylic acids.

In the last decade, phosphoryl-substituted aminocarboxylic and ketocarboxylic acids have attracted the attention of chemists. Synthesis and investigation of the properties of these compounds have been developed as one of the most important directions in the organophosphorus chemistry of biologically active compounds. One can point out several sources of the development of this trend. For example, they include the elucidation of the important mediatory role of γ-aminobutyric and glutamic acids [1], discovery of the biological activity of β-aminoethylphosphonic acid [2], the herbicide activity of glyphosate [3], and solution of the structure of the antibiotic—SF-1293—bialophos, which is a peptide with a terminal methylhydroxyphosphinyl group [4]. The phosphorus moiety of bialophos—phosphinothricin—turned out to be a very interesting biologically active compound with a wide range of activity [5]. The herbicidal activity of a similar compound, γ-methylhydroxyphosphinyl-α-ketobutyric acid, a possible precursor of phosphinothricin in nature, was subsequently discovered [6]. Investigation into the field of phosphinothricin has become very popular, and we have not remained alien to it.

The present report includes three parts bound by one idea: The first one is the investigation of the synthesis of phosphinothricin itself and its analogues; the second part is devoted to the study of substituted α-ketocarboxylic acids, which is full of surprises; and the third one deals with the development of the cycloalkylation method as an approach to aminophosphinocarboxylic acids.

With regard to the synthesis of phosphinothricin and its analogues, we were interested in the literature method [7] that is based on the addition of Schiff bases to alkyl vinylphosphinates (Reaction 1). There were several reasons for our interest in this method.

First, we had a facile method for the synthesis of alkyl vinylphosphinates based on dichlorophosphines [8]. It is presented in Scheme 1.

Although this is a multistep synthesis, it can be performed as a one-pot operation affording in 80% yield (based on dichlorophosphine) the desired alkyl vinylphosphinate. Secondly, we have been engaged for a long time in the study of addition reactions to a vinyl group bonded to the phosphorus atom [9, 10]. Thirdly, we were interested in the in-

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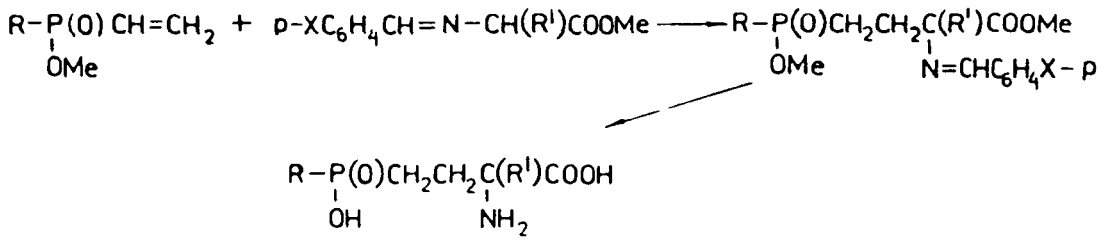
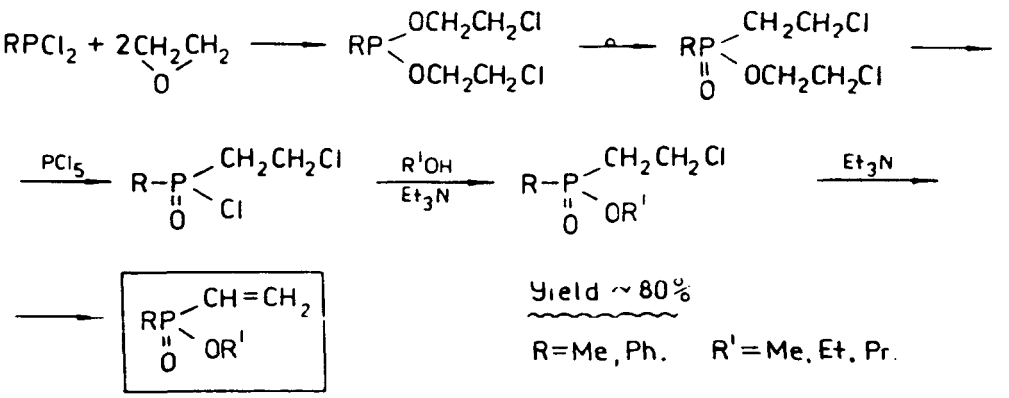


REACTION 1

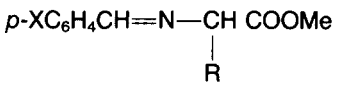


SCHEME 1

vestigation of the acidity and reactivity of α-methinyl acids. The Schiff bases of α-aminoacids and aldehydes belong to this class of compound.

Therefore, we obtained a series of Schiff bases by the traditional method. Then we investigated their α-methinyl acidities in DMSO using an indicator method [11]. Phenylfluorene (pK 18.5) was used as standard and K^+ as counterion. The results of measurement of the equilibrium CH-acidity are presented in Table 1.

TABLE 1 Equilibrium CH-Acidities in Dimethyl Sulfoxide Solution at 25°C



No.	R	X	pK_a	$\lambda_{max.}$, nm
1	H	Me_2N	21.9	430
2	H	H	19.7	440
3	H	Cl	19.3	450
4	H	Br	19.2	450
5	Me	Me_2N	22.6	430
6	Me	H	20.9	440
7	Me	Cl	20.0	460
8	Me	Br	20.2	460
9	*i*-Pr	Me_2N	25.6	440
10	*i*-Pr	H	23.7	450
11	*i*-Pr	Cl	22.7	460
12	Pr	H	22.5	450
13	Ph	H	18.4	460, 350

As evident, the azomethines studied belong to CH-acids of medium strength. Within each series, the bathochromic shift of the UV-absorption maximum is diagnostic of the CH-acidity. Introduction of the alkyl substituents into the aminoacid moiety of the molecule decreases the CH-acidity, but introduction of a phenyl group leads to an increase of it.

The data in Table 1 allow one to consider the possibility of a $\sigma\rho$-correlation of the pK_a values for these acids. At first we calculated the constants $\sigma^-_{CH_2}$ and σ^-_{CH} for the azomethine groups from Equation 1. This equation had been derived earlier by us [12] on the basis of data obtained by Shatenshtein and his coworkers.

$$pK_a = 48.77 - 22.83 \sum \sigma^-_{CH_x};\ n = 35;$$

$$r = 0.995,\ s = 0.62,\ s_\rho = 0.41 \quad (1)$$

The results of these calculations are presented in Table 2. The same table gives the values of $\sigma^-_{CH_2}$ and σ^-_{CH} for azomethine groups obtained from the data of Bordwell and coworkers [13]. Equation 2 has been derived by us especially for Bordwell's data [12]:

$$pK_a = 49.13 - 23.35 \sum \sigma^-_{CH_x};\ n = 89;$$

$$r = 0.989,\ s = 1.03,\ s_\rho = 0.38 \quad (2)$$

As evident, these data are nearly identical.

TABLE 2 The $\sigma^{-}_{CH_x}$ Constants of Azomethine Groups

	$\sigma^{-}_{CH_2}$		σ^{-}_{CH}	
	Our Data	*Bordwell's Data*	*Our Data*	*Bordwell's Data*
p-Br	0.58	—	0.50	—
p-Cl	0.57	0.58	0.48	0.52
H	0.55	0.56	0.44	0.44
p-NMe_2	0.46	—	0.36	—

A satisfactory correlation was obtained between the calculated $\sigma^{-}_{CH_x}$ constants and the CH-acidities of all of the sets of azomethines studied (Equation 3):

$$pK_a = 51.80 - 25.317 \sum \sigma^{-}_{CH_x};\ n = 13;$$
$$r = 0.961,\ s = 0.60,\ s_p = 2.19 \quad (3)$$

However, the pK_a vs. $\sigma^{-}_{CH_x}$ plot shows (Figure 1) that all the points can be referred to three groups. The first one applies to glycine derivatives, the second to alanine derivatives, and the third to valine derivatives. Within each group, a good or excellent linear relationship between pK_a and $\sigma^{-}_{CH_x}$ is observed. The occurrence of these sets may be attributed to the different steric effects of the substituents R′ on the equilibrium dissociation of the CH-acids.

The study of the addition of Schiff bases to the vinylphosphoryl compounds has revealed that the reaction occurs easily in the presence of catalytic amounts of strong nitrogen bases in aprotic dipolar solvents, such as DMSO and DMF (Reaction 2). These data offer a contrast to the results of the previous workers [7]. In the case of the Schiff bases of glycine and alanine derivatives, yields are almost quantitative; for the valine esters, they are significantly lower. The best solvent to use is well dried DMSO, and the best catalysts are DBU (diazobicycloundec-7-ene) and analogous strong nitrogen bases. The

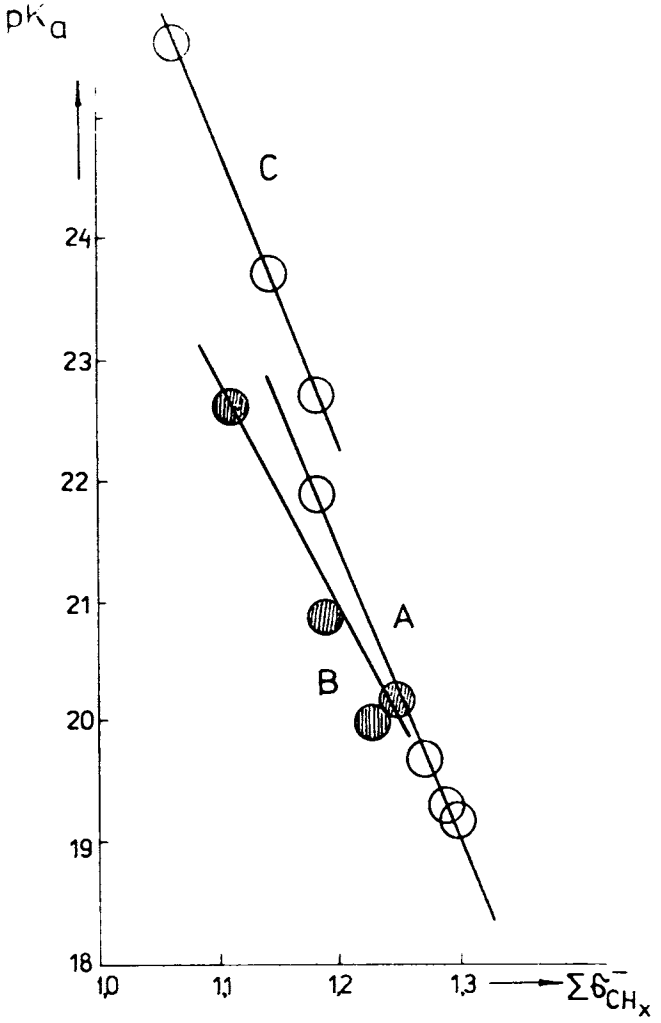
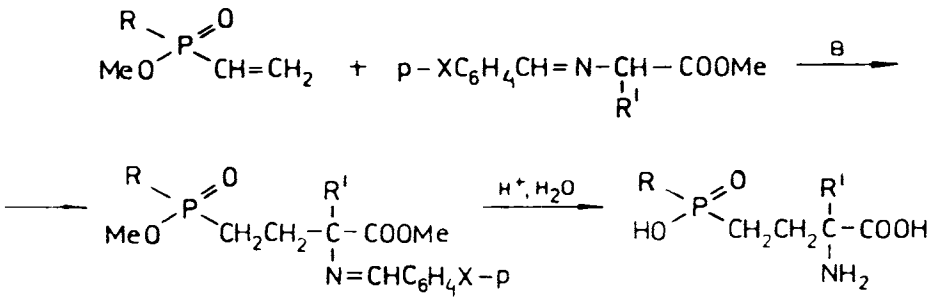


FIGURE 1 The Hammett correlation of CH-acidity of Schiff bases of derivatives of aminoacid esters in DMSO. A—glycine, B—alanine, C—valine.



REACTION 2

R = Me, Ph

R′ = H, Me, Et, Pr, i-Pr, i-Bu,

X = H, Br, Cl, NMe_2

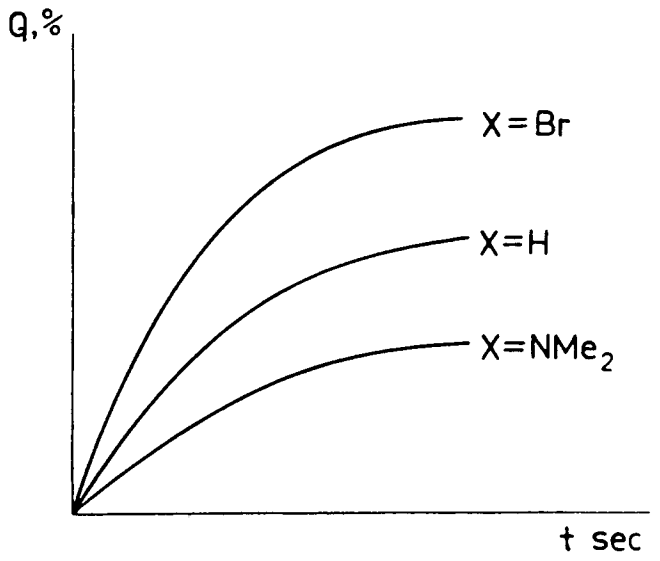


FIGURE 2 The kinetic curves for the addition reactions of Schiff bases of glycine esters $XC_6H_4CH{=}NCH_2COOEt$ with vinylphosphinates in DMSO.

reaction does not occur with weaker bases, for example, triethylamine. The reaction proceeds faster with increasing basicity and concentration of the catalyst. We managed to follow the reaction kinetics by the ^{31}P NMR method. Kinetic curves for the addition of azomethines, which are derivatives of glycine, to vinylphosphinate are presented in Figure 2. As seen, the reaction is significantly accelerated on going from a weaker CH-acid (X = NMe_2) to stronger ones (X = H and Br).

The best interpretation of the experimental results is obtained by the following scheme for the addition reaction:

First stage. Formation of the azomethine complex with the base-catalyst:

$$AH + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [AH\cdots\cdots B]$$

Second stage. Reaction of the complex with the vinylphosphinate (V):

$$[AH\cdots\cdots B] + V \xrightarrow{k_2} AV^- + BH^+$$

Third stage. Fast proton transfer reaction of the carbanion (AV^-) with BH^+:

$$AV^- + BH^+ \xrightarrow{k_3} AVH + B$$

(AVH: the end-product of the reaction).

In the case of the glycine derivatives, the first stage is a fast one. The rate-limiting step is the second stage, and the whole process is a second order one.

In the case of alanine or valine derivatives, the first stage is the rate-limiting one, and the whole process is first order (the concentration of base-catalyst is constant).

TABLE 3 Second-Order Rate Constants k' for the Addition of p-$XC_6H_4CH{=}N{-}CH_2{-}COOMe$ to $R(MeO)P(O)CH{=}CH_2$, DMSO, 20°, DBU (5 mol.%)

No.	R	X	pK_a	n	$k^1 \cdot 10^4$ $l \cdot mol^{-1} \cdot s^{-1}$	Correlation Coefficient, r
1	Ph	H	19.7	7	45.93 ± 0.03	0.994
1[a]	Ph	H	19.7	6	9.3 ± 0.1	0.987
2	Me	Br	19.2	6	13.20 ± 0.01	0.991
3	Me	H	19.7	7	9.4 ± 0.001	0.999
4	Me	Me_2N	21.9	5	0.42 ± 0.002	0.994

[a] DBU: 1 mol.%

TABLE 4 First-Order Rate Constants k' for the Addition of p-$XC_6H_4CH{=}NCH(CH_3)COOMe$ to $Me(MeO)P(O)CH{=}CH_2$, DMSO, 20°, DBU (5 mol.%)

N	X	pK_a	n	$k^1 \cdot 10\ s^{-1}$	Correlation Coefficient, r
5	Br	21.2	6	0.54 ± 0.000	0.997
6	H	20.9	5	0.45 ± 0.01	0.996
7	Me_2N	22.6	6	0.054 ± 0.000	0.982

$$AH + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [AH\cdots B] \quad \text{slow}$$

$$\left.\begin{array}{l} [AH\cdots B] + V \xrightarrow{k_2} AV^- + BH^+ \\ AV^- + BH^+ \xrightarrow{k_3} AVH + B \end{array}\right\} \quad \text{fast}$$

$$\frac{-d[V]}{dt} = k'[V]; \qquad k' = k_1[B]$$

In both cases the reaction rate constants are proportional to the CH-acidity of the Schiff base and to the catalyst basicity. This is supported experimentally.

As depicted in Table 3, the glycine derivatives' reactions are second order. The alanine derivatives (R′ = Me), on the contrary, undergo first order reactions (Table 4). Thus, in the addition reaction of Schiff bases of the alanine derivatives, formation of the complex ($AH\cdots B$) is hindered. The steric effect is probably similar to that characteristic of the hindered CH-dissociation of alanine derivatives, mentioned above.

Thus, the addition of Schiff bases of α-aminoacid esters to vinylphosphinates in DMSO in the presence of DBU and other strong organic bases represents a good method for the synthesis of phosphinothricin and its analogues. However, we have found and elaborated another more facile method. It relies on the addition of Schiff bases to vinyl-

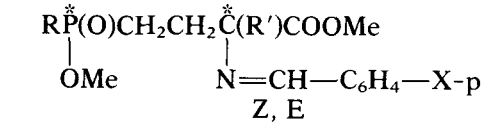
TABLE 5 Phase Transfer Catalysis of the Reaction, $R(MeO)P(O)CH{=}CH_2 + p\text{-}XC_6H_4CH{=}NCH_2COOMe$; System ClC_6H_5/H_2O 10:1, KOH, Equimolar Amounts of Components, Catalyst: Bu_4NCl (0.05 mol/l)

R	X	°C	Reaction Time (min)	Yield %, (^{31}P NMR)
Ph	H	0	30	80
Ph	H	−10	1	97
Ph	H	−15	10	98
Me	H	−25	10	96
Me	H	−25	30	85
Me	Br	−25	8	100
Me	Me_2N	−25	30	29

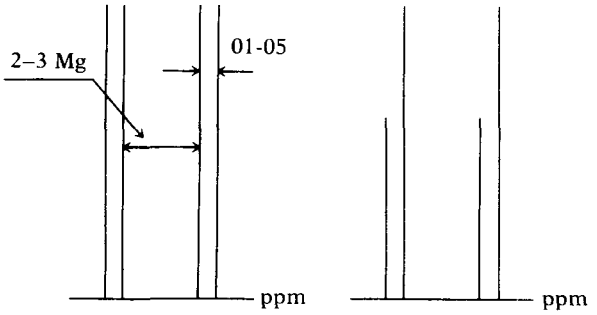
phosphinates under the conditions of phase transfer catalysis.

Chlorobenzene appeared to be the best organic solvent with the aqueous:organic phase ratio of 1:10. Good results are obtained with KOH and NaOH when one equivalent of alkali is used. From the multitude of catalysts investigated, tetrabutylammonium chloride (0.005 mol/l) turned out to be the best. The concentration of each reaction component is 1:1, the temperature range is maintained from −25 to −10°C, and the reaction time is 1 to 30 min. An increase in temperature and prolongation of the reaction time lead to side processes and reduce the yield. Examples are shown in Table 5, involving the addition reactions to Schiff base of glycine derivative under various conditions. As in the case of the homogenous addition, the phenylphosphinate reacts more rapidly than the methyl derivative. On decreasing the CH-acidity of the azomethine, the reaction slows down and the yield decreases. Bulky substituents in the aminoacid moiety of the molecule slow down the reaction and decrease the yield due to side processes occurring without participation of the phosphorus moiety.

Some additional considerations about the stereochemical aspects of the addition reactions of azomethines to vinylphosphinates are required. Since there are two asymmetric centers in the addition products, phosphorus and the carbon of the aminoacid, the formation of diasteroisomers (threo- and erythro) cannot be ruled out.



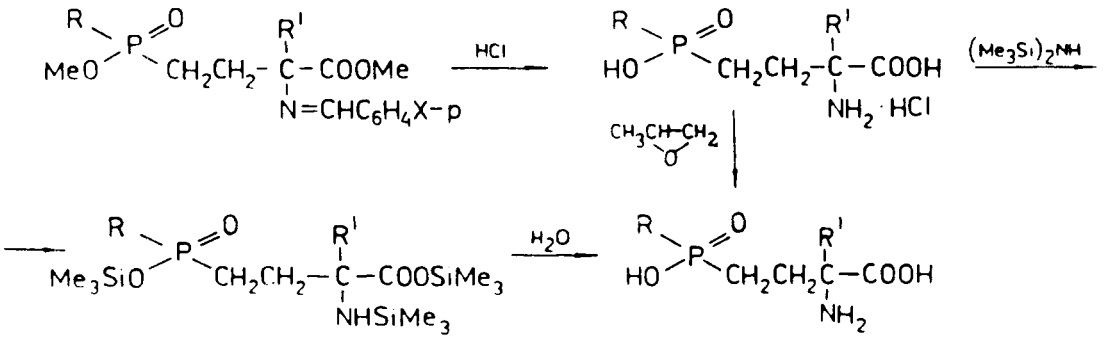
NMR ^{31}P δ 42–46 ppm (R = Ph)
δ 52–56 ppm (R = Me)



R^1 = H − Z : E = 1:1 R^1 = Alk − F > Z

Besides, isomerism about the C=N bond is possible, although Schiff bases ordinarily exist as anti isomers only (*E*-isomers) [11]. Therefore, ^{31}P NMR spectra should display, and indeed do display, four pairs of signals. The closely situated pairs of signals (0.1–0.5 ppm) probably correspond to the geometrical isomers, and the other two correspond to threo and erythro isomers, respectively. In the cases of the glycine derivatives, the *Z* and *E* isomer ratios are 1:1. On introduction of substituents into the amino acid moieties of the molecules, the ratios change in favor of the *E* isomer.

The products of the Michael addition reaction were hydrolyzed in an acidic medium. Free acids were isolated via formation and aqueous hydrolysis of trimethylsilyl esters or by treatment with propylene oxide (Scheme 2).



SCHEME 2

TABLE 6 Yields and Physical Constants of Phosphinothricin and Its Analogues, $R(HO)P(O)CH_2CH_2CR'(NH_2)COOH$

No.	R	R'	Yield	mp °C	mp lit.	δ, ^{31}P	$\nu_{P=O}$
1	Me	H	75	232	229–31	44.7	1240
2	Ph	H	50	237	236–39	34.6	1240
3	Me	Me	44	210	209–12	35.0	1235
4	Ph	Me	39	228	—	34.5	1235
5	Me	Pr	27	207	—	36.2	1240
6	Ph	Pr	42	212	—	29.9	1240

Summing up, the application of catalysts, i.e. strong nitrogen bases, in DMSO medium or under conditions of phase transfer catalysis have led to simple and facile syntheses of phosphinothricin and its analogues (Table 6).

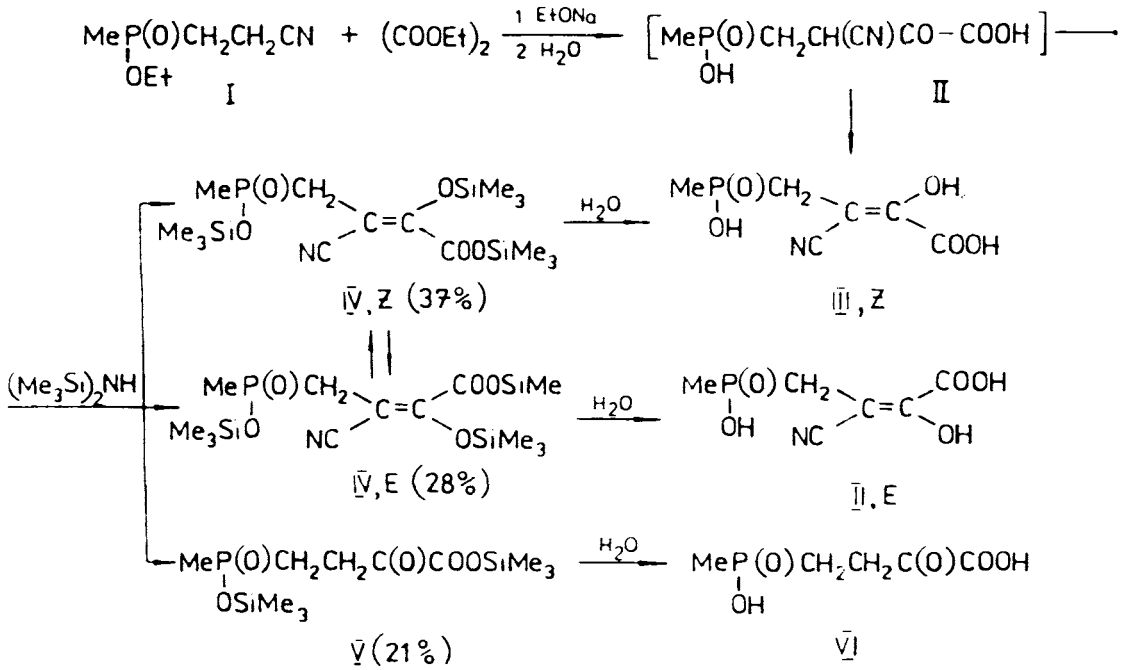
Let us now consider the synthesis and reactions of phosphorylated α-ketocarboxylic acids, in particular γ-(methylhydroxyphosphinyl)-α-ketobutyric acid and its analogues. The acid is evidently related to phosphinothricin in the same way that ketoglutaric acid is related to glutamic acid. The role of the latter in the biochemical amination processes is well known. This acid is known also to exhibit herbicidal activity similar to that of glyphosate. Ketoacids of this type are of interest from the synthetic point of view as well: phosphinothricin and its analogues can be prepared by the reductive amination method [6].

Unexpected results were obtained in the attempts to synthesize the CN derivatives of γ-(methylhydroxyphosphinyl)-α-ketobutyric acid. Initial attempts were undertaken to prepare them under the conditions of the Claisen condensation from β-phosphorylated propionitrile and diethyl oxalate (Scheme 3).

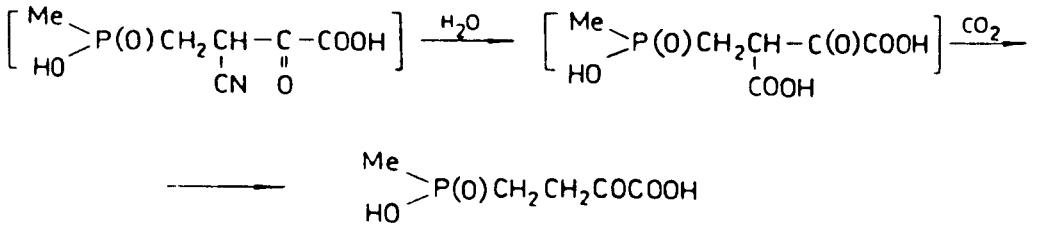
This condensation and the subsequent hydrolysis gave, not the CN derivative of the phosphorylated ketoacid (II), but the *Z* isomer of its enol form (III). It turned out to be quite stable and no ketonization was detected. Its structure, i.e. the phosphorylated nitrile of α-hydroxycitraconic acid, was established by various spectroscopic methods: ^1H, ^{13}C, ^{31}P NMR, IR, and MS. This acid dissociates in three steps, the corresponding pK_a values being 2.0, 3.5 and 13.0.

Hydrolysis, removal of sodium chloride and subsequent treatment of the reaction mixture with hexamethyldisilazane led to three products: the trisilyl ester of the *Z*-enol form (IV-*Z*, 37%), the trisilyl ester of the *E*-enol form (IV-*E*, 28%), and an unexpected disilyl ester of γ-(methylhydroxyphosphinyl)-α-ketobutyric acid (V, 21%). The latter compound possessed no CN group. On treatment with water, it was converted into the free acid, isolated as the diammonium salt.

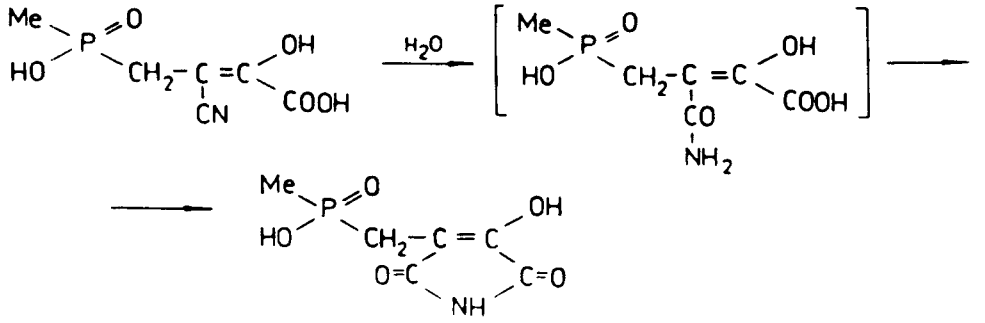
The ratio of geometric isomers (*Z*:*E*) is 57:43. It is of interest that, on treatment with hexamethyldisilazane, the pure *Z* isomer of the enol form (III, *Z*) affords the *Z* form of the trisilyl ester only (IV, *Z*). However, on vacuum distillation, the ester is converted into an equilibrium mixture with the



SCHEME 3



REACTION 3



REACTION 4

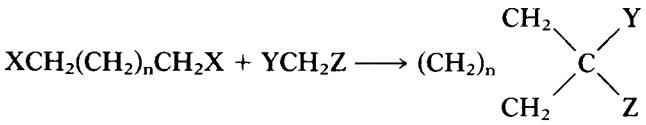
same *Z*:*E* isomer ratio of 57:43. This isomerization is similar to the well-known transformation of citraconic acid into mesaconic acid. The fact that, in our case, the transformation leads to an equilibrium mixture testifies to a small difference in energies of these geometric isomers (about one kj/mol). Aqueous hydrolysis of the silyl esters gives isomeric *Z* and *E* acids in the same ratio of 57:43.

Formation of the ketobutyric acid without the CN group evidently occurs during the hydrolysis of the Claisen condensation products. The CN group is hydrolyzed and the ketocarboxylic acid initially formed is decarboxylated (Reaction 3).

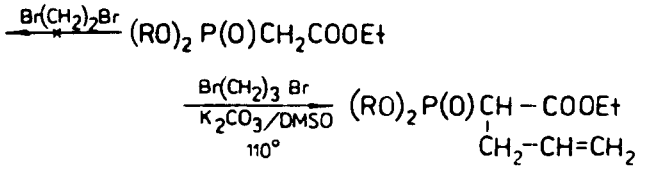
Of interest is the behavior of the phosphorylated hydroxycitraconic acid during either 10 hours of reflux of a dilute aqueous solution or on prolonged storage. In this case, the CN group is converted into an amide group and then a cyclization reaction occurs that affords the cyclic imide (Reaction 4). Although the analysis and spectral data confirmed the imide structure, its unusual formation in aqueous solution influenced us to undertake an X-ray diffraction study. The imide structure is presented in Figure 3. The five-membered ring is nearly planar (the sum of angles is 539.9°). This is undoubtedly a result of the interaction of three π-bonds and two lone pairs on nitrogen and hydroxyl oxygen atoms. The enolic oxygen atom lies in the same plane with the ring.

The third part of this investigation is devoted to a study of the cycloalkylation reaction as a method for the synthesis of phosphorylated derivatives of aminocarboxylic acids. It is known that, on treatment with ammonia, cyclopropane derivatives are susceptible to ring cleavage to afford amines [14]. Therefore, the objective was to elaborate a facile method for synthesis of the phosphoryl substituted cycloalkanes with subsequent ring opening on treatment with ammonia to give aminophosphinocarboxylic acids.

It is well known that cycloalkylation reactions [15] involve the attack on dihalogenoalkanes by the carbanions that are formed from the compounds with active methylene groups. Here X = halogen atom and Y and Z = electronacceptor groups.



Good results in this reaction are ordinarily obtained in DMSO medium in the presence of potash [16]. Although attempts were undertaken to carry out the reaction in this manner, its application to our proposed organophosphorus chemistry was unsuccessful [17].



However, we have found that dibromoethane and other α,ω-dibromoalkanes undergo cycloaddition reactions with phosphorylacetic derivatives in the system K_2CO_3 /DMSO at 20°C/ [18] (Scheme 4).

This reaction was studied by us with various

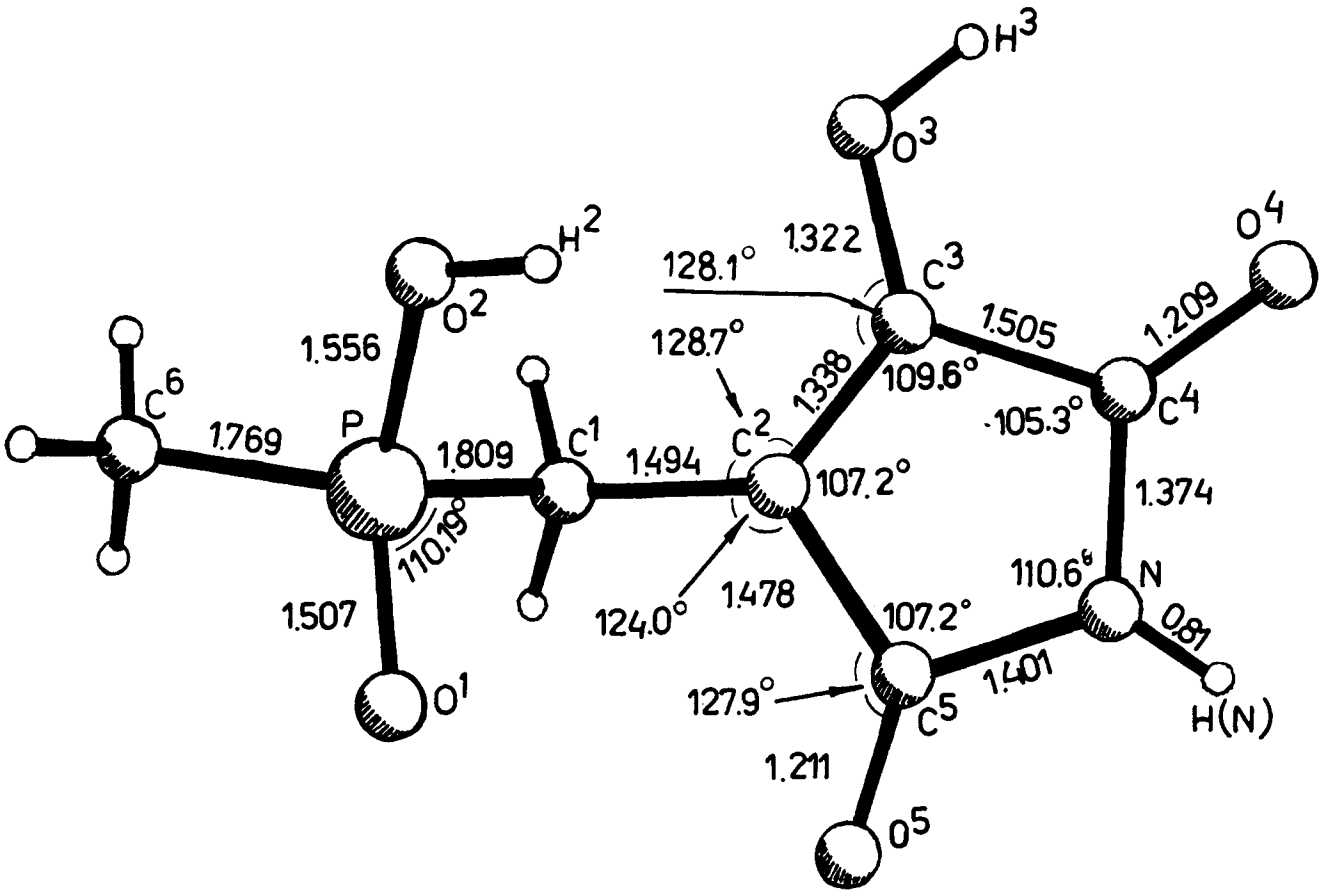
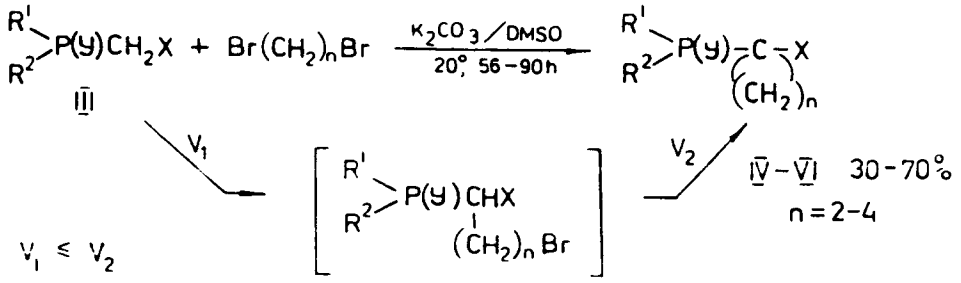


FIGURE 3 The structure of 4-methylhydroxyphosphinyl-3-hydroxycitraconimide.

compounds, including thiophosphoryl ones. Yields of phosphoryl substituted cycloalkanes ranged from 30 to 70%. The reaction rate was increased by use of the traditional phase transfer catalysts. Progress of the reaction was followed by ^{31}P NMR spectroscopy. The spectra of each reaction mixture displayed only signals of the starting compounds and the cycloaddition product. The intermediate ω-halogenalkylated compound was not detected. It gives evidence that, after the primary halogenated product had been formed, the ring closed so fast that the intermediate could not be detected by ^{31}P NMR spectroscopy. It is of interest that the intermediate haloalkyl product can be isolated in 10–

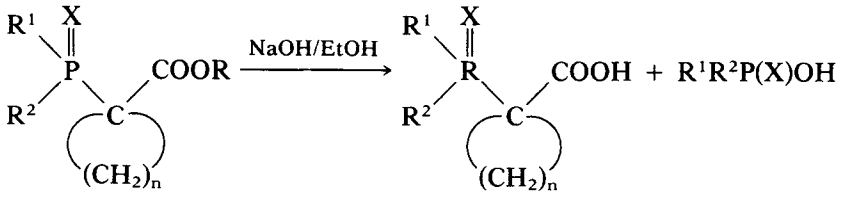


SCHEME 4

25% yield in the cycloalkylation of malonic ester carried out under the same conditions [16].

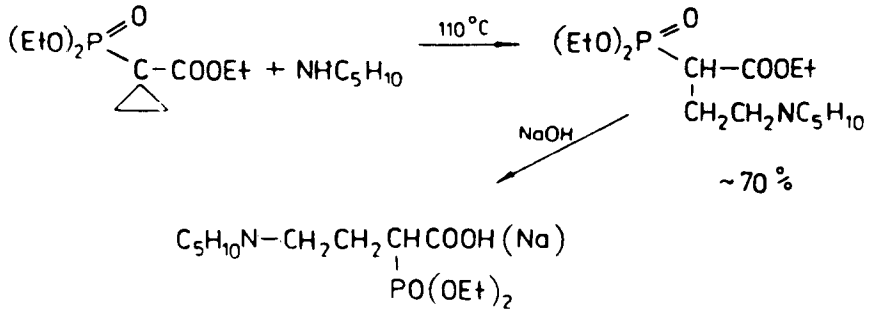
The cycloalkylation rate is in fact dependent on the CH-acidity of the phosphoryl compound having an active methylene group. Thus, the following relationship between the acidity and reaction rate is observed: phosphonates (R = R′ = EtO; pK_a = 17.5–19.5) react faster than phosphinates (R = Me, R′ = EtO; pK_a = 18.2–20.0); acetonitrile derivatives (Y = CN, pK_a = 17.5–18.2) react faster than those of ethylacetate (Y = COOEt, pK_a = 17.5–20.0); the latter react slower than malonic ester (pK_a = 16.7); and acetamide derivatives (Y = $CONEt_2$, pK_a = 22.1) do not undergo the reaction at all. Thiophosphoryl compounds, being approximately one to two orders of magnitude more acidic than the corresponding phosphoryl compounds, react faster. An exception is the acetamide derivative. The values of pK_a are measured in DMSO with K^+ as the counterion [19–21].

The reaction rate decreased on going from dibromalkanes to dichloroalkanes. Functionalized dihalogenoalkanes are oxidized in DMSO, but the phosphorus component shows no changes. It should be noted that the cyclopropanes obtained are quite stable, and they do not decompose up to 200°C. Meanwhile, the cyclobutanes and the cyclopentanes are less stable. When heated, they decompose with P—C bond cleavage and formation of the corresponding phosphinic and phosphoric acids. Under mild alkaline hydrolysis (aqueous alcoholic alkali, 20°C), the carbethoxy group can be hydrolyzed, but the ring and ester groups at the phosphorus atom remain intact (Reaction 5).

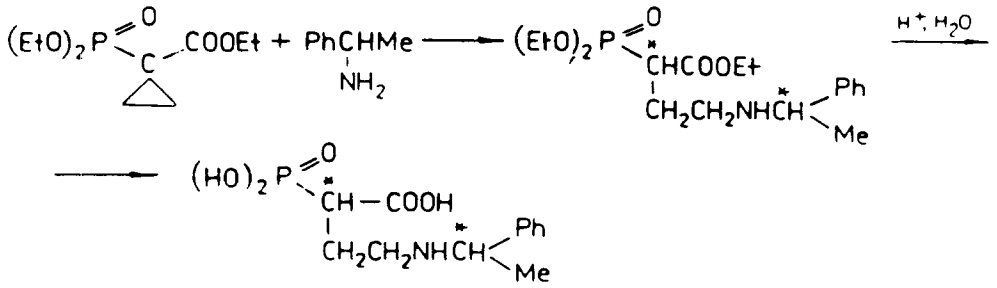


R^1 = R^2 = OEt, Ph; R^1 = Me, R^2 = OEt, OBu-i; R = Et, Bzl; X = O,S; n = 2–4

REACTION 5



REACTION 6



REACTION 7

In the case of phosphoryl derivatives, partial cleavage of the P—C bond and formation of the corresponding phosphorus acid take place. Thiophosphoryl derivatives are significantly less stable toward hydrolysis. Hydrolysis in acidic medium leads to the cleavage of both the P—C bond and the ring.

The last stage, i.e. opening of the cycloalkane ring by amines, was carried out with the cyclopropane derivatives (Reactions 6 and 7). The addition of piperidine and α-phenylethylamine to diethoxyphosphinyl-α-carbethoxycyclopropane was investigated. The reactions occur on heating in toluene and afford the corresponding amines with yields of approximately 70%. Direction of the three-membered ring cleavage was established by the PMR method. An alternative ring opening should have led to a markedly different PMR spectrum.

Hydrolysis in acidic medium of the triester obtained gave the free acid, which was isolated as a sodium salt.

Reaction with α-phenylethylamine follows the analogous pathway. Since there are two asymmetric centers in the compound obtained, ^{31}P NMR and PMR spectra display the diasteromeric anisochronism. It increases somewhat on saponification of the ester groups.

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