Stereoselectivity in Fragmentation and Rearrangement of α-Hydroxyimino-phosphinates and -phosphonates. A Synthetic Approach to Acylphosphon- and phosphor-amidates. Crystal Structures of Methyl (*E*)-α-Hydroxyimino-benzylphenylphosphinate and Methyl Benzoylphenylphosphonamidate

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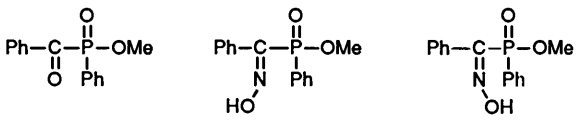
Reaction of methyl benzoylphenylphosphinate **1** with hydroxylamine gave methyl α-hydroxyiminobenzylphenylphosphinate **2** as a mixture of *E* and *Z* isomers with the *E* isomer predominating. Pure (*E*)-**2** when heated gave methyl *N*-benzoylphenylphosphonamidate **3** as the sole product. In contrast, (*Z*)-**2** when heated gave, as a result of fragmentation, mainly methyl hydrogen phenylphosphonate **4** and benzonitrile, together with methyl *N*-phenylcarbamoylphenylphosphinate **5** as the minor product; the latter results from Beckmann rearrangement of (*Z*)-**2**. Analogous behaviour is exhibited by the two geometrical isomers of dimethyl α-hydroxyiminobenzylphosphonate **8**. The crystal structures of methyl (*E*)-α-hydroxyiminobenzylphenylphosphinate (*E*)-**2** and methyl benzoylphenylphosphonamidate **3** are reported.

Recently we reported initial results from our study concerning the oxyiminophosphonic functional group.[1] Our interest in this area arose from the assumption (subsequently confirmed[2]) that the combination of the oxime and phosphonic functions provides a new type of bifunctional group that possesses interesting metal binding properties. Furthermore, it is assumed that such a hydroxyiminophosphonic functionality can easily be incorporated into virtually any type of organic molecule that has, or may be attached to, a carboxy group, thus allowing the design of molecules with potential biological or technological importance.

In addition, it was of interest to extend our studies to phosphinate derivatives, since the replacement of one of the alkoxy groups of a phosphonate by an aryl or alkyl group may result in molecules with modified properties in a number of ways. The introduction of a P-aryl (or alkyl) group into the molecule might be expected to: (1) alter the basicity of the phosphorus oxygens, (2) endow the molecule with increased lipophilicity, and (3) provide steric bulk at the vicinity of the phosphorus atom which, in turn, might help in preventing the formation of polymeric complexes.[2,3] In addition, it was reasonable to expect that the oxyiminophosphinic acids may be developed to a new class of phosphonylating agents, in analogy to the phosphorylating capability demonstrated by oxyiminophosphonates.[4] Here we describe the results of our studies concerning the preparation, characterization, and the reactivity of the two geometrical isomers of methyl α-hydroxyiminobenzylphenylphosphinate as representative compounds of this class. In addition, the thermal behaviour of the two geometrical isomers of dimethyl α-hydroxyiminobenzylphosphonate[1] is described.



1 (*E*)-**2** (*Z*)-**2**

Results and Discussion

Structure and Properties of Methyl α-Hydroxyiminobenzylphenylphosphinates.—Methyl benzoylphenylphosphinate **1** was prepared by the Arbuzov reaction of dimethyl phenylphosphonite using a slightly modified literature procedure.[5] Reactions of **1** with hydroxylamine hydrochloride in alcoholic solution, in the presence of pyridine, gave methyl α-hydroxyiminobenzylphenylphosphinate **2** as mixtures of isomers. The major component in these mixtures (85–90% of the total)† could be isolated in pure form by repeated crystallizations from chloroform and was identified by single crystal X-ray crystallography as the *E* isomer (*vide infra*). On this basis the ^{31}P chemical shifts of the two isomeric oximes could be assigned, and used subsequently for determining the compositions of the isomeric mixtures. Similarly to what was reported for oxyiminophosphonates,[1] in the phosphinate series too, the *E* isomer resonates in its ^{31}P NMR spectrum at lower field (δ 30.4 ppm) than with the *Z* isomer (δ 25.6 ppm). However, the analogy is not extended to the ^{1}H NMR spectra since the $POCH_3$ signals of the two geometrical isomers appear in the reverse order in the two systems.[1]

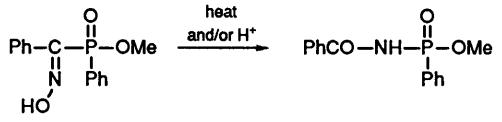
The thermal behaviour of the oximes **2** could be studied using either the pure (*E*)-**2** isomer or mixtures of (*E*)-**2** and (*Z*)-**2** in different proportions. [These different mixtures became available through the fractional crystallizations. Since we were unable to isolate (*Z*)-**2** in a pure state, its behaviour is inferred from that of the isomeric mixture]. The results from these

† Since the procedure for the preparation of methyl α-hydroxyiminobenzylphenylphosphinate involves acidic treatment during the work-up, and since we found that *Z*→*E* isomerization of α-hydroxyiminophosphonates is catalyzed by acid,[1] and *E*/*Z* ratio obtained in the various preparations is somewhat incidental. In a separate experiment we found that under equilibrium conditions a *Z*/*E* ratio of 1:11 is obtained.

Table 1. Thermal behaviour of (*E*)- and (*Z*)-methyl α-hydroxyiminobenzylphenylphosphinate **2**

Starting compd.	Solvent	Temp. (°C)	Time (h)	Products (%) 3	4	5
100% (*E*)	toluene	110	30	100	—†	—†
100% (*E*)	toluene	110	5.5*	100	—†	—†
100% (*E*)	benzene	80	60	100	—†	—†
(*E*)/(*Z*) = 7:1‡	benzene	80	20	87	13	—†
(*E*)/(*Z*) = 1:2	benzene	80	20	36	56	8

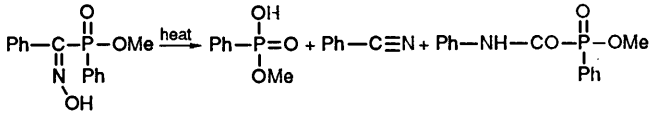
* This experiment was carried out in the presence of a catalytic amount toluene-*p*-sulphonic acid. † Not detected. ‡ The yields of the products in this experiment were estimated from the integrated ^{31}P NMR spectrum of their mixture.



(*E*)-**2** **3**

studies are summarized in Table 1. From this table it can be seen that when heated pure (*E*)-**2** gave methyl *N*-benzoylphenylphosphonamidate **3** as the sole product. This Beckmann rearrangement can be carried out without acid catalysis. To go to completion, it was necessary to reflux (*E*)-**2** in toluene for 30 h or in benzene for *ca.* 60 h. However, in the presence of a catalytic amount of toluene-*p*-sulphonic acid the reaction was over in 5.5 h.

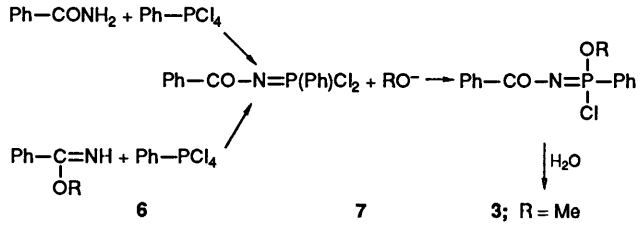
In contrast, the thermal behaviour of the mixture of (*E*)-**2** and (*Z*)-**2** was found to depend on the isomeric composition. The 7:1 (*E*):(*Z*) mixture required *ca.* 20 h under reflux in benzene to go to completion, and afforded a 7:1:1 mixture of **3**, methyl hydrogen phenylphosphonate **4**, and benzonitrile. The shorter reaction time observed in this case as compared to that of the pure (*E*)-**2** can be rationalized as resulting from the catalytic effect of the acidic **4** emerging during the reaction. This effect is amplified in the reaction of the 1:2 mixture of (*E*)-**2** and (*Z*)-**2**. In this case, in addition to benzonitrile, the phosphorus-containing products were **3**, **4**, and methyl *N*-phenylcarbamoylphenylphosphinate **5**, a new product which seems to result from the Beckmann rearrangement of (*Z*)-**2**. These results indicate that the two geometrical isomers of **2** do not interconvert under the reaction conditions, but each is transformed stereoselectivity to its characteristic products.



(*Z*)-**2** **4** **5**

The identification of the amide **3** is based upon X-ray crystallography (*vide infra*) and upon analytical and spectral data. In the IR spectrum it shows the expected characteristic absorption for the amide carbonyl at 1666 cm^{-1} in addition to other peaks expected for the aromatic and the phosphonyl groups. Both the ^{31}P NMR (δ 18 ppm, q) and the ^{1}H NMR spectra of **3** are also fully consistent with the rearranged structure.

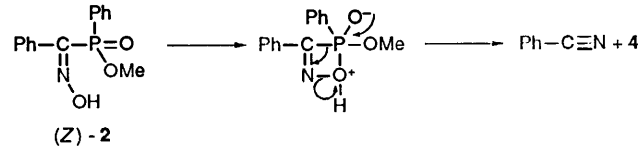
This rearrangement represents a simple convenient synthetic method to acylphosphonamidates, since starting materials are easily accessible by the following sequence of simple high-yield reactions: Arbuzov reaction, oxime formation, its isomerization to the more stable *E* form and the latter's thermal rearrangement. The alternative methods to **3** require reaction of benzamide or alkyl benzimidate with tetrachloro(phenyl)-phosphorane ($PhPCl_4$, **6**) leading to *N*-benzoyl-*P*-phenylphosphonimide dichloride **7**, followed by treatment with sodium alkoxide, both steps proceeding in reportedly low yields.[6,7]



Methyl hydrogen phenylphosphonate **4** was identified by comparison of its ^{1}H and ^{31}P spectroscopic properties with those of an authentic sample. Methyl *N*-phenylcarbamoylphenylphosphinate **5** was isolated only in very small quantity by preparative TLC. Because of the small quantity available, its structure assignment is based on spectroscopic properties. These included the mass spectrum, the IR, the ^{1}H and ^{31}P NMR spectra which were all consistent with the structure assigned (see Experimental section).

Comparison of the mass spectra of the two amides **3** and **5** reveals significant differences in fragmentation which clearly result from the differences in structures of the two isomers. The main fragmentation in both compounds is bond fission α to C=O. In compound **3** this leads to the fragment of *m/z* 105 corresponding to $[PhC{=}O]^+$. However the base peak in the spectrum of **3** is *m/z* 142 presumably due to $[PhPO_2H_2]^+$. In contrast, the base peak in the case of **5** is *m/z* 155 $[PhP(=O)OMe]^+$, formed by α cleavage, (this peak appears also in the spectrum of **3** at a much lower intensity) accompanied by a weaker peak at *m/z* 141 ($[PhPO_2H]^+$). For details, see Experimental section.

Our results indicate that while (*E*)-**2** undergoes only Beckmann rearrangement, the geometrical isomer (*Z*)-**2** behaves differently. Its main course of reaction is fragmentation presumably through intramolecular attack of the oxime oxygen on the phosphorus[1] (see Scheme 1) resulting in the formation of benzonitrile and methyl hydrogen phenylphosphonate, and only a small proportion goes through the Beckmann rearrangement to **5**. The decreased tendency of (*Z*)-**2** to rearrange might indicate a relatively low migratory aptitude of the phenyl group as compared to that of the phosphonyl



(*Z*)-**2**

Scheme 5.

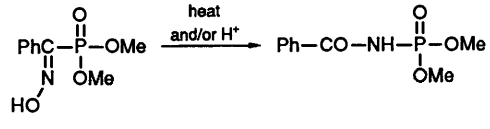
Table 2. Thermal fragmentation of **8** in refluxing benzene[a]

	Starting compd. **8**		Products (%)[a]			
Time (h)	% *E*	% *Z*	**9**	DMHP	TMPP	PhCN
0	35	65	0	0	0	0
8	20	0	10	47	24	60
24	10	0	18	38	32	62
34	8	0	20	47	25	68
48	7	0	22	51	20	70
0	100	0	0	0	0	0
8	100	0	0	0	0	0
24	84	0	14	0	2	0
34	77	0	16	4	3	0
48	62	0	30	5	3	8

[a] The proportions of the phosphorus-containing products and starting materials were estimated from the integrated signals of ^{31}P NMR. The amounts of starting material **8** and of product **9** could be confirmed by HPLC during the determination of the proportion of benzonitrile (on an RP-8 column using a 60:40 mixture of 0.05% TFA in water:MeOH, flow = 1.0 ml/min, analysed at 250 nm).

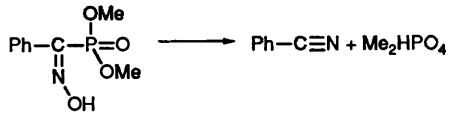
group,* but on the other hand it may also be the result of the competition of the C–P bond-breaking reaction, which is not possible in the *E* isomer, but seems to be the favoured path in this case.

Thermal Behaviour of Dimethyl α-Hydroxyiminobenzylphosphonate.—In view of the above mentioned results we re-examined the behaviour of the geometrical isomers of dimethyl α-hydroxyiminobenzylphosphonate [(*E*) and (*Z*)-**8**] recently described.[1] Previously we noted that (*Z*)-**8** undergoes relatively rapid thermal fragmentation to benzonitrile and dimethyl phosphate (Scheme 2) while the *E* isomer seemed to exhibit relative stability under the reaction conditions.[1] Reinvestigation of the thermal behaviour of (*E*)-**8** revealed that it slowly undergoes thermal Beckmann rearrangement to dimethyl benzoylphosphoramidate (**9**). This compound was identified by comparison of its analytical data with those described in the literature.



(*E*)-**8** **9**

Dimethyl benzoylphosphoramidate **9** was previously prepared by the reaction of sodium methoxide either with *N*-benzoyltrichlorophosphazene or with benzoylphosphoramidic dichloride.[8] Although both of the methods mentioned above were reported to proceed in high yields, we consider the Beckmann rearrangement reported here as a good alternative synthetic approach to this type of compounds, in view of its simplicity and the fact that it does not require the intermediacy of strongly acidic reagents.



(*Z*)-**8**

Scheme 2.

Results from reinvestigation of the thermal behaviour of pure *E* and *E* + *Z* mixture of dimethyl α-hydroxyiminobenzylphosphonate **8** are summarized in Table 2.

Monitoring the progress of the reaction of a mixture of isomers of **8** (*E*/*Z* = 35/65) in refluxing benzene by ^{31}P NMR spectrometry showed relatively rapid disappearance of the *Z* isomer with the concomitant appearance of three new peaks: one at 2.88 ppm (septet, *J* 11 Hz), identified as dimethyl hydrogen phosphate (DMHP) a second signal at 1.74 ppm (octet, *J* 10 Hz) identified as dimethyl benzoylphosphoramidate **9** and a broad signal at *ca.* −10 ppm, which is identified as tetramethyl pyrophosphate[7] (TMPP). Because of the closeness of their chemical shifts, the identities of the two former peaks were confirmed by the addition of authentic samples of DMHP and compound **9** to the mixture. In addition to ^{31}P NMR spectrometry, the reaction was also monitored by HPLC. By this method the formation of benzonitrile and of **9** as well as the decrease in the quantities of starting materials **8** could be monitored. The results obtained by HPLC for the quantities of **8** and **9** were in good agreement with those from ^{31}P NMR spectrometry. Benzonitrile was identified by comparison of its IR and NMR spectra and retention time with those of an authentic sample.

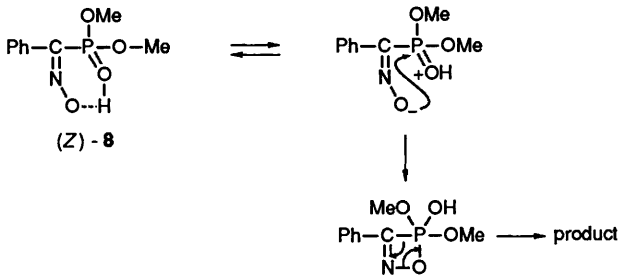
In a control experiment the thermal fragmentation of **8** was carried out in the presence of an equimolar amount of dimethyl hydrogen phosphate. In this experiment, ^{31}P NMR analysis revealed a considerable increase in the proportion of the signal at −10 ppm.[1] On the other hand, dimethyl hydrogen phosphate when heated alone, or with benzonitrile produced no signal at −10 ppm. All this is consistent with the assumption regarding the identity of the −10 ppm signal as that of tetramethyl pyrophosphate.

Examination of the results listed in Table 2 reveals that when heated for 8 h (*Z*)-**8** is converted completely into benzonitrile, DMHP, and TMPP. During the same period of time about a third of the *E* isomer was found to rearrange to **9**. Further heating of the reaction mixture, after all the *Z*-oxime has been consumed, causes little changes in the proportions of DMHP, TMPP, and benzonitrile. The gradual increase in the amounts of these can be attributed to the formation of more (*Z*)-**8** by slow, acid (DMHP)-catalysed *E*/*Z* equilibration. The main change seen during extended heating of the mixture is the slow, gradual increase in the amount of the Beckmann product **9**.

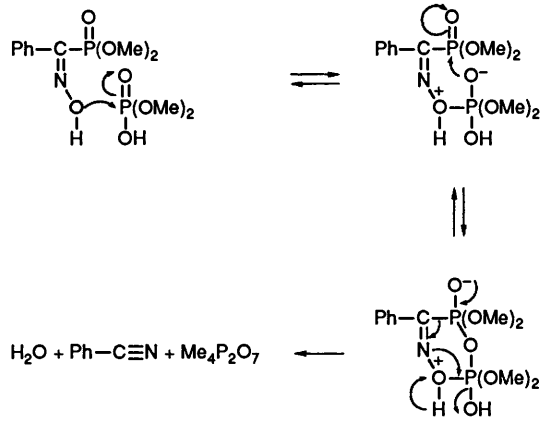
When the behaviour of the pure *E* isomer (bottom of Table 2) is compared to that of the mixture, it can be seen that in contrast to the behaviour of the mixture, heating of the pure *E*

* There exist conflicting results about the relative migratory aptitudes of aryl *versus* dialkoxyphosphoryl groups in reactions involving competitive migrations of these groups to electron deficient centres. The reactions studied include: (*a*) epoxide rearrangements to carbonyl compounds: R. H. Churi and C. E. Griffin, *J. Org. Chem.*, 1966, **88**, 1824; A. J. Kirby and S. G. Warren, *The Organic Chemistry of Phosphorus*, Elsevier, London, 1967, pp. 333–334; S. G. Warren, *Angew. Chem., Int. Ed. Engl.*, 1968, **7**, 606; M. Sprecher and D. Kost, *Tetrahedron Lett.*, 1969, 703; (*b*) Baeyer–Villiger oxidations of dialkyl aroylphosphonates: M. Sprecher and E. Nativ, *Tetrahedron Lett.*, 1968, 4405; and (*c*) The Schmidt reaction of dialkyl aroylphosphonates, D. Kost and M. Sprecher, *Tetrahedron Lett.*, 1970, 2535.

A recent report (M. P. Kaushik and R. Vaidyanathswamy, *Chem. Ind.*, 1989, 389) describes the rearrangement and nitrile formation from four aroylphosphonate oximes of unreported stereochemistry in refluxing acetic acid. These authors claim that their results indicate that the phosphoryl group possesses higher migratory aptitude than the aryl groups. In our view, because of its stereoselective nature, the Beckmann rearrangement is not a suitable model to supply that information. In this rearrangement always the group *anti* to the leaving OH migrates. Therefore in *E*-oximes *only* the phosphoryl group can migrate, which is what we show in the present paper, while in the *Z*-oximes *only* the aryl groups could do so. In the latter cases however, the fragmentation reaction seems to be faster and therefore no rearrangement is seen.



Scheme 3.



Scheme 4.

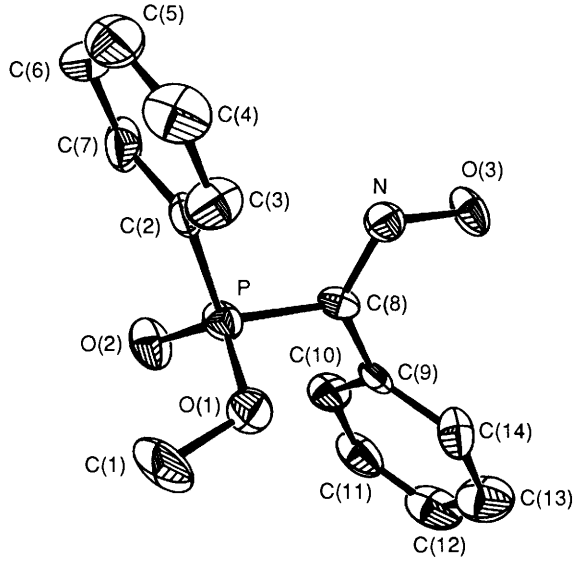


Fig. 1. Structure of molecule (*E*)-**2** showing 50% probability thermal ellipsoids and atom labelling scheme.

isomer produces Beckmann rearrangement at a much slower rate [compare 10% rearrangement from 35% *E*-oxime in the thermolysis of the mixture in 8 h, *vs.* 14% rearrangement from 100% *E*-oxime in the thermolysis of the pure *E*-oxime in 24 h]. This difference in rates can be attributed to the low percentage of acid (DMHP) in the initial stages of the reaction mixture of the pure (*E*)-**8**. In contrast, the acceleration observed in the formation of **9** in the later stages of this reaction, can be attributed to the presence of a significant amount of acid (DMHP).

The results in Table 2 further suggest that the formation of both dimethyl hydrogen phosphate and that of tetramethyl

Table 3. Crystallographic data for (*E*)-**2** and **3**

	(*E*)-**2**	**3**
Elem. formula	$C_{14}H_{14}NO_3P$	$C_{14}H_{14}NO_3P$
Mol. weight	275	275
Space group	$P2_1/c$	*Pbcn*
a (Å)	14.554(2)	10.283(1)
b (Å)	8.149(1)	11.808(1)
c (Å)	11.935(1)	25.581(2)
β (°)	106.41(1)	
V (Å)	1358(1)	2863(1)
d (calc.) g cm^{-3}	1.34	1.27
Z	4	8
μ, cm^{-1}	1.61	1.52
Range of 2θ, °	4–45	4–45
No. of unique data	1744	1847
No. of data with $F_o^2 > 3\sigma(F_o^2)$	1283	1206
R_1[a]	0.0829	0.0594
R_2[a]	0.1030	0.0639

[a] $R_1 = |\Sigma|F_o| - |F_c||/\Sigma|F_o|$. $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{\frac{1}{2}}$

Table 4. Positional parameters for (*E*)-**2**[a]

Atom	*x*	*y*	*z*
P	0.224 1(2)	0.019 2(3)	0.801 1(2)
O(1)	0.314 8(5)	−0.090 2(8)	0.858 7(5)
O(2)	0.197 0(5)	0.027 3(8)	0.673 0(5)
O(3)	0.263 5(5)	0.418 9(8)	0.990 2(5)
N	0.229 4(5)	0.267(1)	0.944 6(6)
C(1)	0.315(1)	−0.257(1)	0.816(1)
C(2)	0.130 2(7)	−0.058(1)	0.855 1(7)
C(3)	0.148 6(7)	−0.150(1)	0.957 1(9)
C(4)	0.072 7(9)	−0.213(1)	0.992(1)
C(5)	−0.019 3(9)	−0.187(1)	0.928(1)
C(6)	−0.038 9(8)	−0.101(1)	0.824(1)
C(7)	0.035 3(7)	−0.032(1)	0.788 0(8)
C(8)	0.268 1(6)	0.213(1)	0.865 2(7)
C(9)	0.346 4(6)	0.297(1)	0.829 6(8)
C(10)	0.329 4(7)	0.356(1)	0.717 1(9)
C(11)	0.400 5(8)	0.433(1)	0.682(1)
C(12)	0.489 9(9)	0.448(1)	0.757(1)
C(13)	0.509 2(8)	0.388(1)	0.871(1)
C(14)	0.438 0(7)	0.310(1)	0.907 2(8)

[a] Estimated standard deviations in the last significant figure are given in parentheses.

pyrophosphate can be linked to the *Z*-oxime. The formation of dimethyl hydrogen phosphate can be rationalized (as suggested before [1]) by assuming a cyclic mechanism which involves pre-equilibrium of (*Z*)-**8** with a zwitterionic intermediate, which is formed *via* an intramolecularly hydrogen bonded species. This should facilitate nucleophilic attack by the oxime oxygen on the phosphorus, leading to a four-membered cyclic intermediate, which then decomposes to products (see Scheme 3).

On the other hand, the formation of pyrophosphate can be reasonably assumed to occur *via* the attack of the highly nucleophilic oxime hydroxy group on the phosphorus of dimethyl phosphate, which can further cyclize to a six-membered ring intermediate. This, in turn, undergoes fragmentation to benzonitrile and tetramethyl pyrophosphate (Scheme 4).

X-Ray Crystallography.—Crystal structure of (E)-**2**. The molecular structure of (*E*)-**2** is depicted in Fig. 1 and crystallographic data are listed in Table 3. The *E* configuration is clearly visible in the ORTEP view. Bond lengths, bond angles, and other geometric features all fall within the ranges expected for similar compounds. We have considered the possibility that

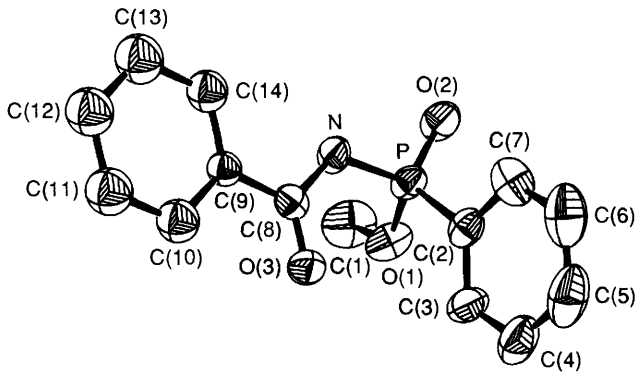


Fig. 2. An ORTEP view of **3** depicting the geometry and atom labelling scheme.

Table 5. Positional parameters for **3**[a]

Atom	*x*	*y*	*z*
P	0.119 2(2)	0.872 3(2)	0.051 59(7)
O(1)	0.079 8(5)	0.744 0(4)	0.050 4(2)
O(2)	0.136 9(5)	0.924 1(4)	−0.004 5(2)
O(3)	0.016 6(4)	0.843 4(4)	0.166 1(2)
N	0.001 0(5)	0.944 0(5)	0.084 7(2)
C(1)	−0.031(1)	0.709 3(8)	0.016 5(4)
C(2)	0.262 0(7)	0.872 1(6)	0.093 9(3)
C(3)	0.296 7(7)	0.784 1(6)	0.130 2(3)
C(4)	0.412 0(8)	0.789 6(8)	0.160 3(3)
C(5)	0.489 7(8)	0.883 2(9)	0.156 3(4)
C(6)	0.454 7(8)	0.971 1(9)	0.121 8(4)
C(7)	0.342 0(8)	0.966 1(6)	0.090 5(3)
C(8)	−0.031 8(6)	0.922 9(5)	0.141 0(3)
C(9)	−0.129 0(6)	0.998 8(5)	0.167 9(3)
C(10)	−0.162 0(7)	0.975 4(6)	0.224 2(3)
C(11)	−0.249 7(8)	1.044 6(6)	0.252 5(3)
C(12)	−0.301 8(7)	1.136 1(7)	0.226 5(3)
C(13)	−0.269 4(8)	1.161 6(7)	0.171 1(3)
C(14)	−0.181 9(7)	1.092 6(6)	0.141 8(3)

[a] Estimated standard deviations in the last significant figure are given in parentheses.

Table 6. Important bond lengths (Å) for (*E*)-**2** and -**3**[a]

(*E*)-**2**		**3**	
Bond		Bond	
P···O(1)	1.580(7)	P···O(1)	1.569(5)
P···O(2)	1.468(6)	P···O(2)	1.469(5)
P···C(2)	1.79(1)	P···N	1.673(6)
P···C(8)	1.796(9)	P···C(2)	1.776(7)
O(1)···C(1)	1.45(1)	O(1)···C(1)	1.45(1)
O(3)···N	1.39(1)	O(3)···C(8)	1.216(8)
N···C(8)	1.31(1)	N···C(8)	1.393(8)
C(8)···C(9)	1.49(1)	C(8)···C(9)	1.485(9)

[a] Estimated standard deviations in the last significant figure are given in parentheses.

the *E* and *Z* isomers might co-crystallise and give rise to two-fold disorder around the C(8)–N bond. The clean difference map in the expected position of the O(3) in the *Z* isomer in conjunction with reasonable thermal parameters reassured us that the crystals contained pure *E* isomer. This conclusion was further supported by ^{31}P and ^{1}H NMR spectroscopy.

Inspection of the packing in the unit cell revealed the existence of an intermolecular hydrogen bond between the phosphonyl oxygen atom O(2) and the oxyimino oxygen atom O(3) of an adjacent molecule (O–O distance 2.661 Å).

Table 7. Important bond angles (°) for (*E*)-**2** and -**3**[a]

(*E*)-**2**		**3**	
Angle		Angle	
O(1)–P–O(2)	115.1(4)	O(1)–O–O(2)	114.7(3)
O(1)–P–C(2)	105.9(4)	O(1)–P–N	108.1(3)
O(1)–P–C(8)	99.1(4)	O(1)–P–C(2)	102.8(3)
O(2)–P–C(2)	112.6(5)	O(2)–P–N	107.4(3)
O(2)–P–C(8)	111.3(4)	O(2)–P–C(2)	113.9(3)
C(2)–P–C(8)	112.1(4)	N–P–C(2)	109.8(3)
P–O(1)–C(1)	117.4(8)	P–O(1)–C(1)	119.1(5)
O(3)–N–C(8)	113.8(7)	P–N–C(8)	122.0(4)
P–C(8)–N	115.3(7)	O(3)–C(8)–N	120.1(6)
P–C(8)–C(9)	119.5(6)	O(3)–C(8)–C(9)	122.3(6)
N–C(8)–C(9)	125.1(8)	N–C(8)–C(9)	117.6(5)

[a] Estimated standard deviations in the last significant figure are given in parentheses.

Crystal structure of **3** The molecular structure of **3** is displayed in Fig. 2 and crystallographic data are listed in Table 3. The crystal structure demonstrates unequivocally that the product is indeed the one which is expected from a Beckmann rearrangement of (*E*)-**2**, and not the rearrangement product of (*Z*)-**2**. The bond lengths, bond angles, and other geometric data do not display any exceptional features (see Tables 3, 5 and 7).

The identity of the nitrogen atoms was confirmed by the reasonable thermal parameters in the refinement and the P–N and C–N bond lengths 1.673(5) A and 1.393(8) Å respectively, further support this. Despite the existence of phenyl rings in the molecules no intermolecular stacking interactions were observed, though an intermolecular hydrogen bond between the oxyimino nitrogen atom (N) and the O(2) of the oxygen atom of an adjacent molecule was observed.

The basic core structure of the phosphonamidate unit of **3** is very similar to that of **9** reported by Mizrahi and Modro.[9] The bond lengths and bond angles are very similar and in both structures the two opposing dipoles (P=O and C=O) are disposed *cis*/*trans* to each other. Also in both structures the phosphonyl and NH groups are *syn* coplanar, while the carbonyl and NH are *anti* coplanar (see Fig. 2).

Experimental

M.p.s were determined on a Thomas-Hoover capillary melting-point apparatus and are uncorrected. Elemental analyses were performed by the Microanalytical Laboratory of The Hebrew University of Jerusalem. IR spectra were determined on an Analect FTIR spectrometer. NMR spectra were obtained on a Bruker WH-300 or on a Varian VXR-300s instrument. ^{1}H and ^{31}P NMR spectra were recorded in deuteriochloroform, hexadeuteriobenzene, or in deuterium oxide solutions. Chemical shifts are reported in ppm downfield from TMS or TSP as internal standards for the ^{1}H spectra and from 85% orthophosphoric acid as external standard for the ^{31}P spectra. Positive chemical shifts are at lowfield with respect to the standard. Mass spectra were obtained on LKB 2091 gas chromatograph-mass spectrometer.

Methyl Benzoyl(phenyl)phosphinate (**1**).—This compound was synthesized in 80% yield by the Arbuzov reaction of dimethyl phenylphosphonite and benzoyl chloride in a slight modification of the method of Razumov and Gazizov: namely, the reaction temperature was kept < 30° C. After the completion of the reaction, the mixture was filtered and the product

was crystallized from dry ether; it had m.p. 75–76 °C (lit.,[5] m.p. 78.5 °C); $\delta_H(CDCl_3)$ 8.38–8.31 (2 H, m), 7.92–7.81 (2 H, m), 7.62–7.52 (2 H, m), 7.50–7.39 (4 H, m), and 3.90 (3 H, d, *J* 11.9 Hz).

(E)- *and* (Z)-*Methyl α-Hydroxyiminobenzyl(phenyl)phosphinate* (**2**).—Methyl benzoylphenylphosphinate (7.8 g, 0.03 mol) was added slowly to a solution of hydroxylamine hydrochloride (2.2 g, 0.033 mol) and pyridine (2.6 g, 0.033 mol) in absolute methanol (100 ml). After the mixture had been stirred for 48 h, it was diluted with water (20 ml) and the methanol evaporated under reduced pressure; dilute hydrochloric acid (1 M; 10 ml) was added to the mixture. The mixture was then extracted with chloroform (5 × 30 ml) and the combined extracts were washed with water (3 × 20 ml), dried ($MgSO_4$), filtered, and evaporated to give a solid product (90%) having an *E*:*Z* ratio of 9:1 (^1H and ^{31}P NMR).

(E)-*Methyl α-Hydroxyiminobenzyl(phenyl)phosphinate* (E)-**2**.—Pure (*E*)-**2**, isolated from the *E*/*Z* mixture by fractional crystallization from chloroform, had m.p. 160–163 °C; ν_{max}(KBr) 3132, 1590, 1193 and 1020; $\delta(CDCl_3)$ 10.45 (1 H, OH, br s), 7.82–7.59 (2 H, m), 7.54–7.50 (1 H, m), 7.47–7.42 (4 H, m), 7.39–7.37 (3 H, m) and 3.75 (3 H, d, *J* 11.25 Hz); $\delta_P(CD_3OD)$ 30.4 (q); *m*/*z* 275 (M^+), (36.27), 156 (55.6) and 155 {100; $[PhP(O)OCH_3]^+$} (Found: C, 60.85; H, 5.0; N, 5.95. Calc. for $C_{14}H_{14}NO_3P$: C, 61.09; H, 5.12; N, 5.08%).

(Z)-*Methyl α-Hydroxyiminobenzyl(phenyl)phosphinate* (Z)-**2**.—This compound was not isolated in pure state. Its spectral data are taken from the spectra of the *E*/*Z* mixture; $\delta(CDCl_3)$ 3.82 (d, *J* 11.4 Hz); $\delta_P(CD_3OD)$ 25.6 (q).

Thermal Beckmann Rearrangement of (E)-*Methyl α-Hydroxyiminobenzyl(phenyl)phosphinate*.—Compound (*E*)-**2** (0.275 g, mmol) was dissolved in solvent (20 ml) and refluxed while being monitored by TLC (silica gel/2% methanol in ether). The reaction carried out in toluene was completed in 30 h, while that in refluxing benzene containing 10 mol% toluene-*p*-sulphonic acid was over in 5.5 h. When the reaction was run in benzene without added acid, its completion required 50 h. After completion of the reactions the solvent was removed under reduced pressure and the residue crystallized from ether to give (in the case in toluene) a 90% yield of methyl *N*-benzoyl(phenyl)-phosphonamidate **3**, m.p. 146–148 °C; ν_{max}(KBr) 1666, 1599, 1224, 1131 and 1028; $\delta_H(CDCl_3)$ δ 9.32 (1 H, br s), 8.09–8.02 (4 H, m), 7.56–7.42 (6 H, m) and 3.92 (3 H, d, *J* 11.85 Hz), $\delta_P(CDCl_3)$ 18.0 ppm (q); *m*/*z* 275 (M^+), (21.7), 198 (41.22, [*M* − C_6H_5), 142 (100, $[PhPO_2H_2]$) (Found: C, 60.75; H, 5.05; N, 4.9. Calc. for $C_{14}H_{14}NO_3P$: C, 61.09; H, 5.12; N, 5.08%).

Thermal Rearrangement/Fragmentation of Mixtures of E- *and* Z-*Methyl α-Hydroxyiminobenzyl(phenyl)phosphinate*.—Mixtures of (*Z*)- and (*E*)-**2**, in various ratios, were dissolved in benzene (0.05 M) and refluxed. The amounts of products **3**, **4** and **5** were estimated from the ^1H NMR spectra of the reaction mixtures, while the amount of benzonitrile was determined by gc: column temp.: 110 °C, injection port and detector temp.: 200 °C. A solution containing (*E*)- + (*Z*)-**2** in the ratio of 7:1 when refluxed for 20 h gave **3** (88%), **4** (12%), and PhCN (11%). A solution of (*E*)- + (*Z*)-**2** in the ratio of 1:2 when refluxed for 2 h gave **3** (36%), **4** (56%), **5** (8%) and PhCN (not determined).

Methyl hydrogen phenylphosphonate **4**. For comparison, this compound was synthesized in our laboratory also by the fragmentation of methyl hydrogen α-hydroxyiminobenzyl-(phenyl)phosphinate in methanol;[10] δ_P 19.0 ppm (q).

Methyl N-*phenylcarbamoyl(phenyl)phosphinate* (**5**). This was isolated by preparative TLC (silica gel/2% methanol in ether); $\nu_{max}(CH_2Cl_2)$ 3359, 1667, 1120 and 1029 cm^{-1}; $\delta_H(CDCl_3)$ 9.13, (1 H, br s), 8.04–7.97 (2 H, dq), 7.66–7.60 (3 H, m), 7.55–7.49 (2 H, m), 7.34 (2 H, t), 7.19–7.14, (1 H, m) and 3.90 (3 H, d, *J* 11.7); δ_P 19.3 (q); *m*/*z* 275 (M^+, 12), 155 (100, $[PhPO_2Me]$) and 140 (40, $[PhPO_2]$).

Thermal Fragmentation and Rearrangement of Dimethyl α-Hydroxyiminobenzylphosphonate (E)- *and* (Z)-**8**.—A mixture of (*E*)- + (*Z*)-**8** (*E*/*Z* 35/65) (0.1 g) was dissolved in dry benzene (5 ml). The reaction mixture was heated to 80 °C and monitored by ^{31}P NMR and HPLC. The results are summarized in Table 2. The experiment was repeated using pure (*E*)-**8** (0.1 g) in dry benzene (5 ml) and the results are listed in the lower part of Table 2.

Thermal Rearrangement of Dimethyl α-Hydroxyiminobenzylphosphate (E)-**8**.—Compound (*E*)-**8** (1 g) was dissolved in benzene (10 ml) and the solution was refluxed for 72 h. Solvent and benzonitrile were removed by vacuum distillation and the residue was dissolved in dichloromethane and passed through a short silica gel column. Evaporation of the eluate gave the product **9** (650 mg) which upon recrystallization from ethyl acetate–hexane afforded white crystals, m.p. 115–116 °C (lit.,[8] m.p. 117–118 °C); ν_{max}(neat) 3195, 2952, 2852, 1681, 1247, 1067 and 1046 cm^{-1}; $\delta_H([^2H_6]benzene$ 10.68 (1 H, d, *J* 8.2 Hz), 8.65 (2 H, m), 7.28 (3 H, m), and 3.65 (6 H, d, *J* 11.5 Hz); $\delta_H(CDCl_3)$ 8.3 (1 H, d), 7.99 (2 H, m), 7.59 (1 H, m), 7.49 (2 H, m) and 3.91 (6 H, d, *J* 11.7 Hz); $\delta_P(C_6H_6)$ 2.88 ppm (octet, *J* 10 Hz).

Crystallizations.—X-Ray quality crystals of the (*E*)-**2** and -**3** were obtained by slow evaporation from methanol. The crystals of **3** were large and well formed, while the crystals of (*E*)-**2** were smaller and of poorer quality.

Data Collection and Processing.—The crystals were mounted on glass fibres using epoxy glue. Data sets were collected on a Philips PW 1100 four-circle computer-controlled diffractometer. Mo-K_α (0.710 69 Å) radiation with a graphite crystal monochromator in the incident beam was used. Unit cell parameters were obtained by a least-squares fit of 25 high angle reflections ($13° < \theta < 16°$). The data sets were collected in the θ–2θ scan mode. The scan width, *w*, for each reflection was 1° with a scan time of 20 s.

Background measurements were made at both limits of each scan. For each data set Lorenz and polarization corrections were applied. None of the data sets displayed any decay in the intensities of the standard reflections and no correction was applied. No absorption correction was applied. Other information pertinent to data collection and processing is given in Table 3.

Structure Analysis and Refinement.—The co-ordinates of the phosphorus atoms of (*E*)-**2** were obtained by the direct program SHELX-86, and those for **3** by MULTAN.[11] The positions of the remaining non-hydrogen atoms were obtained from subsequent refinements and difference Fourier maps. Anisotropic thermal parameters were used for all phosphorus, oxygen, nitrogen and carbon atoms of (*E*)-**2**. Owing to the low ratio of observed reflections to refined variables in **3**, the carbons of the second phenyl ring [C(9)–C(14)] were refined isotropically. The aromatic hydrogen atoms were placed in their calculated positions, were constrained to 'ride' on the carbon atoms and were refined using a common thermal parameter. For both structures **3** and (*E*)-**2** the methyl hydrogens were placed in their calculated positions and refined using a group thermal parameter.

Using SHELX-76,[12] full-matrix, least-squares refinements were carried out on 178 and 148 variables for structures (*E*)-**2** and

-3, respectively. The refinements, using unit weights, converged to reasonable discrepancy factors which are listed in Table 3.

Final non-hydrogen positional parameters, together with their estimated standard deviations, for (*E*)-**2**, appear in Table 4 and for **3** in Table 5. Important interatomic distances, together with their standard deviations, are given in Table 6. Important bond angles, with their standard deviations are given in Table 7. Listings of anisotropic thermal parameters, positional and thermal parameters of the hydrogen atoms, and the bond lengths, bond angles of the phenyl rings are available on request from Crystallographic Data Centre Cambridge.* Fig. 1 depicts a labelling scheme of (*E*)-**2**. Fig. 2 depicts the molecular geometry and labelling scheme of **3**.

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