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Tandem Wolff Rearrangement-"*tert*-Amino Effect" Sequence: Synthesis of 2-Oxoindolinium Enolate Derivatives

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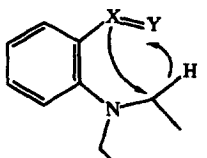
Abstract: The thermolysis of 1-diazo-2-oxo-(2-*N,N*-disubstituted aminophenyl)ethylphosphonates 1 gave rise to 2-oxoindolinium enolate derivatives 4 through Wolff rearrangement and interaction of the *tert*-amino moiety with the ketene functionality. Variable amounts of either ammonium ylides 5 or of products resulting from their transformations were also formed during the course of the reaction. If the amino moiety was substituted by a benzyl or an allyl group, indolinones, resulting from [1,3] or [1,2] benzylic or allylic shifts, were isolated in place of compounds 4 and 5.

INTRODUCTION

The formation of heterocycles by ring closure of *ortho*-substituted *N,N*-dialkylanilines (the "*tert*-amino effect") has been reviewed by Meth-Cohn and Suschitzky,[1a] Verboom and Reindhoudt[1b] and more recently by Meth-Cohn.[1c] According to Meth-Cohn, five types of *tert*-amino effect processes are distinguished by the size of the ring formed or by its mode of formation in the key step of the reaction. The most frequently encountered examples are type 1 and 2 reactions which are two-step processes involving first hydrogen abstraction from the α position of the *tert*-amino function followed by cyclization of a dipolar intermediate to a five or six-membered ring and type 4 reactions with initial attack of the nitrogen atom on the unsaturated *ortho* substituent X=Y.



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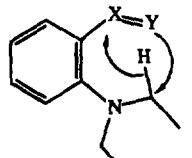

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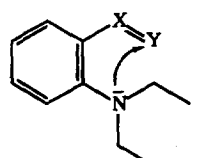

Type 4

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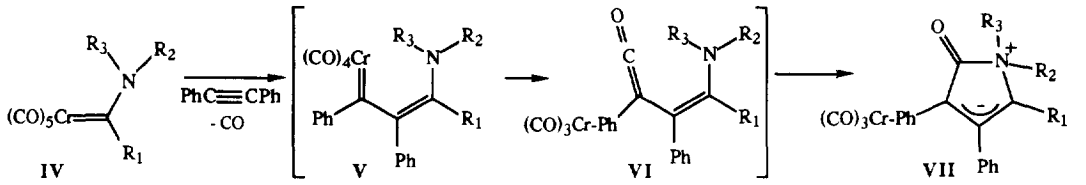
The "*tert*-amino effect" has been exemplified by various "*ortho* 2π substituents" such as C=C, C=O, C=N, NO_2, N=N, $N=SO_2$. However, to the best of our knowledge, there was no study about the reaction of the *tert*-amino moiety with a ketene functionality as the X=Y substituent.[2]

Examples of intermolecular interaction between ketenes and tertiary amines are known to proceed through zwitterionic species which then rearrange.[3-5] A related intramolecular transformation has been reported by the Rudler group.[6] The reaction of aminocarbene chromium complexes **IV** with alkynes gives rise to intermediate enamino ketenes **VI** which afford nitrogen ylide chromium complexes **VII** resulting from a through-space interaction of the tertiary amine with the carbonyl group of the ketene function; however no metal-free ylides deriving from **VII** could be obtained (Scheme 1).



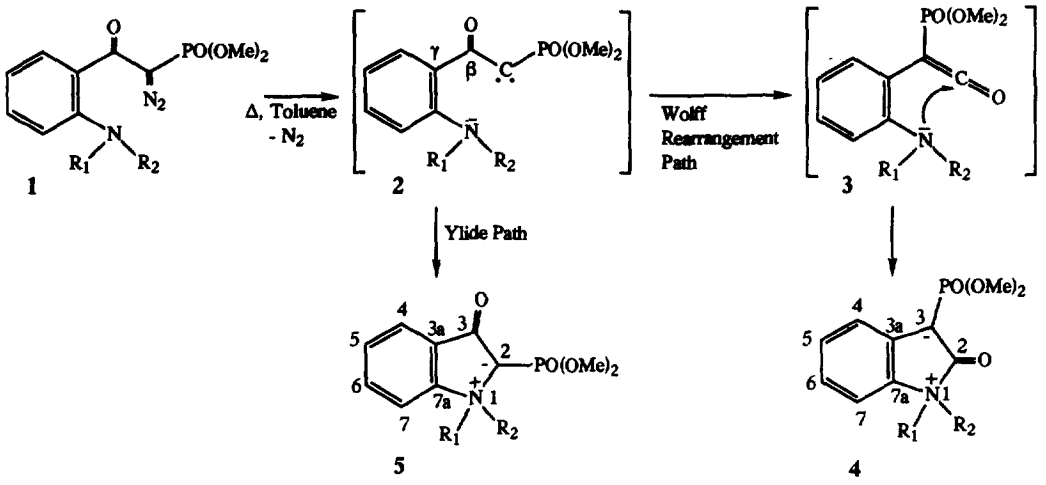
Scheme 1

Recent results from our laboratory have demonstrated that dimethylphosphono vinyl or aryl ketenes are easily generated by the thermal Wolff rearrangement of α-diazo-β-keto-γ,δ-alkenyl(or β-aryl)phosphonates.[7] Consequently the thermolysis of 1-diazo-2-oxo-(2-*N,N*-disubstituted aminophenyl)ethylphosphonates **1** should afford intermediate 2-ketenyl-*N,N*-disubstituted anilines **3** and thus allow the study of the interaction between the *tert*-amino and ketene moieties (Scheme 2). In a preliminary communication,[8] we have investigated the thermolysis of the β-aryl-α-diazo-β-ketophosphonates **1a,b** *ortho*-substituted by piperidine or pyrrolidine and shown that the attack of the nitrogen lone pair onto the ketene functionality led to the formation of mesoionic compounds **4a,b** (*tert*-amino effect process of type 4); during the course of the reaction, no product resulting from a hydrogen shift was observed but variable amounts of stable ammonium ylides **5** were formed (Table 1). The general pathway of the Wolff rearrangement involves initial loss of N_2 to form the keto carbene **2**, which can react either by migration of the aryl group to afford the ketene **3**, or by a variety of other processes.[9] Thus the formation of the ylide **5**, by interaction between the *tert*-amino group and the carbene moiety, appears as a competing process to the Wolff rearrangement. Most often ammonium ylides are intermediate species which can evolve, depending on their structures, either by Stevens [1,2] shift or [2,3] sigmatropic rearrangement.[10-13] Only a few examples of stable ammonium ylides are known, resulting from either intermolecular[14,15] or intramolecular[6,16] reactions. In particular the reaction of the 5-nitro-2-(piperidin-1-yl)benzoyl chloride with diazomethane was found to give a mixture of the expected diazoketone together with the 5-nitro-3-oxo-1-spiropiperidinoindolinium enolate,[16] resulting presumably from a similar amino-carbene interaction as for the analogous **5a**.

As compared to the thermolysis of 2-dialkylaminobenzoyldiazophosphonates **1**, a very similar chemistry has been observed in the thermolysis of 2-dialkylaminobenzoylazides **VIII** (Scheme 3). Martin, Meth-Cohn and Suschitzky[16] and very recently Waldron and co-workers[17] have reported that the decomposition of **VIII** produced a mixture of isocyanates **IX** resulting from the Curtius rearrangement and 1,1-dialkylindazol-1-ium-3-

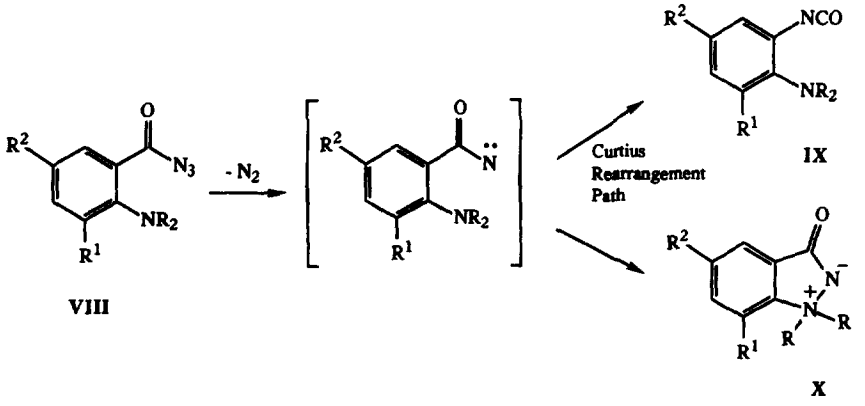
olates **X** through direct interaction of the *tert*-amino moiety with a nitrene intermediate (or by a concerted mechanism from the azide), the ratios of the two products depending upon the nature of the R, R^1 and R^2 substituents. However no further evolution of the isocyanates **IX** to mesoionic compounds was observed.

The present report describes full results concerning the influence of the *tert*-amino moiety on the decomposition pathways followed during the thermal decomposition of the α-diazo-β-ketophosphonates **1**.



a: R_1, R_2 = -$(CH_2)_5$-
b: R_1, R_2 = -$(CH_2)_4$-
c: R_1, R_2 = -CH_2-CH=CH-CH_2-
d: R_1, R_2 = -$(CH_2)_6$-
e: R_1, R_2 = -$(CH_2)_2$-O-$(CH_2)_2$-
f: R_1, R_2 = -CH_2-CH=CH-$(CH_2)_2$-
g: R_1= -C_2H_5, R_2 = -C_2H_5
h: R_1= -CH_3, R_2 = -CH_2-CH=CH_2
i: R_1= -CH_3, R_2 = -CH_2-C_6H_5

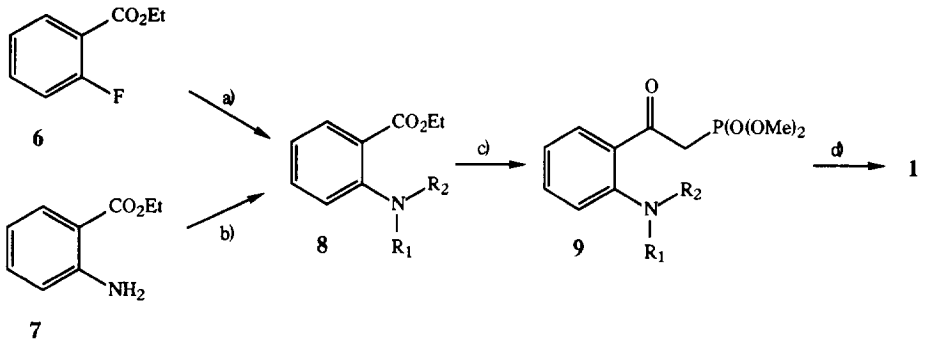
Scheme 2



Scheme 3

RESULTS AND DISCUSSION

The ethyl *N,N*-disubstituted anthranilates **8a-b,d-i** were prepared from ethyl 2-fluorobenzoate **6** by fluorine substitution with the requisite secondary amine in the presence of potassium carbonate,[18] whereas compound **8c** was obtained by reaction of ethyl anthranilate **7** with (*Z*)-2-butene-1,4-diol dimesylate[19] (Scheme 4). Subsequent condensation of esters **8** with dimethyl lithiomethylphosphonate followed by diazotransfer with tosyl azide yielded the α-diazo-β-ketophosphonates **1a-i**.



a) R_1R_2NH, K_2CO_3; b) (*Z*)-$MsOCH_2CH{=}CHCH_2OMs$, C_6H_6; c) $LiCH_2P(O)(OMe)_2$, THF; d) TsN_3, K_2CO_3, CH_3CN.

Scheme 4

As reported in our preliminary communication,[8] the thermolysis of **1a** in refluxing toluene gave rise to a 49:51-mixture of **4a** and **5a** whose structures were established by X-ray crystallography.[20] The structure of the oxoindolinium enolate **4a**[21] deserves comment. Examination of the four N(1)-C bonds showed normal lenghts of 1,508 Å for N(1)-C(8) and N(1)-C(12) (C_{sp^3}-N^+ = 1,510 Å)[22] and of 1,458 Å for N(1)-C(7a) (C_{ar}-N^+ = 1,465 Å) and a very long N(1)-C(2) bond of 1.645 Å. This remarkable value together with a rather short C(2)-C(3) bond of 1.382 Å and an O(1)-C(2)-C(3) bond angle of 140.0° suggested a significant contribution of the open valence tautomer **A** as a canonical form to the structure **4a** (Scheme 5). An other important contributor to the overall structure must be the cyclic valence tautomer **B** in relation with the C(2)-O(1) bond of 1,210 Å (typical C=O double bond: 1,20 Å) coupled with the very strong infrared carbonyl absorption at 1750 cm^{-1}. Previous to this work, the same structural analysis has been reported first by Thiessen and Hope for the molecular geometry and bonding in the sydnone ring (1,2,3-oxadiazol-5-ones)[23] and then by other groups for isoxazolium enolates[24] and imidazo[1,2-c]pyrimidin-3-ones.[25] It appeared that the characteristic bond lenghts and bond angles in **4a** compared well with the literature values for the related spiro mesoionic compounds **XI**[6a] and **XII**[24a] (Table 2) but, except for the C(2)-O(1) bond, are quite different from those reported for the mesoionic compound **XIII**.[25] Thus the N(1)-C(2) bond length in **XIII** (nearly that of a C-N single bond at 1.47 Å) is shorter than in **4a**, **XI** and **XII** and this is presumably due to the delocalisation of the positive charge to the nitrogen atoms N(1) and N(4) in **XIII** which may stabilize and thus favour the cyclic valence tautomers with respect to the open valence tautomer. Such a stabilization is impossible for **4a**, **XI** and **XII**, the positive charge being located on the tetrasubstituted nitrogen atom. This analysis is confirmed by a similar comparison between the C(2)-C(3) bond

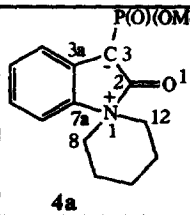
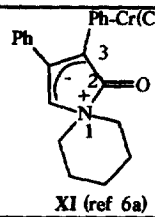
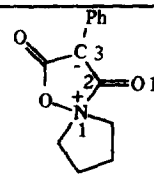
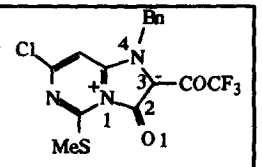
lengths and N(1)-C(2)-0(1) and O(1)-C(2)-C(3) bond angles in **4a**, **XI**, **XII** and **XIII**. As previously observed by the Rudler[6a] and Edstrom[25] groups, the weakness of the N(1)-C(2) bond is illustrated by the facile acid-catalysed ring opening of **4a** by water to give the acid **10** which decarboxylated immediately to yield methylenephosphonate **11** (Scheme 6).

The ^{13}C-NMR chemical shifts for the mesoionic compound **4a** with C-2 at δ 170.2 and C-3 at δ 62.3 are close to those reported by Rudler[6a] for **XI**, respectively at δ 169.1 and δ 67.3, but very different from those for the ammonium ylide **5a**, with C-2 at δ 105.8 ($^1J_{CP}$ = 226.8 Hz) and C-3 at δ 172.1 ($^2J_{CP}$ = 16.8 Hz). Compounds **4a** and **5a** are also easily differentiated by their infrared carbonyl absorption, respectively at 1750 cm^{-1} and 1620 cm^{-1}. These characteristic spectral parameters were used in the sequel to support the structures of the other mesoionic compounds **4** (Table 3) and ylides **5**.

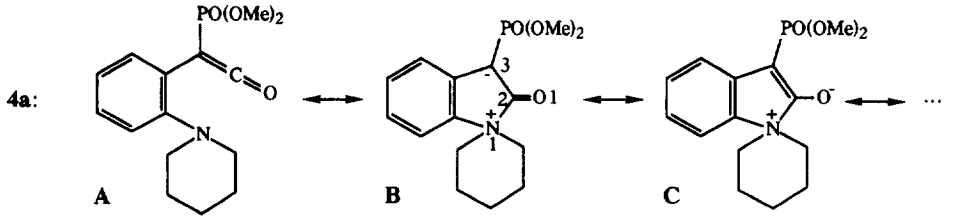
Table (1): Thermal Decomposition of the Diazophosphonates **1a-i** and **18**

Starting Compounds	Ratios of Products	Total yield (%)
1a	**4a:5a** = 49:51	87
1b	**4b:5b** = 98:2	88
1c	**4c:5c** = 100:0	66
1d	**4d:5d** = 94:6	72
1e	**4e:(5e+12)** = 58:42	91
1f	**4f:(13+14)** = 51:49	77
18	**19:20** = 87:13	60
1g	**4g:21** = 90:10	74
1h	**22h:23h** = 53:47	82
1i	**22i:23i** = 73:27	96

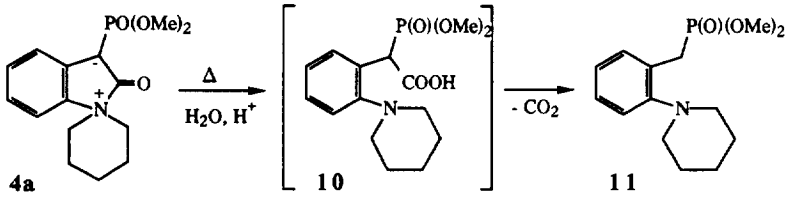
Table (2): Characteristic Bond Lenghts [Å] and Angle Values [°] in some Mesoionic Compounds*

Bonds or angles	 **4a**	 **XI** (ref 6a)	 **XII** (ref 24a)	 **XIII** (ref 25)
N(1)-C(2)	1.645	1.590	1.545	1.457
C(2)-C(3)	1.382	1.368	1.387	1.408
C(2)-O(1)	1.210	1.225	1.218	1.219
N(1)-C(2)-O(1)	114.8	115.7	116.0	121.4
O(1)-C(2)-C(3)	140.0	138.6	137.7	135.3
N(1)-C(2)-C(3)	105.1	105.7	106.4	-

* The atoms are numbered for an easy comparison between the different compounds.



Scheme 5



Scheme 6

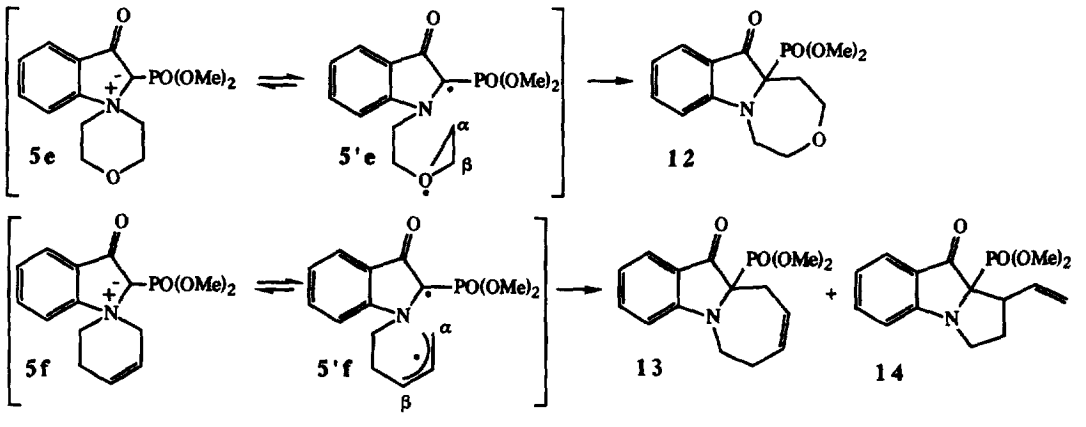
The replacement of the piperidino substituent by a pyrrolidino substituent resulted in the formation of the mesoionic compound **4b** together with a minute amount of the ylide **5b**. Similar results were observed when an insaturation was introduced in the five membered ring (pyrrolino: **c**) or in the case of a saturated seven membered ring (perhydroazepino: **d**) (Table 1).

The decomposition of the diazo **1e**, bearing a morpholino substituent, yielded a 58:13:29-mixture of **4e**, **5e** and oxazepinoindolinone **12** (Scheme 7). Refluxing the ylide **5e** in toluene for 24 h afforded quite quantitatively the indolinone **12** which should therefore be the result of a Stevens [1,2] shift. It has been shown that the Stevens rearrangement normally involves a radical pair mechanism.[26,27] Thus the facile formation of the oxazepinoindolinone **12** from **5e** can be rationalized by the intermediate formation of the stabilized biradical **5'e** in which the cyclization either to the α- or β-position gives rise to the same product. The decomposition of the diazo **1f**, bearing a tetrahydropyridino substituent, afforded a 51:49-mixture of mesoionic compound **4f** and tricyclic compounds (**13+14**) resulting from rearrangement of the ylide **5f** which, in this case, was not isolated. In a similar manner as for **12**, the formation of **13** and **14** can be explained by the intermediate formation of the stabilized biradical **5'f**, in which radical recombination either to the α- or β-position leads respectively to **13** or **14**. Pure samples of tricyclic compounds **12** and **13** were isolated and their structures were characterized by their ^{13}C-NMR spectra showing resonances for a ketonic carbonyl respectively at δ 197.6 or 197.9 and for a carbon atom bonded to the phosphorus atom respectively at δ 72.8 or 75.3 ($^{1}J_{CP}$ = 154.4 or 152.7 Hz); furthermore the resonances of the two methoxy groups were splitted in two doublets, due to the 2-bonds C-P coupling and to the presence of an asymetric carbon in these structures. We were not able to isolate a pure sample of **14**; its structure was inferred from the presence of characteristic vinylic protons resonances at δ 6.15 (m, 1H) and δ 5.55 (m, 2H) in the ^{1}H-NMR spectrum of a mixture constituted by **13** and **14**.

Table (3): ν_{CO} (cm^{-1}) and ^{13}C-NMR Data* of Mesoionic Compounds **4** and **19** [δ (ppm) and J (Hz)]

Compound (ν_{CO})	C-2	C-3	C-3a	C-5, C-6, C-4**, C-7	C-7a	R_1, R_2	$PO(OMe)_2$
4a 1750	170.2 $^2J_{CP}$ = 24.8	62.3 $^1J_{CP}$ = 219.3	139.3 $^2J_{CP}$ = 15.0	130.1, 120.0, 119.9, 118.7	137.7 $^3J_{CP}$ = 13.0	55.8, 21.0, 20.3	52.3 $^2J_{CP}$ = 5.3
4b 1735	170.5 $^2J_{CP}$ = 25.0	61.2 $^1J_{CP}$ = 220.2	139.5 $^2J_{CP}$ = 15.0	130.1, 120.8, 119.4, 116.0	140.4 $^3J_{CP}$ = 13.2	61.6, 25.1	52.2 $^2J_{CP}$ = 5.4
4c 1750	169.6 $^2J_{CP}$ = 25.6	63.4 $^1J_{CP}$ = 219.9	138.9 $^2J_{CP}$ = 14.9	130.3, 120.9, 119.1, 114.8	141.6 $^3J_{CP}$ = 13.3	125.0, 67.9	52.0 $^2J_{CP}$ = 5.3
4d 1750	173.0 $^2J_{CP}$ = 24.7	61.4 $^1J_{CP}$ = 219.7	138.0 $^2J_{CP}$ = 15.0	130.1, 120.6, 119.6, 117.0	139.8 $^3J_{CP}$ = 13.4	61.5, 29.7, 23.5	52.2 $^2J_{CP}$ = 5.3
4e 1760	170.7 $^2J_{CP}$ = 25.6	61.2 $^1J_{CP}$ = 219.4	139.1 $^2J_{CP}$ = 14.8	130.6, 120.6, 120.2, 117.9	137.4 $^3J_{CP}$ = 12.9	61.1, 54.7	52.4 $^2J_{CP}$ = 5.4
4f 1750	169.8 $^2J_{CP}$ = 25.2	62.4 $^1J_{CP}$ = 219.5	139.1 $^2J_{CP}$ = 14.8	130.4, 120.6, 119.7, 117.9	137.1 $^3J_{CP}$ = 13.0	124.8, 122.1, 52.6, 52.4, 21.2	52.29 (d) and 52.25 (d) $^2J_{CP}$ = 5.3
4g 1735	165.5 $^2J_{CP}$ = 24.8	68.3 $^1J_{CP}$ = 217.3	142.1 J_{CP} = 15.1	130.5, 120.9, 119.3, 116.7	131.1 $^3J_{CP}$ = 13.3	55.2, 8.1	52.0 $^2J_{CP}$ = 5.1
19 1740	167.8 $^2J_{CP}$ = 22.7	62.2 $^1J_{CP}$ = 219.3	133.7 J_{CP} = 14.5	126.8, 138.6, 125.6	151.4 $^3J_{CP}$ = 14.1	55.1, 21.6, 19.9	52.3 $^2J_{CP}$ = 5.4

*The ^{13}C-NMR chemical shifts and coupling constants of compound **4a** were attributed on the basis of *H,H*-COSY, *H,C*-COSY and *H,C*-Heteronuclear Multi Bond Correlation. Chemical shifts and coupling constants of other compounds **4** were deduced on the basis of their spectral similarities with **4a**. ** No 3-bonds coupling was observed between P and C(4).

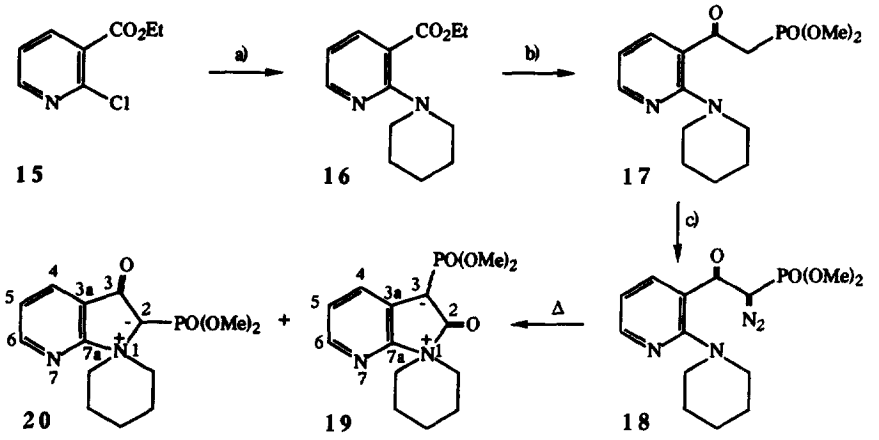


Scheme 7

It appeared that the ring size of the amino functionality strongly influenced the decomposition towards the Wolff rearrangement path or the ylide path, but that the presence of an insaturation or of an heteroatom in the ring had a minor influence. Thus five or seven membered rings (**b,c,d**) gave rise to mixtures containing mainly compounds **4** resulting from the Wolff rearrangement whereas six membered rings (**a,e,f**) afforded mixtures containing nearly equal amounts of **4** and products resulting from the ylide path (Table 1). The Wolff rearrangement as well as the ylide formation[28] are irreversible processes and therefore both compounds **4** and **5** must be considered as kinetic products. Hence the orientation of the thermolysis must be related to the competition between the Wolff rearrangement and the attack of the nitrogen atom lone pair onto the carbene moiety. A similar analysis has been reported by Waldron and Raza[17b] to explain the results in the thermal decomposition of 2-dialkylaminobenzoylazides **VIII**[16,17] (Scheme 3). The orientation of the reaction resulted from a competition between the Curtius rearrangement leading to the isocyanate **IX** and the cyclisation to the indazolium olate **X**, arising probably from the trapping of the intermediate nitrene by the lone pair of electrons on the nearby amino group. The availabilty and the orientation of the lone pair on the nitrogen were determined to be the key factors and the (**IX/X**) ratios were interpreted by electronic and steric effects of the R, R^1 and R^2 substituents. Thus in the decomposition of compounds **VIIIa** ($R^1 = R^2 = H$, R = Me) and **VIIIb** ($R^1 = R^2 = H$, R = Et), the (**IXa/Xa**) and (**IXb/Xb**) ratios were found to be respectively 56/31 and 9/79; the prevailing orientation directed towards the zwitterionic product **X** in the case of the ethyl groups was explained by a greater electron availability on the nitrogen atom and a greater steric hindrance. Unfortunately in our case, we found no evident steric, electronic or stability factors in relation with the ring size of the amino functionality to rationalize the observed products ratios.

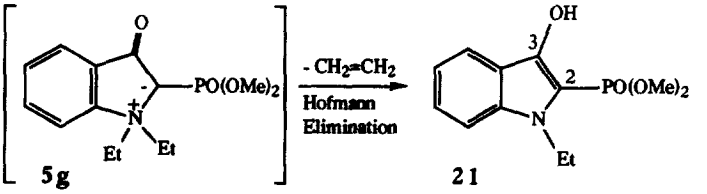
Although the present work was centered on the nature of the amino moiety, we investigated the effect of the replacement of the benzene ring by a pyridine ring. Starting from ethyl 2-chloronicotinate **15**, we prepared the diazophosphonate **18** in a similar manner as described above (Scheme 8); its thermolysis afforded a 87:13-mixture of mesoionic compound **19** and ammonium ylide **20**, showing that the orientation of the reaction was dependent on the aromatic moiety. As compared with the decomposition of **1a**, this result could be related, for electronic and steric reasons, to an unfavorable orientation of the nitrogen atom lone pair lowering its interaction with the carbene moiety and thus favoring the Wolff rearrangement product **19**. A possible influence of the pyridine ring on the rate of Wolff rearrangement could be also considered. In conclusion, we think that the decomposition paths of the diazophosphonates **1a-f** or **18** are governed by fine parameters which are difficult to evidence in view of our present results.

We next turned our attention to the thermolysis of diazophosphonates **1** bearing an acyclic *tert*-amino moiety. The diazophosphonate **1g** possessing two ethyl groups as the amino substituents yielded the mesoionic compound **4g** as the major product together with a small amount of the hydroxyindole **21** formed by Hofmann elimination from the non-isolated ylide **5g** (Scheme 9). The structure of the hydroxyindole **21** was supported by the presence of an OH stretching band at 3260 cm^{-1} and by the resonances at δ 100.1 ($^1J_{CP}$ = 218.6 Hz) for C-2 and δ 151.6 ($^2J_{CP}$ = 15.8 Hz) for C-3.



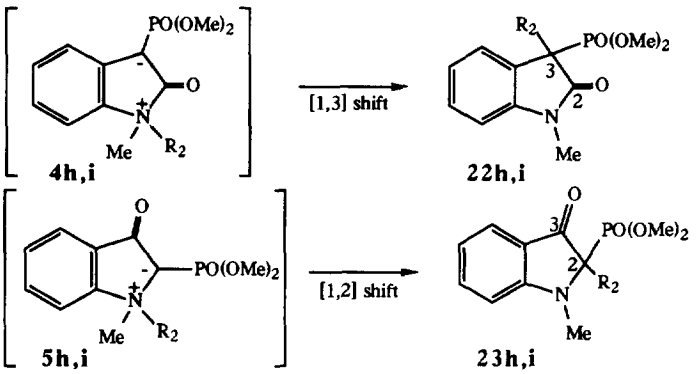
a) Piperidine, K_2CO_3; b) $LiCH_2P(O)(OMe)_2$, THF; c) TsN_3, K_2CO_3, CH_3CN.

Scheme 8



Scheme 9

Neither mesoionic compound **4** nor ammonium ylide **5** were isolated in the case of diazophosphonates **1** bearing an alkyl group of strong migratory aptitude on the nitrogen atom. Thus the thermolysis of compounds **1** possessing an allyl group (**h**) or a benzyl group (**i**) as the R_2 amino substituent gave rise to mixtures of indolinones **22** and **23** (Scheme 10). The 2-indolinones **22** were formed through the corresponding mesoionic compounds **4** by a [1,3] shift of the allyl or benzyl group. It should be noticed that no [1,3] shift had occured in the case of cyclic *tert*-amino moieties (**a-f**), even when an allyl system was present in the ring (**e,f**); these results are different from the [1,3] nitrogen-to-carbon migrations of various alkyl groups observed by Rudler[6a,b] when ylide complexes **VII**, **XI** or related compounds were refluxed in toluene.[29] The formation of 3-indolinones **23** resulted from a Stevens rearrangement of the ylides **5h,i** which showed a similar behaviour as the ylides **5e,f**. The lactam structures of **22h,i** were in agreement with resonances at δ 173.0-172.8 ($^2J_{CP}$ = 2.8-2.7 Hz) for C-2 and at δ 54.7-56.3 ($^1J_{CP}$ = 137.4-137.5 Hz) for C-3 whereas the ketonic structures of **23h,i** were supported by resonances at δ 73.1-74.5 ($^1J_{CP}$ = 148.4-142.6 Hz) for C-2 and at δ 196.2-196.1 ($^2J_{CP}$ = 2.4-3.0 Hz) for C-3. The resonances of the two methoxy groups in **22** or **23** were splitted in two doublets, due to the 2-bonds C-P coupling and to the presence of an asymetric carbon, respectively C-3 or C-2.



Scheme 10

We have also synthesized the diazophosphonate of type **1** bearing a methyl group and a phenyl group as the amino substituents. Its decomposition gave a complex mixture of unidentified products and therefore these experiments are not included in the experimental section. As compared with dialkyl substituents, this negative result can be explained by the lowering of the nitrogen nucleophilicity, resulting from the introduction of the phenyl substituent, which prevents the interaction of nitrogen with the intermediate carbene or ketene moities to take place.

CONCLUSION

The nature of the products obtained by thermal decomposition of 1-diazo-2-oxo-(2-*N*,*N*-disubstituted aminophenyl)ethylphosphonates **1** depends strongly on the structure of the *tert*-amino substituent. The reaction allows the synthesis of 2-oxoindolinium enolate derivatives **4** if the amino moiety is part of a ring or bears substituents of low migratory aptitude. Ammonium ylides **5** or products resulting from their transformations are also formed during the course of the decompositions, especially when the amino moiety is part of a 6-membered ring. If the amino moiety is acyclic and bears a substituent of strong migratory aptitude, indolinones **22** or **23**, resulting from [1,3] or [1,2] benzylic or allylic shifts, were directly obtained in place of compounds **4** and **5**.

EXPERIMENTAL

General.

Diethyl ether was distilled from potassium hydroxide, pentane from phosphorus pentoxide, tetrahydrofuran from sodium benzophenone ketyl. Benzene and toluene were dried over sodium. Organic solutions were dried over anhydrous sodium sulfate. Column chromatographies were performed using Merck Silica gel 60 (70-230 mesh) and TLC were carried out using Merck Kieselgel 60 F254 plates. Melting points were determined on a Kofler block apparatus. IR spectra were recorded on a Perkin Elmer 1310 infrared spectrophotometer. Nuclear magnetic resonance spectra were recorded in $CDCl_3$ on a Brucker AC200 (200/50 MHz) spectrometer. All NMR recordings were referenced to $CHCl_3$ resonances (7.26 and 77.0 ppm). Splitting patterns abbreviations are: s, singulet; d, doublet; t, triplet; m, multiplet; b, broad; p, pseudo. Multiplicity (^{13}C NMR) was determined by DEPT sequencies. Elemental analyses were performed by Service Central d'Analyse, Centre National de la Recherche Scientifique, 69300 Vernaison, France.

SYNTHESIS OF AMINOESTERS (8a-i) and (16)

The ethyl 2-fluorobenzoate **6** was obtained by reaction of 2-fluorobenzoyl chloride with absolute ethanol in refluxing ethanol (yield: 91 %). The ethyl 2-chloronicotinate **15** was obtained by reaction of 2-chloronicotinic acid with thionyl chloride in refluxing benzene followed by treatment of the intermediate 2-chloronicotinoyl chloride with absolute ethanol at room temperature (yield: 95 %).

General Procedure for the Preparation of Aminoesters 8a,b,d,e,f,h,i and 16: a mixture of 2-fluorobenzoate **6** (3 g, 17.8 mmol) or ethyl 2-chloronicotinate **15** (3.3 g, 17.8 mmol), potassium carbonate (2.9 g, 21.4 mmol) and of the requisite secondary amine (21.4 mmol) in 10 ml of DMF (**a,b,d,e,f,i**) or toluene (**h**) was refluxed for 24 h. After cooling, the resulting mixture was poured into water (120 ml) and extracted with ethyl acetate (3 x 30 ml). The organic layers were dried, filtered and concentrated to afford a residue which was purified by chromatography eluting with pentane-ethyl acetate 10:90 to afford **8a,b,d,e,f, h,i and 16**.

Ethyl 2-piperidinobenzoate (8a)

Yield 3.45 g (83 %). Oil. IR ($CHCl_3$): 1720, 1595. ^{1}H-NMR: δ 7.58 (dd, 1H, J = 7.7, 1.8); 7.35 (ddd, 1H, J = 8.3, J = 7.3, J = 1.8); 7.00 (dd, 1H, J = 8.3, J = 1.1); 6.92 (td, 1H, J = 7.5, J = 1.1); 4.31 (q, 2H, J = 7.1); 2.97 (t, 4H, J = 5.2); 1.74-1.43 (m, 6H); 1.36 (t, 3H, J = 7.1). ^{13}C-NMR: δ 168.5; 153.1; 132.2; 131.1; 124.7; 120.7; 118.8; 60.8; 53.8; 26.2; 24.3; 14.3. Anal Calcd for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21; N, 6.00. Found: C, 71.85; H, 8.36; N, 5.96.

Ethyl 2-pyrrolidinobenzoate (8b)

Yield 2.77 g (71 %). Oil. IR ($CHCl_3$): 1725, 1595. ^{1}H-NMR : δ 7.57 (dd, 1H, J = 7.8); 7.30 (ddd, 1H, J = 8.2, J = 7.2, J = 1.7); 6.77 (d, 1H, J = 8.2); 6.70 (pdd, 1H, J = 7.7, J = 7.2); 4.35 (q, 2H, J = 7.1); 3.27-3.20 (m, 4H); 1.97-1.90 (m, 4H); 1.37 (t, 3H, J = 7.1). ^{13}C-NMR: δ 169.1; 147.9; 131.7; 131.0; 117.5; 115.6; 114.0; 60.7; 50.8; 25.9; 14.4. Anal Calcd for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81; N, 6.39. Found: C, 71.19; H, 7.54; N, 6.25.

Ethyl 2-perhydroazepinobenzoate (8d)

Yield 3.21 g (73 %). Oil. IR (neat): 1705, 1595. ^{1}H-NMR: δ 7.52 (dd, 1H, J = 7.7, J = 1.8); 7.28 (ddd, 1H, J = 7.7, J = 8.1, J = 1.8); 6.95 (d, 1H, J = 8,1); 6.73 (pt, 1H, J = 7.7); 4.33 (q, 2H, J = 7.1); 3.33 (m, 4H); 1.76 (m, 4H); 1.59 (m, 4H); 1.45 (t, 3H, J = 7.1). ^{13}C-NMR: δ 169.4; 151.2; 131.5; 130.9; 120.4; 117.1 (2C); 60.7; 52.9; 28.5; 28.1; 14.3. Anal Calcd for $C_{15}H_{21}NO_2$: C, 72.84; H, 8.56; N, 5.66. Found: C, 72.89; H, 8.47; N, 5.61.

Ethyl 2-morpholinobenzoate (8e)

Yield 1.60 g (41 %). Oil. IR ($CHCl_3$): 1720, 1595. ^{1}H-NMR: δ 7.75 (dd, 1H, J = 7.9, J = 1.9); 7.42 (m, 1H); 7.04 (d, 1H, J = 7.8); 7.02 (m, 1H); 4.35 (q, 2H, J = 7.1); 3.91-3.80 (m, 4H); 3.10-3.00 (m, 4H); 1.39 (t, 3H, J = 7.1). ^{13}C-NMR : δ 167.6; 151.9; 132.3; 131.2; 124.8; 121.6; 118.7; 66.9; 60.7; 52.6; 14.1. Anal Calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.16; H, 7.68; N, 5.92.

Ethyl 2-(2-(1,2,3,6-tetrahydropyridino)benzoate (8f)

Yield 3.00 g (73 %). Oil. IR ($CHCl_3$): 1715, 1595. ^{1}H-NMR; δ 7.68 (dd, 1H, J = 7.7, J = 1.6); 7.37 (t, 1H, J = 7.7); 7.02 (d, 1H, J = 8.3); 6.96 (ddd, 1H, J = 8.3, J = 7.7, J = 1.6); 5.87 (dm, 1H, J = 10.0); 5.76 (dm, 1H, J = 10.0); 4.35 (q, 2H, J = 7.1); 3.61 (m, 2H); 3.21 (t, 2H, J = 5.5); 2.30 (tm, 2H, J = 5.5); 1.37 (t, 3H, J = 7.1). ^{13}C-NMR: δ 168.4; 151.9; 132.3; 131.4; 125.8; 125.3; 123.6; 120.3; 118.1; 60.8; 50.5; 50.4; 26.1; 14.3. No correct microanalysis could be obtained for this compound.

Ethyl 2-(N-allyl,N-methylamino)benzoate (8h)

Yield 3.04 g (78 %). Oil. IR (neat): 1710, 1595. ^{1}H-NMR: δ 7.64 (dd, 1H, J = 7.7, J = 1.7); 7.34 (ddd, J = 8.3, J = 7.4, J = 1.7); 6.98 (d, 1H, J = 8.3); 6.87 (td, 1H, J = 7.4, J = 0.9); 5.93 (ddt, 1H , J = 17.1, J = 10.2, J = 5.9); 5.30-5.10 (m, 2H); 4.37 (q, 2H, J = 7.1); 3.71 (d, 2H, J = 5.9); 2.80 (s, 3H); 1.39 (t, 3H, J = 7.1). ^{13}C-NMR : δ 168.5; 151.6; 134.8; 131.9; 131.2; 122.5; 119.3; 118.2; 117.3; 60.8; 59.4; 39.9; 14.3. Anal Calcd for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81; N, 6.39. Found: C, 71.38; H, 7.80; N, 6.53.

Ethyl 2-(N-benzyl,N-methylamino)benzoate (8i)

Yield 2.97 g (62 %). Oil. IR ($CHCl_3$): 1725, 1595. ^{1}H-NMR: δ 7.65 (dd, 1H, J = 7.7, J = 1.7); 7.36-7.21 (m, 6H); 6.97 (dd, 1H, J = 8.4, J = 1.0); 6.88 (td, 1H, J = 7.4, J = 1.0); 4.32 (q, 2H, J = 7.1); 4.31 (s, 2H); 2.74 (s, 3H); 1.34 (t, 3H, J = 7.1). ^{13}C-NMR: δ 168.7; 151.7; 138.2; 131.9; 131.2; 128.3; 127.9; 127.0; 123.1; 119.6; 118.7; 60.9; 59.8; 40.9; 14.3. Anal Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.61; H, 7.21; N, 5.15.

Ethyl 2-piperidinonicotinate (16)

Yield 3.25 g (78 %). Oil. IR ($CHCl_3$): 1705, 1580. ^{1}H-NMR: δ 8.25 (dd, 1H, J = 4.7, J = 2.0); 7.92 (dd, 1H, J = 7.6, J = 2.0); 6.67 (dd, 1H, J = 7.6, J = 4.7); 4.35 (q, 2H, J = 7.1); 3.36 (br s, 4H); 1.65 (br s, 6H); 1.38 (t, 3H, J = 7.1). ^{13}C-NMR: δ 167.7; 159.6; 150.3; 140.4; 113.9; 113.2; 60.9; 50.4; 25.9; 24.6; 14.3. Anal Calcd for $C_{13}H_{18}N_2O_2$: C, 66.64; H, 7.74; N, 11.96. Found: C, 66.77; H, 7.72; N, 11.72.

Procedure for the Preparation of Aminoester 8c: the ethyl anthranilate **7** (2.7 g, 16.3 mmol) was added slowly to a mixture of (Z)-2-butene-1,4-diol dimesylate (8 g, 32.7 mmol) and ethyldiisopropylamine (4.2 g, 32.7 mmol) in benzene (160 ml). After refluxing for 24 h, the benzene was evaporated in vacuum. To the residue was added water (50 ml) and then a saturated aqueous ammoniac solution up to pH 10. After extraction with ethyl acetate (3 x 50 ml), the organic layers were dried, filtered and concentrated to afford a residue which was purified by chromatography eluting with pentane-ethyl ether 90:10.

Ethyl 2-pyrrolinobenzoate (8c)

Yield 2.97 g (84 %). Mp 41-43°C. IR ($CHCl_3$): 1700, 1600. ^{1}H-NMR : δ 7.51 (dd, 1H, J = 7.5, J = 1.7); 7.31 (dt, 1H, J = 7.5, J = 1.8); 6.73 (m, 2H); 5.88 (s, 2H); 4.36 (q, 2H, J = 7.1); 4.12 (s, 4H); 1.39 (t, 3H, J = 7.1). ^{13}C-NMR: δ 169.6; 146.4; 131.6; 130.8; 125.7; 117.4; 115.6; 114.2; 60.9; 56.8; 14.3. Anal Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.76; H, 6.97; N, 6.54.

Procedure for the Preparation of Aminoester 8g: a mixture of 2-fluorobenzoate **6** (17.8 mmol), potassium carbonate (2.9 g, 21.4 mmol) and diethylamine (1.56 g, 21.4 mmol) was introduced into a high-pressure autoclave and heated at 145 °C for 24 h. After cooling the residue was poured into water (120 ml) and extracted with ethyl acetate (3 x 30 ml). The organic layers were dried, filtered and concentrated to afford a residue which was purified by chromatography eluting with pentane-ethyl acetate 10:90 to afford **8g**.

Ethyl 2-(N,N-diethylamino)benzoate (8g)

Yield 2.28 g (58 %). Oil. IR ($CHCl_3$): 1700, 1590. ^{1}H-NMR: δ 7.55 (dd, 1H, J = 7.7, J = 1.7); 7.34 (ddd, 1H, J = 8.3, J = 7.3, J = 1.7); 7.05 (dd, 1H, J = 8.3, J = 0.9; 6.93 (ptd, 1H, J = 7.6, 0.9); 4.34 (q, 2H, J = 7.1); 3.15 (q, 4H, J = 7.1); 1.37 (t, 2H, J = 7.1); 1.05 (t, 4H, J = 7.1). ^{13}C-NMR : δ 168.9; 150.3; 131.3; 130.4; 127.0; 121.2; 120.7; 60.7; 47.0; 14.3; 12.4. Anal Calcd for $C_{13}H_{19}NO_2$: C, 70.56; H, 8.65; N, 6.33. Found: C, 70.10; H, 8.53; N, 6.18.

SYNTHESIS OF β-KETOPHOSPHONATES (9a-i) and (17)

General Procedure: to a stirred solution of dimethyl methylphosphonate (3.5 g, 28.2 mmol) in anhydrous THF (70 ml) cooled at -80°C, was added dropwise, under nitrogen, 17.6 ml (28.2 mmol) of *n*-butyllithium 1.6 M in hexanes. The mixture was kept for 45 mn at -60 °C and then a solution of amino ester **8a-i** or **16** (14.1 mmol) in anhydrous THF (30 ml) was added slowly. The reaction mixture was allowed to react at room temperature for 3.5 h, and was then quenched with a saturated ammonium chloride solution (200 ml). The aqueous phase was extracted with ethyl acetate (5 x 60 ml), the organic layers were washed with brine, dried, filtered and concentrated to afford a residue which was purified by chromatography eluting with ethyl acetate. The samples obtained after this purification contained variable amounts of residual dimethyl methylphosphonate and were characterized by their IR spectra [ν_{CO}: 1680-1650 cm^{-1}] and by their ^{1}H-NMR spectra [CH_2P δ 4.04-3.68 ($^2J_{HP}$ = 22.7-21.6) and $PO(OMe)_2$: δ 3.79-3.52 ($^3J_{HP}$ = 11.2)].

SYNTHESIS of α-DIAZO-β-KETOPHOSPHONATES (1a-i) and (18)

General Procedure: to a mixture of β-ketophosphonate **9a-i** or **17** (10 mmol), obtained as described above, and potassium carbonate (1.72 g, 12.5 mmol) in acetonitrile (40 ml) cooled in a water-ice bath, under nitrogen, was added dropwise with stirring a solution of tosyl azide[30,31] (2.46 g, 12.5 mmol) in acetonitrile (30 ml). The cooling bath was removed and the mixture was stirred at room temperature. The disappearance of compound **9** or **17** was monitored by tlc. After 1-2.5 h, potassium carbonate was filtered off and acetonitrile was evaporated *in vacuo* to afford a residue which was purified by chromatography eluting with ethyl acetate (**1a,b,g,i**) or ethyl acetate:pentane 70:30 (**1c-f,h** and **18**).

Dimethyl 1-diazo-2-oxo-2-(2-piperidinophenyl)ethylphosphonate (1a)

Yield 2.73 g (81 %). Mp 93-94°C. IR ($CHCl_3$): 2125, 1625, 1265, 1055, 1030. ^{1}H-NMR: δ 7.32 (td, 1H, J = 7.8, J = 1.7); 7.23 (dd, 1H, J = 7.8, J = 1.7); 7.10-7.02 (m, 2H); 3.86 (d, 6H, $^3J_{HP}$ = 11.9); 2.96 (t, 4H, J = 5.2); 1.78-1.68 (m, 4H); 1.60-1.52 (m, 2H). ^{13}C-NMR: δ 189.8 (d, $^2J_{CP}$ = 7.0); 132.2; 131.8 (d, $^3J_{CP}$ = 5.9); 129.5; 122.6; 118.4; 63.3 (d, $^1J_{CP}$ = 224.1); 54.3; 54.2 (d, $^2J_{CP}$ = 6.3); 26.4; 23.9. Anal Calcd for $C_{15}H_{20}N_3O_4P$: C, 53.41; H, 5.98; N, 12.46; P, 9.18. Found: C, 53.17; H, 5.95; N, 12.48; P, 8.65.

Dimethyl 1-diazo-2-oxo-2-(2-pyrrolidinophenyl)ethylphosphonate (1b)

Yield 2.17 g (67 %). Mp 95-96°C. IR ($CHCl_3$): 2110, 1620, 1250, 1050, 1030. ^{1}H-NMR: δ 7.34-7.24 (m, 2H); 6.79-6.70 (m, 2H); 3.84 (d, 6H, $^3J_{HP}$ = 11.9); 3.25-3.18 (m, 4H); 1.98-1.91 (m, 4H). ^{13}C-NMR: δ 189.1 (d, $^2J_{CP}$ = 8.2); 146.9; 132.0; 129.1; 123.4 (d, $^3J_{CP}$ = 4.7); 116.5; 114.4; 63.8 (d, $^1J_{CP}$ = 220.7); 54.1 (d, $^2J_{CP}$ = 6.2); 51.0; 25.8. Anal Calcd for $C_{14}H_{18}N_3O_4P$: C, 52.01; H, 5.61; N, 13.00; P, 9.58. Found: C, 51.78; H, 5.43; N, 13.00; P, 9.36.

Dimethyl 1-diazo-2-oxo-2-(2-pyrrolinophenyl)ethylphosphonate (1c)

Yield 2.76 g (86 %). Mp Oil. IR ($CHCl_3$): 2110, 1620, 1250, 1060, 1030. ^{1}H-NMR: δ 7.40-7.20 (m, 2H); 6.80-6.70 (m, 2H); 5.90 (s, 2H); 4.11 (s,4H); 3.85 (d, 6H, $^3J_{HP}$ = 11.8). ^{13}C-NMR: δ 189.1 (d, $^2J_{CP}$ = 8.8); 145.4; 131.9; 128.4; 125.9; 122.4 (d, $^3J_{CP}$ = 4.1); 116.0; 114.6; 64.3 (d, $^1J_{CP}$ = 220.4); 57.1; 54.1 (d, $^2J_{CP}$ = 6.2). Anal Calcd for $C_{14}H_{16}N_3O_4P$: C, 52.34; H, 5.02; N, 13.08; P, 9.64. Found: C, 52.33; H, 5.05; N*, 12.38; P, 9.08. *No better analysis could be obtained.

Dimethyl 1-diazo-2-oxo-2-(2-perhydroazepinophenyl)ethylphosphonate (1d)

Yield 3.27 g (93 %). Oil. IR ($CHCl_3$): 2120, 1630, 1260, 1050. ^{1}H-NMR: δ 7.30-7.20 (m, 2H); 6.94 (d, 1H, J = 8.1); 6.85 (br t, 1H, J = 7.5); 3.82 (d, 6H, $^3J_{HP}$ = 11.9); 3.28-3.22 (m, 4H); 1.80-1.50 (m, 8H). ^{13}C-NMR: δ 190.0 (d, $^2J_{CP}$ = 7.3); 151.3; 131.7; 129.3; 128.3 (d, $^3J_{CP}$ = 5.4); 119.9; 117.9; 63.3 (d, $^1J_{CP}$ = 221.4); 54.7; 54.1 (d, $^2J_{CP}$ = 6.2); 28.5; 27.7. Anal Calcd for $C_{16}H_{22}N_3O_4P$: C, 54.70; H, 6.31; N, 11.96; P, 8.82. Found: C, 54.87; H, 6.30; N, 11.60; P, 8.31.

Dimethyl 1-diazo-2-oxo-2-(2-morpholinophenyl)ethylphosphonate (1e)

Yield 3.02 g (89 %). Mp 145-147°C. IR ($CHCl_3$): 2120, 1625, 1270, 1050, 1030. ^{1}H-NMR: δ 7.52-7.35 (m, 2H); 7.20-7.00 (m, 2H,); 3.91 (d, 6H, $^3J_{HP}$ = 11.9); 3.85 (m, 4H); 3.03 (m, 4H). ^{13}C-NMR: δ 189.4 (d, $^2J_{CP}$ = 7.2); 149.8; 132.2; 131.5 (d, $^3J_{CP}$ = 5.7); 129.3; 123.3; 118.0; 66.9; 63.2 (d, $^1J_{CP}$ = 222.8); 54.0 (d, $^2J_{CP}$ = 6.3); 52.9. Anal Calcd for $C_{14}H_{18}N_3O_5P$: C, 49.56; H, 5.35; N, 12.38; P, 9.13. Found: C, 49.51; H, 5.53; N, 12.29; P, 8.81.

Dimethyl 1-diazo-2-oxo-2-(2-(1,2,3,6-tetrahydropyridino)phenyl)ethylphosphonate (1f)

Yield 3.32 g (99 %). Mp 101-103°C. IR ($CHCl_3$): 2120, 1620, 1250, 1050, 1030. ^{1}H-NMR: δ 7.47-7.34 (m, 2H); 7.10-7.06 (m, 2H); 5.86 (dm, 1H, J = 10.1); 5.75 (dm, 1H, J = 10.1); 3.88 (d, 6H, $^3J_{HP}$ = 12.0); 3.54 (m, 2H); 3.20 (t, 2H, J = 5.6); 2.40-2.30 (m, 2H). ^{13}C-NMR: δ 189.7 (d, $^2J_{CP}$ = 7.2); 150.5; 132.2; 132.1 (d, $^3J_{CP}$ = 5.8); 129.3; 125.7; 124.9; 123.0; 118.7; 63.2 (d, $^1J_{CP}$ = 220.7); 54.1 (d, $^2J_{CP}$ = 6.0); 51.9; 49.9; 26.1. Anal Calcd for $C_{15}H_{18}N_3O_4P$: C, 53.73; H, 5.41; N, 12.53; P, 9.24. Found: C, 53.36; H, 5.46; N, 12.70; P, 8.62.

Dimethyl 1-diazo-2-(2-(N,N-diethylamino)phenyl)-2-oxoethylphosphonate (1g)

Yield 2.77 g (85 %). Oil. IR ($CHCl_3$): 2120, 1635, 1290, 1265, 1055, 1035. ^{1}H-NMR: δ 7.42-7.27 (m, 2H); 7.08-7.00 (m, 2H); 3.91 (d, 6H, $^3J_{HP}$ = 12.0); 3.17 (q, 4H, J = 7.1); 1.05 (t, 6H, J = 7.1). ^{13}C-NMR: δ 190.2 (d, $^2J_{CP}$ = 7.0); 149.3; 132.5 (d, $^3J_{CP}$ = 5.9); 131.5; 129.1; 122.3; 120.7; 63.1 (d, $^1J_{CP}$ = 220.0); 54.1 (d, $^2J_{CP}$ = 6.0); 46.4; 11.5. Anal Calcd for $C_{14}H_{20}N_3O_4P$: C, 51.69; H, 6.20; N, 12.92; P, 9.52. Found: C, 51.66; H, 6.34; N, 12.94; P, 9.10.

Dimethyl 1-diazo-2-oxo-2-(2-(N-allyl,N-methylamino)phenyl)ethylphosphonate (1h)

Yield 2.75 g (85 %). Oil. IR (neat): 2120, 1635, 1270, 1060, 1030. ^{1}H-NMR: δ 7.42-7.30 (m, 2H); 7.06-6.99 (m, 2H); 5.84 (ddt, 1H, J =17.4, J = 9.8, J = 6.3); 5.21 (dd, 1H, J =17.4, J = 1.4); 5.19 (dd, 1H, J = 9.8, J = 1.4); 3.89 (d, 6H, $^3J_{HP}$ = 11.9); 3.64 (d, 2H, J = 6.3); 2.76 (s, 3H). ^{13}C-NMR: δ 189.7 (d, $^2J_{CP}$ = 7.3); 150.4; 133.9; 131.9; 130.7 (d, $^3J_{CP}$ = 5.5); 129.3; 123.1; 118.7; 118.3; 63.4 (d, $^1J_{CP}$ = 220.8); 60.5; 54.1 (d, $^2J_{CP}$ = 6.2); 40.1. Anal Calcd for $C_{14}H_{18}N_3O_4P$: C, 52.01; H, 5.61; N, 13.00; P, 9.58. Found: C, 51.46; H, 5.70; N, 12.71; P, 9.24.

Dimethyl 1-diazo-2-oxo-2-(2-(N-benzyl,N-methylamino)phenyl)ethylphosphonate (1i)

Yield 3.58 g (96 %). Mp 75-77°C. IR ($CHCl_3$): 2120, 1625, 1260, 1050, 1030. ^{1}H-NMR: δ 7.43-6.97 (m, 9H); 4.23 (s, 2H); 3.87 (d, 6H, $^3J_{HP}$ = 11.9); 2.69 (s, 3H). ^{13}C-NMR: δ 189.8 (d, $^2J_{CP}$ = 7.3); 150.4; 137.0; 132.0; 130.8 (d, $^3J_{CP}$ = 5.3); 129.1; 128.4; 128.3; 127.5; 122.2; 119.2; 63.4 (d, $^1J_{CP}$ = 236.5); 61.6; 54.1 (d, $^2J_{CP}$ = 6.1); 40.1. Anal Calcd for $C_{18}H_{20}N_3O_4P$: C, 57.91; H, 5.40; N, 11.25; P, 8.30. Found: C, 57.67; H, 5.41; N, 11.24; P, 8.23.

Dimethyl 1-diazo-2-oxo-2-(3-(2-piperidinopyridinyl))ethylphosphonate (1l)

Yield 2.98 g (88 %). Mp 66-68°C. IR ($CHCl_3$): 2100, 1620, 1260, 1060, 1030. ^{1}H-NMR: δ 8.32 (dd, 1H, J = 4.8, J = 2.0); 7.67 (dd, 1H, J = 7.5, J = 2.0); 6.86 (dd, 1H, J = 7.5, J = 4.8); 3.90 (d, 6H, $^3J_{HP}$ = 11.9); 3.32

(m, 4H); 1.80-1.60 (m, 6H). ^{13}C-NMR: δ 188.0 (d, $^{2}J_{CP}$ = 7.5); 159.1; 150.4; 138.9; 122.4 (d, $^{3}J_{CP}$ = 5.7); 115.7; 63.1 (d, $^{1}J_{CP}$ = 222.5); 54.2 (d, $^{2}J_{CP}$ = 6.3); 51.4; 26.0; 24.3. Anal Calcd for $C_{14}H_{19}N_4O_4P$: C, 49.71; H, 5.66; N, 16.56; P, 9.16. Found: C, 49.92; H, 5.60; N, 16.97; P, 8.98.

THERMOLYSIS OF α-DIAZO-β-KETOPHOSPHONATES (1a-i) and 18

General Procedure: to the α-diazo-β-ketophosphonate **1** or **18** (500 mg) was added anhydrous benzene (15 ml) and benzene was evaporated *in vacuo*. Compounds **1** or **18** were then dissolved in anhydrous toluene (50 ml) and the solution was refluxed under nitrogen until the disappearance of compound **1** or **18** was completed as judged by TLC. The toluene was then evaporated *in vacuo* and the residue was purified. For ^{13}C-NMR data of mesoionic compounds **4** and **19**, see Table (2). No microanalysis was made for the ylides **5b,d** and **20** which were isolated only in small quantities.

Thermolysis of 1a: Time of decomposition, 3.5 h. Purification of the residue by chromatography on silica gel yielded **4a** after elution with acetone and **5a** after elution with ethyl acetate-methanol 50:50.

3-Dimethylphosphono-2-oxo-1-spiropiperidinoindolinium enolate (4a)

Yield 197 mg (43 %). Mp = 170-172 °C. IR ($CHCl_3$): 1750, 1600, 1580, 1055, 1025 cm^{-1}. ^{1}H-RMN: δ 7.57 (d, 1H, J = 8.0); 7.52 (d, 1H, J = 7.9); 7.30 (pt, 1H, J = 7.7); 6.94 (pt, 1H, J = 7.8); 3.69 (d, 6H, $^{3}J_{HP}$ = 11.5); 3.55 (td, 2H, J = 13.2, J = 3.8); 2.88 (pd, 2H, J = 13.2); 2.33-2.18 (m, 2H); 2.07-1.98 (m, 3H); 1.76-1.71 (m, 1H). Anal Calcd for $C_{15}H_{20}NO_4P$: C, 58.25; H, 6.52; N, 4.53; P, 10.01. Found: C, 58.10; H, 6.79; N, 4.58; P, 9.77.

2-Dimethylphosphono-3-oxo-1-spiropiperidinoindolinium enolate (5a)

Yield 202 mg (44 %). Mp = 219-221 °C. IR ($CHCl_3$) : 1620, 1585, 1035 cm^{-1}. ^{1}H-RMN: δ 7.95 (d, 1H, J = 8.2); 7.82 (d, 1H, J = 6.4); 7.65 (pt, 1H, J = 7.4); 7.52 (pt, 1H, J = 6.8); 4.87 (td, 2H, J = 13.4, J = 4.0); 3.74 (d, 6H, $^{3}J_{HP}$ = 12.1) ; 3.22 (pd, 2H, J = 13.4); 2.47-2.31 (m, 2H); 2.12-1.97 (m, 3H); 1.89-1.77 (m, 1H). ^{13}C-RMN: δ 172.11 (d, $^{2}J_{CP}$ = 16.8); 150.88 (d, $^{3}J_{CP}$ = 8.6); 135.44 (d, $^{3}J_{CP}$ = 15.7); 130.85; 129.10; 123.79 (d, J_{CP} = 0.7); 119.27 (d, J_{CP} = 1.2); 105.75 (d, $^{1}J_{CP}$ = 226.8); 64.40; 52.77 (d, $^{2}J_{CP}$ = 5.6); 22.72; 19.50. Anal Calcd for $C_{15}H_{20}NO_4P$: C, 58.25; H, 6.52; N, 4.53; P, 10.01. Found: C, 58.13; H, 6.39; N, 4.50; P, 9.95.

Thermolysis of 1b: Time of decomposition, 1 h. Purification of the residue by chromatography on silica gel yielded **4b** after elution with acetone and a small amount of **5b** after elution with ethyl acetate-methanol 50:50.

3-Dimethylphosphono-2-oxo-1-spiropiperidinoindolinium enolate (4b)

Yield 402 mg (88 %). Mp 140-141°C. IR ($CHCl_3$): 1735, 1600, 1575, 1050, 1020. ^{1}H-NMR: δ 7.47 (dd,1H, J = 7.8, J = 1.2); 7.23 (td, 1H, J = 7.8, J = 1.1); 7.05 (pd, 1H, J = 8.0); 6.88 (td, 1H, J = 7.7, J = 1.2); 4.05-3.70 (m, 8H with a doublet at 3.76, $^{3}J_{HP}$ = 11.4); 3.40-3.25 (m, 2H); 2.50-2.35 (m, 2H). Anal Calcd for $C_{14}H_{18}NO_4P$: C, 56.95; H, 6.14; N, 4.74; P, 10.49. Found: C, 56.69; H, 6.09; N, 4.73; P, 10.20.

2-Dimethylphosphono-3-oxo-1-spiropiperidinoindolinium enolate (5b)

Yield 9 mg (2 %). Oil. IR ($CHCl_3$): 1600, 1580, 1030. ^{1}H-NMR: δ 7.80 (dd, 1H, J = 8.4, J = 1.5); 7.60-7.32 (m, 3H); 4.80-4.64 (m, 2H); 3.80-3.60 (m, 8H with a doublet at 3.75, $^{3}J_{HP}$ = 11.9); 2.80-2.55 (m, 2H); 2.55-2.30 (m, 2H).

Thermolysis of 1c: Time of decomposition, 1 h. Purification of the residue by recrystallisation from toluene yielded **4c** .

3-Dimethylphosphono-2-oxo-1-spiro(3-pyrrolino)indolinium enolate (4c)

Yield 301 mg (66 %). Mp 173-175°C. IR ($CHCl_3$): 1750, 1605, 1580, 1055, 1020. ^{1}H-NMR: δ 7.47 (dd,1H, J = 7.8, J = 0.9); 7.26 (ddd, 1H, J = 7.8, J = 7.6; J = 0.9); 7.14 (d, 1H, J = 7.9); 6.88 (m, 1H); 6.09 (m, 2H); 4.78 (d, 2H, J = 13.7); 4.09 (d, 2H, J = 13.1); 3.80 (d, 6H, $^3J_{HP}$ = 11.5). Anal Calcd for $C_{14}H_{16}NO_4P$: C, 57.34; H, 5.50; N, 4.78; P, 10.56. Found: C, 57.41; H, 5.51; N, 4.80; P, 10.68.

Thermolysis of 1d: Time of decomposition, 2.5 h. Purification of the residue by chromatography on silica gel yielded **4d** after elution with acetone and a small amount of **5d** after elution with ethyl acetate-methanol 50:50.

3-Dimethylphosphono-2-oxo-1-spiroperhydroazepinoindolinium enolate (4d)

Yield 304 mg (66 %). Mp 193-195°C. IR ($CHCl_3$): 1750, 1600, 1575, 1055, 1025. ^{1}H-NMR: δ 7.52 (dd, 1H, J = 8.2, J = 1.4); 7.25 (m, 2H); 6.92 (td, 1H, J = 7.7, J = 1.3); 3.82 (m, 2H); 3.80 (d, 6H, $^3J_{HP}$ = 11.4); 3.24 (dd, 2H, J = 13.8, J = 8.6); 2.50-2.30 (m, 2H); 2.20-1.80 (m, 6H). Anal Calcd for $C_{16}H_{22}NO_4P$: C, 59.44; H, 6.86; N, 4.33; P, 9.58. Found: C, 59.14; H, 6.90; N, 4.31; P, 9.11.

2-Dimethylphosphono-3-oxo-1-spiroperhydroazepinoindolinium enolate (5d)

Yield 28 mg (6 %). Mp 197-199°C. IR ($CHCl_3$): 1620, 1600, 1580, 1055, 1035. ^{1}H-NMR: δ 7.79 (dd, 1H, J = 8.8, J = 6.5); 7.65 (dd, 1H, J = 6.9, J = 1.9); 7.51 (m, 2H); 4.59 (dd, 2H, J = 13.6, J = 9.4); 3.72 (d, 6H, $^3J_{HP}$ = 11.8); 3.64 (dd, 2H, J = 13.6, J = 6.7); 2.60-2.40 (m, 2H); 2.20-1.70 (m, 6H).^{13}C-NMR: δ 171.7 (d, $^2J_{CP}$ = 17.3); 153.2 (d, $^3J_{CP}$ = 8.8); 134.3 (d, $^3J_{CP}$ = 15.6); 130.4; 129.8; 123.5; 117.1; 107.4 (d, $^1J_{CP}$ = 227.9); 71.6; 52.4 (d, $^2J_{CP}$ = 5.7); 28.6; 25.7.

Thermolysis of 1e: Time of decomposition, 3 h. Purification of the residue by chromatography on silica gel yielded **12** and then **4e** after elution with acetone and **5e** after elution with ethyl acetate-methanol 50:50. A second purification of the sample of **5e** by chromatography with ethyl acetate-methanol 50:50 as eluent was necessary to obtain pure **5e**.

3-Dimethylphosphono-2-oxo-1-spiromorpholinoindolinium enolate (4e)

Yield 243 mg (53 %). Mp 203-205°C. IR ($CHCl_3$): 1760, 1595, 1575, 1050, 1025. ^{1}H-NMR: δ 7.62-7.46 (m, 2H); 7.31 (dt, 1H, J = 7.7, J = 1.0); 6.96 (td, 1H, J = 7.7, J = 1.2); 4.49 (td, 2H, J = 13.1, J = 4.3); 4.22 (ddd, 2H, J = 13.1, J = 9.0, J = 3.0); 3.89-3.61 (m, 8 H, with a doublet at 3.78, $^3J_{HP}$ = 11.5); 3.04 (dt, 2H, J = 13.1, J = 3.0). HRMS (EI) m/z calcd for $C_{14}H_{18}NO_5P$ (M^+) 311.0923, found 311.0912. LRMS (EI) m/z (rel.int.): 311 (37.1); 280 (48.1); 268 (44.6); 253 (68.7); 238 (21.6); 225 (25.9); 174 (100); 91 (37.7); 77 (24.7).

2-Dimethylphosphono-3-oxo-1-spiromorpholinoindolinium enolate (5e)

Yield 55 mg (12 %). Mp 218-220°C (dec.). IR ($CHCl_3$): 1620, 1585, 1135, 1040. ^{1}H-NMR: δ 8.10 (d, 1H, J = 8.1); 7.93 (d, 1H, J = 7.3); 7.66 (pt, 1H, J = 7.4); 7.53 (dd 1H, J = 8.1; J = 7.3); 5.19 (td, 2H, J = 13.0, J = 4.5); 4.47 (td, 2H, J = 13.0, J = 2.0); 4.15 (dd, 2H, J = 13.0, J = 4.5); 3.81 (d, 6 H, $^3J_{HP}$ = 12.0); 3.20 (dd, 2H, J = 13.0, J = 2.0). ^{13}C-NMR: δ 171.7 (d, $^2J_{CP}$ = 16.8); 150.9 ($^3J_{CP}$ = 8.4); 135.4 ($^3J_{CP}$ = 15.4); 131.2; 129.4; 124.0; 118.7; 105.7 (d, $^1J_{CP}$ = 226.9); 62.6; 62.5; 52.7 (d, $^2J_{CP}$ = 5.7). HRMS (EI) m/z calcd for $C_{14}H_{18}NO_5P$ (M^+) 311.0923, found 311.0915. LRMS (EI) m/z (rel.int.): 311 (34.1); 268 (14.6); 202 (100); 172 (26.1); 110 (34.1); 77 (18.1).

5a-Dimethylphosphono-6-oxo-1,4-oxazepano[4,5-a]indoline (12)

Yield 119 mg (26 %). Oil. IR ($CHCl_3$): 1690, 1610, 1580, 1250, 1060, 1030. ^{1}H-NMR: δ 7.58 (d, 1H, J = 7.8); 7.47 (pt, 1H, J = 7.8); 6.86-6.75 (m, 2H); 3.95-3.92 (m, 2H); 3.85-3.70 (m, 5 H with a doublet at 3.77, $^3J_{HP}$ = 10.7); 3.60 (d, 3 H, $^3J_{HP}$ = 10.4); 3.51-3.30 (m, 1 H); 2.86-2.51 (m, 3 H). ^{13}C-NMR: δ 197.6 (d,

$^2J_{CP}$ = 1.3); 160.8 (d, $^3J_{CP}$ = 7.3); 137.8; 125.2; 121.9 (d, $^3J_{CP}$ = 1.3); 119.1; 110.4; 72.8 (d, $^1J_{CP}$ = 154.4); 68.2 (d, $^4J_{CP}$ = 2.5); 66.8 (d, $^3J_{CP}$ = 14.6); 54.9 (d, $^2J_{CP}$ = 7.2); 53.9 (d, $^2J_{CP}$ = 7.7); 47.1; 35.9. HRMS (EI) m/z calcd for $C_{14}H_{18}NO_5P$ (M^+) 311.0923, found 311.0920. LRMS (EI) m/z (rel.int.): 311 (17.2); 202 (100); 172 (14.0); 144 (5.1); 105 (3.7); 77 (6.8).

Thermolysis of 1f: Time of decomposition, 3 h. The ^{1}H-NMR spectrum of the crude residue showed that it contained of 51:40:9-mixture (determined by ^{1}H-NMR) of **4f**, **13** and **14**. The purification of the residue by chromatography on silica gel yielded 57 mg of **13** and 175 mg of a mixture of **13+14** after elution with ethyl acetate-acetone 80:20 and then 119 mg of **4f** after elution with acetone, the total yield being 77 %.

3-Dimethylphosphono-2-oxo-1-spiro-(1',2',3',6'-tetrahydropyridino)indolinium enolate (4f)

Isolated yield 119 mg (26 %). Mp 142-144°C. IR ($CHCl_3$): 1750, 1600, 1575, 1050, 1025. ^{1}H-NMR: δ 7.57 (dd, 1H, J = 7.3, J = 1.0); 7.34-7.24 (m, 2H); 6.89 (td, 1H, J = 7.3, J = 1.3); 6.18 (m, 1H); 6.02 (m, 1H); 4.38 (m, 1H); 3.79 (d, 6H, $^3J_{HP}$ = 11.4); 3.67 (m, 1H); 3.23 (m, 1H); 2.93 (m, 1H); 2.74-2.48 (m, 2H). Anal Calcd for $C_{15}H_{18}NO_4P$: C, 58.63; H, 5.90; N, 4.56; P, 10.08. Found: C, 58.19; H, 5.88; N, 4.68; P, 9.71.

5a-Dimethylphosphono-6-oxo-(2,3,6,7-tetrahydro-1H-azepino)[1,2-a]indoline (13)

Isolated yield 57 mg (12 %). Mp 113-115°C. IR ($CHCl_3$): 1690, 1610, 1580, 1060, 1030. ^{1}H-NMR: δ 7.56 (d, 1H, J = 7.7); 7.43 (ddd, 1H, J = 8.3, J = 7.5, J = 1.3); 6.90 (d, 1H, J = 8.3); 6.77 (dd, 1H, J = 7.7, J = 7.5); 5.23 (br s, 2H); 4.12-3.55 (m, 2H); 3.75 (d, 3H, $^3J_{HP}$ = 10.7); 3.57 (d, 3H, $^3J_{HP}$ = 10.5); 3.25-3.07 (m, 1H); 2.89-2.76 (m, 1H); 2.69-2.52 (m, 1H); 2.35-2.26 (m, 1H). ^{13}C-NMR: δ 197.9; 161.0 (d, $^4J_{CP}$ = 7.4); 137.0; 130.5; 124.9; 123.0 (d, $^3J_{CP}$ = 1.3); 121.5 (d, $^3J_{CP}$ = 16.4); 118.9; 111.2; 75.3 (d, $^1J_{CP}$ = 152.7); 54.8 (d, $^2J_{CP}$ = 7.2); 53.8 (d, $^2J_{CP}$ = 7.7); 40.3; 28.6 (d, $^2J_{CP}$ = 2.4); 28.0. Anal Calcd for $C_{15}H_{18}NO_4P$: C, 58.63; H, 5.90; N, 4.56; P, 10.08. Found: C, 58.47; H, 6.00; N, 4.36; P, 9.02.

Thermolysis of 1g: Time of decomposition, 3.5 h. Purification of the residue by chromatography on silica gel yielded **21** after elution with ethyl acetate-pentane 75:25 and **4g** after elution with ethyl acetate-methanol 80:20.

3-Dimethylphosphono-1,1-diethylindolium-2-olate (4g)

Yield 306 mg (67 %). Mp 163-165°C. IR ($CHCl_3$): 1735, 1605, 1575, 1050, 1020. ^{1}H-NMR: δ 7.55 (d, 1H, J = 7.8); 7.30 (td, 1H, J = 7.6, 1.9); 7.02-6.94 (m, 2H); 3.77 (d, 6H, $^3J_{HP}$ = 11.5); 3.66-3.48 (m, 2H); 3.34-3.21 (m, 2H); 0.93 (t, 6H, J = 7.1). ^{13}C-NMR: δ 165.5 (d, $^3J_{CP}$ = 24.8); 142.1 (d, J_{CP} = 15.1); 131.1 (d, J_{CP} = 13.3); 130.5; 120.9; 119.3; 116.7; 68.3 (d, $^1J_{CP}$ = 217.3); 55.2; 52.0 (d, $^2J_{CP}$ = 5.1); 8.1. Anal Calcd for $C_{14}H_{20}NO_4P$: C, 56.56; H, 6.78; N, 4.71; P, 10.42. Found: C, 56.27; H, 6.56; N, 4.79; P, 10.38.

Dimethyl 1-ethyl-3-hydroxy-2-indolephosphonate (21)

Yield 29 mg (7 %). Oil. IR ($CHCl_3$): 3260, 1605, 1045, 1020. ^{1}H-NMR: δ 9.00-8.60 (brs, 1H); 7.76 (d, 1H, J = 8.1); 7.59-7.22 (m, 2H); 7.07 (td, 1H, J = 7.3, 0.9 Hz); 4.11 (q, 2H, J = 7.1); 3.76 (d, 6H, $^3J_{HP}$ = 11.6); 1.31 (t, 3H, J = 7.1). ^{13}C-NMR: δ 151.6 (d, $^2J_{CP}$ = 15.8); 137.2 (d, $^3J_{CP}$ = 12.4); 126.4; 120.1; 118.8; 117.7 (d, $^3J_{CP}$ = 15.3); 109.6 (d, $^4J_{CP}$ = 2.0); 100.1 (d, $^1J_{CP}$ = 218.6); 52.84 (d, $^2J_{CP}$ = 4.5); 40.0; 14.3. Anal Calcd for $C_{12}H_{16}NO_4P$: C, 53.53; H, 5.99; N, 5.20; P, 11.50. Found: C, 53.68; H, 5.83; N, 5.44; P, 11.34.

Thermolysis of 1h: Time of decomposition 2.5 h. Purification of the residue by chromatography on silica gel, eluting with ethyl acetate, yielded **23h** and then **22h**.

Dimethyl 3-allyl-1-methyl-2-oxo-3-indolinephosphonate (22h)

Yield 196 mg (43 %). Mp 75-77°C. IR ($CHCl_3$): 1705, 1605, 1490, 1050, 1030. ^{1}H-NMR: δ 7.48 (dt, 1H, J = 7.4, J = 1.5); 7.32 (tt, 1H, J = 7.7, J = 1.5, $^6J_{HP}$ = 1.5); 7.10 (br t, 1H, J = 7.4); 6.84 (d, 1H, J = 7.7); 5.38-5.15 (m, 1H); 5.01 (br d, 1H, J = 16.9); 4.87 (br d, 1H, J = 9.8); 3.84 (d, 3H, $^3J_{HP}$ = 10.9); 3.56 (d, 3H, $^3J_{HP}$

= 10.7); 3.23 (s, 3H); 3,03 (m, 2H). ^{13}C-NMR: δ 173.0 (d, $^{2}J_{CP}$ = 2.8); 144.2 (d, $^{3}J_{CP}$ = 7.8); 130.7 (d, $^{3}J_{CP}$ = 14.4); 128.5 (d, J_{CP} = 2.8); 125.6 (d, J_{CP} = 3.7); 124.9 (d, J_{CP} = 6.0); 122.7 (d, J_{CP} = 3.1); 119.7; 108.1 (d, $^{2}J_{CP}$ = 1.8); 54.7 (d, $^{1}J_{CP}$ = 137.4); 54.7 (d, $^{2}J_{CP}$ = 6.8); 53.8 (d, $^{2}J_{CP}$ = 7.6); 36.3 (d, $^{2}J_{CP}$ = 4.4); 26.6. Anal Calcd for $C_{14}H_{18}NO_4P$: C, 56.95; H, 6.14; N, 4.74; P, 10.49. Found: C, 56.65; H, 6.32; N, 4.71; P, 10.31.

Dimethyl 2-allyl-1-methyl-3-oxo-2-indolinephosphonate (23h)

Yield 178 mg (39 %). Oil. IR ($CHCl_3$): 1690, 1610, 1580, 1060, 1030. ^{1}H-NMR: δ 7.59 (br d, 1H, J = 7.7); 7.54-7.43 (m, 1H); 6.82 (d, 1H, J = 8.3); 6.72 (t, 1H, J = 7.1); 5.40-5.10 (m, 2H); 5.00-4.90 (m, 1H); 3.84 (d, 3H, $^{3}J_{HP}$ = 10.8); 3.63 (d, 3H, $^{3}J_{HP}$ = 10.7); 3.20 (s, 3H); 3.10-2.90 (m, 2H). ^{13}C-NMR: δ 196.2 (d, $^{2}J_{CP}$ = 2.4); 161.0 (d, $^{3}J_{CP}$ = 6.0); 137.7; 130.2 (d, $^{3}J_{CP}$ = 5.6); 124.7; 120.6 (d, $^{4}J_{CP}$ = 1.6); 120.0; 117.8; 108.6; 73.1 (d, $^{1}J_{CP}$ = 148.4); 54.4 (d, $^{2}J_{CP}$ = 7.0); 53.7 (d, $^{2}J_{CP}$ = 7.7); 34.9; 29.7. Anal Calcd for $C_{14}H_{18}NO_4P$: C, 56.95; H, 6.14; N, 4.74; P, 10.49. Found: C, 56.83; H, 6.23; N, 4.84; P, 9.84.

Thermolysis of 1i: Time of decomposition 3.5 h. The purification of the residue by chromatography on silica gel, eluting with ethyl acetate, yielded 69 mg of **23i**, 232 mg of a 22:78-mixture of **23i+22i** and 144 mg of **22i**, the total yield being of 96 %.

Dimethyl 3-benzyl-1-methyl-2-oxo-3-indolinephosphonate (22i)

Isolated yield 69 mg (15 %). Mp 116-117°C. IR ($CHCl_3$): 1705, 1610, 1055, 1035. ^{1}H-NMR: δ 7.61 (dt, 1H, J = 7.5, 1.7); 7.21 (tt, 1H, J = 7.7, 1.5); 7.10 (pd, 1H, J = 7.0); 7.05-6.93 (m, 3H); 6.90-6.83 (m, 2H); 6.57 (d, 1H, J = 7.7); 3.91 (d, 3H, $^{3}J_{HP}$ = 10.9); 3.71 (A part of a H_AH_BP system, 1H, J_{AB} = 13.2, $^{3}J_{AP}$ = 6.9); 3.61 (d, 3H, $^{3}J_{HP}$ = 10.7); 3.46 (B part of a H_AH_BP system, 1H, J_{AB} = 13.2, $^{3}J_{BP}$ = 8.0); 2.99 (s, 3H). ^{13}C-NMR: δ 172.8 (d, $^{2}J_{CP}$ = 2.7); 144.0 (d, $^{3}J_{CP}$ = 8.1); 134.4 (d, $^{2}J_{CP}$ = 15.7); 129.8; 128.9 (d, J_{CP} = 2.7); 127.6; 126.7; 126.0 (d, J_{CP} = 3.5); 124.6 (d, $^{2}_{CP}$ = 5.6); 122.4 (d, J_{CP} = 2.9); 108.0 (d, J_{CP} = 1.6); 56.3 (d, $^{1}J_{CP}$ = 137.5); 54.7 (d, $^{2}J_{CP}$ = 6.8); 53.8 (d, $^{2}J_{CP}$ = 7.5); 37.9 (d, $^{2}J_{CP}$ = 4.2); 26.3. Anal Calcd for $C_{18}H_{20}NO_4P$: C, 62.61; H, 5.84; N, 4.06; P, 8.97. Found: C, 62.79; H, 6.10; N, 4.03; P, 8.46.

Dimethyl 2-benzyl-1-methyl-3-oxo-2-indolinephosphonate (23i)

Isolated yield 144 mg (31 %). Oil. IR ($CHCl_3$): 1690, 1615, 1055, 1035. ^{1}H-NMR: δ 7.50 (pd, 1H, J = 7.6); 7.35 (td, 1H, J = 7.7, 1.4); 7.06 (s, 5H); 6.69-6.60 (m, 2H); 3.89 (d, 3H, $^{3}J_{HP}$ = 10.8); 3.76 (A part of a H_AH_BP system, 1H, J_{AB} = 14.2, $^{3}J_{AP}$ = 11.1); 3.64 (d, 3H, $^{3}J_{HP}$ = 10.7); 3.45 (B part of a H_AH_BP system, 1H, J_{AB} = 14.2, $^{3}J_{BP}$ = 10.5); 3.22 (s, 3H). ^{13}C-NMR: δ 196.1 (d, $^{2}J_{CP}$ = 3.0); 160.7 (d, $^{3}J_{CP}$ = 5.0); 137.5; 133.9 (d, $^{3}J_{CP}$ = 15.5); 129.6; 128.1; 127.0; 124.5; 120.4 (d, J_{CP} = 1.3); 117.6; 108.2; 74.5 (d, $^{1}J_{CP}$ = 142.6); 54.3 (d, $^{3}J_{CP}$ = 7.2); 53.9 (d, $^{3}J_{CP}$ = 7.8); 35.9; 30.4. Anal Calcd for $C_{18}H_{20}NO_4P$: C, 62.61; H, 5.84; N, 4.06; P, 8.97. Found: C, 62.25; H, 5.92; N, 4.16; P, 8.83.

Thermolysis of 18: Time of decomposition 1.5 h. Purification of the residue by chromatography on silica gel yielded **19** after elution with acetone and a small amount of **20** after elution with ethyl acetate-methanol 50:50.

7-Aza-3-dimethylphosphono-2-oxo-1-spiropiperidinoindolinium enolate (19)

Yield 238 mg (52 %). Mp 179-181°C. IR ($CHCl_3$): 1740, 1590, 1575, 1260, 1060, 1035. ^{1}H-NMR: δ 7.88 (d, 1H, J = 4.9); 7.82 (d, 1H, J = 7.8); 7.19 (dd, 1H, J = 7.8, J = 4.9); 3.78 (d, 6H, $^{3}J_{HP}$ = 11.5); 3.54 (m, 2H); 3.02 (m, 2H); 2.75 (m, 2H); 2.10-1.90 (m, 3H); 1.90-1.60 (m, 1H). Anal Calcd for $C_{14}H_{19}N_2O_4P$: C, 54.19; H, 6.17; N, 9.03; P, 9.98. Found: C, 53.83; H, 6.19; N, 9.16; P, 9.70.

7-Aza-2-dimethylphosphono-3-oxo-1-spiropiperidinoindolinium enolate (20)
Yield 37 mg (8 %). Mp 193-195°C. IR ($CHCl_3$): 1620, 1595, 1570, 1035. ^{1}H-NMR: δ 8.41 (dd, 1H, J = 4.9, J = 1.7); 8.15 (dd, 1H, J = 7.5, J = 1.7); 7.51 (dd, 1H, J = 7.5, J = 4.9); 4.78 (m, 2H); 3.75 (d, 6H, $^3J_{HP}$ = 11.9); 3.17 (m, 2H); 3.10-2.80 (m, 2H); 2.10-1.90 (m, 1H); 1.90-1.60 (m, 3H). ^{13}C-NMR: δ 170.0 (d, $^2J_{CP}$ = 15.9); 163.7; 147.2; 132.5; 127.8 (d, $^3J_{CP}$ = 14.5); 125.9; 105.5 (d, $^1J_{CP}$ = 225.9); 64.1; 52.6 (d, $^2J_{CP}$ = 5.6); 22.4; 20.3.

REACTION OF WATER WITH THE 3-DIMETHYLPHOSPHONO-2-OXO-1-SPIROPIPERIDINOINDOLINIUM ENOLATE (4a)

A mixture of **4a** (187 mg, 0.6 mmol), water (4 ml) and silica gel (~ 5 mg) was refluxed for 4 h. After cooling, and extraction with ethyl acetate (3 x 15 ml), the organic layer was dried, filtered and concentrated to give a residue which was purified by chromatography eluting with ethyl acetate to afford **11**.

Dimethyl (2-piperidinophenyl)methylphosphonate (11)
Yield 156 mg (89 %). Oil. IR ($CHCl_3$): 1595,1250,1055,1030. ^{1}H-NMR: δ 7.47 (dt, 1H, J = 7.5, J = 2.0); 7.23-7.02 (m, 3H); 3.70 (d, 6H, $^3J_{HP}$ = 10.8); 3.41 (d, 2H, $^2J_{HP}$ = 22,2); 2.96-2.71 (m, 4H); 1.83-1.48 (m, 6H). ^{13}C-NMR: δ 153.3 (d, $^3J_{CP}$ = 8.4); 130.6 (d, $^3J_{CP}$ = 5.0); 127.8 (d, J_{CP} = 3.2); 127.4 (d, $^2J_{CP}$ = 8.0); 124.0 (d, J_{CP} = 3.2); 121.1 (d, J_{CP} = 2.4); 54.4; 53.0 (d, $^2J_{CP}$ = 6.7); 26.7; 26.2 (d, $^1J_{CP}$ = 138.7); 24.2. Anal Calcd for [$C_{14}H_{22}NO_3P$,0.5 H_2O]*: C, 57.52; H, 7.93; N, 4.79; P, 10.60. Found: C, 57.43; H, 7.76; N, 4.68; P, 10.38. *Identical microanalyses were obtained with samples of **11** prepared by independent experiments.

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