Pergamon

Tetrahedron, Vol. 52, No. 38, pp. 12597-12612, 1996

0040-4020/96 $15.00 + 0.00

PII: S0040-4020(96)00748-X

A Comparative Study of the Interaction of Salicylaldehydes with Phosphonoacetates under Knoevenagel Reaction Conditions. Synthesis of 1,2-Benzoxaphosphorines and their Dimers.

Anka Bojilova, R. Nikolova, Christo Ivanov
Department of Organic Chemistry, University of Sofia, Y. Bourchier avenue 1, Sofia, 1126, Bulgaria.

Nestor A. Rodios*
Laboratory of Organic Chemistry, Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki GR 54006, Macedonia, Greece.

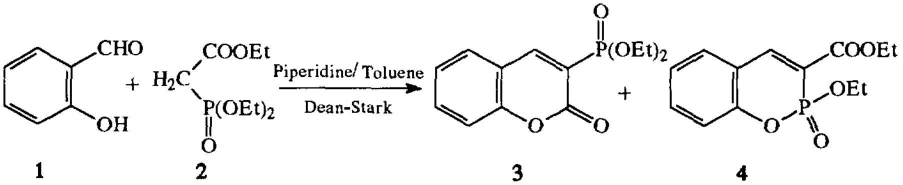
A. Terzis and C. P. Raptopoulou

NCR Demokritos, Institute of Material Sciences, Athens, Greece

Abstract: The reaction of salicylaldehydes **5** with phosphonoacetates **6** gives the coumarin-3-phosphonates **7** and the 1,2-benzoxaphosphorine-3-carboxylates **8** in yields and **7**:**8** ratios depending on the reaction conditions. A mechanistic explanation is given for the stereoselectivity of these reactions. Irradiation of compounds **8** or direct exposure to sunlight causes their head-to-tail dimerization, giving the dimers **11** and in one case its phosphorous epimer **12**. Their structure was confirmed by x-ray crystallographic analyses. Some spectroscopic characteristics of diagnostic importance for compounds **7**, **8**, **11** and **12** are also discussed. Copyright © 1996 Published by Elsevier Science Ltd

INTRODUCTION

In the context of our work on the behaviour of coumarins, bearing at 3-position an electron-withdrawing group, towards nucleophilic reagents[1-5] and acid anhydrides[6-10] under Perkin reaction conditions, we tried to prepare the 3-phosphono-coumarins by reacting salicylaldehyde **1** with triethylphosphonoacetate **2** in the presence of piperidine in refluxing toluene (Knoevenagel reaction conditions). From this reaction, except for the expected diethyl coumarin-3-phosphonate (**3**), which was obtained in good yield (70%), a small amount (9%) of a new heterocyclic compound, the 1,2-benzoxaphosphorine-3-ethylcarboxylate (**4**) was isolated[11].

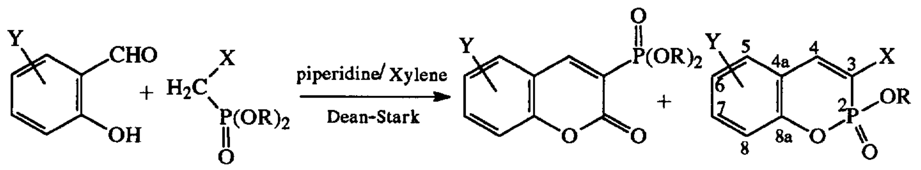


Other authors, who also investigated the above reaction have isolated[12-15] only the coumarin-3-phosphonates **3**, whereas in one case[16] derivatives of both **3** and **4** were obtained.

The different results obtained by various authors prompted us to undertake a more systematic study of the above reaction and especially of the experimental conditions that influence the formation of the two main reaction products **3** and **4** and the yields in which these are obtained. To this study we were also forced by the fact that the 1,2-benzoxaphosphorines **4** were unstable in solution, tending to give head-to-tail dimers under the action of sunlight or during the separation of the reaction mixture on the column in a much more easier way than the corresponding coumarins[17-19].

RESULTS AND DISCUSSION.

The interaction of salicylaldehydes **5** with the phosphonoacetates **6**, performed under different experimental conditions, gave two main products, the coumarin-3-phosphonates **7** and the phosphacoumarins **8**.

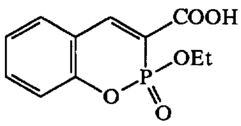


5 **6** **7** **8**

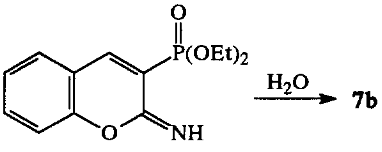
a Y = H
b Y = 5-Br
c Y = 5-Cl
d Y = 4-NEt_3

a R = Me, X = COOEt
b R = Et, X = COOEt
c R = Et, X = $COOSiMe_3$
d R = Et, X = CN

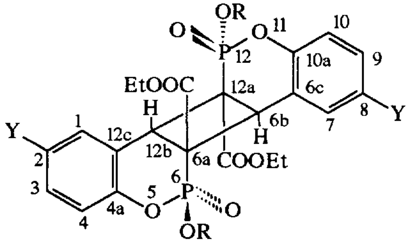
7/8	R	X	Y
a	Me	COOEt	H
b	Et	COOEt	H
c	Et	$COOSiMe_3$	H
d	Et	CN	H
e	Et	COOEt	6-Br
f	Et	COOEt	6-Cl
g	Et	COOEt	7-NEt_2



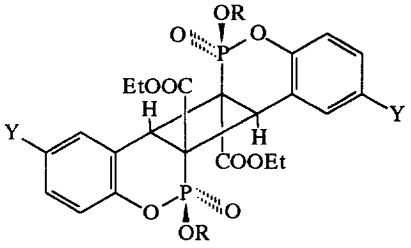
9



10



11 (a-c)



12 (b)

a R = OMe, Y =H; **b** R = OEt, Y = H
e R = OEt, Y =6-Br; **f** R = OEt, Y =6-Cl

From the reaction of salicylaldehyde **5a** with the trimethylsilyl ester **6c** the ethyl oxaphosphorin-3-carboxylate **8b** and the carboxylic acid **9** were isolated, as a result of the reesterification with ethanol and the hydrolysis respectively of the initially formed trimethylsilyl 1,2-benzoxaphosphorine-3-carboxylate **8c**. As was expected, from the reactions of the salicylaldehyde **5a** with the phosphonates **6b**, **6c** and **6d** the same diethyl coumarin-3-phosphonate **7b** was isolated, obviously in the last case as a result of the hydrolysis, under the reaction conditions, of the initially formed iminocoumarin **10**[20].

Table 1. Reaction Conditions and Yields of Products **7b** and **8d** obtained from the Interaction of Acetonitrile Ethyl Phosphonate **6d** and Salicylaldehyde **5a**

Method	Reaction conditions	Overall yield (%)	Yield (%)		
			7b	**8d**	7:8
A	Toluene (60 ml)/ piperidine/Dean-Stark trap	69	45	24	1.8:1
A_1	Toluene (40 ml)/ piperidine/Dean-Stark short distance trap	52	17	35	0.5:1
A_2	Toluene (40 ml)/ piperidine + acetic acid (2-3 drops)/Dean-Stark short distance trap	38	31	7	4.2:1
A_3	Abs. ethanol (40 ml)/piperidine + acetic acid (2-3 drops)	37	34	3	11.3:1
B	Tetrahydrofuran/titanium tetrachloride/ pyridine	49	49	0	49 -
C	toluene/β-alanine/piperidine acetate/ Dean-Stark short distance trap	55	47	8	5.8:1
D	Toluene/piperidine/mol. siev. 4A, reflux, 3h	60	42	18	2.3:1
E	Toluene/ mol. siev. 4A, reflux, 3h	34	34	0	34 -
F	Without solvent; alumina (Al_2O_3), 25°, 1h	33	33	0	33 -
G	Without solvent; Na 13X-zeolite, 25°, 10 min	45	45	0	45 -
H	Without solvent; florisil, 25°, 48h	37	37	0	37 -

From the reactions of **5a-c** and **6a,b** small amounts of the corresponding 1,2-benzoxaphosphorine head-to-tail dimers **11** and **12** were also isolated.

In order to explore the influence of the reaction conditions on the yields and the products formed from the above condensation reactions, salicylaldehyde **5a** and acetonitrile diethylphosphonate **6d** were reacted under different experimental conditions (Methods A-H), and the findings are presented in Table 1. The results of the condensation of the benzaldehydes **5a-d** with the phosphonoacetates **6a-c**, carried out mainly under Methods A, A_1, B and C, are given in Table 2. With the exception of the reaction of 7-dimethylamino-benzaldehyde **5d** with **6b** under Method B (Table 2), the overall yields of the reaction products, mainly **7** and **8**, obtained from the above reaction range from 20-98%.

An inspection on the results given in the Tables 1 and 2 reveals that, when the reactions between **5** and **6** were taking place in solution and in the presence of a base (the usual Knoevenagel conditions), both the coumarin-3-phosphonates **7** and the 1,2-benzoxaphosphorines **8** were isolated (Methods A, A_1, A_2, A_3, C and D) whereas in the absence of base or without solvent and in the presence of an adsorbent (Methods E, F, G and H, Table 1) only the coumarin-3-phosphonates **7**, but not the oxaphosphorins **8**, were isolated. Compounds **7** were also the only product from the above reactions, when carried out in tetrahydrofuran in the presence of base and titanium tetrachloride[21,22], (Method B, Tables 1 and 2).

The regioselectivity of the reactions studied (Tables 1 and 2) could be explained (Scheme 1) by accepting a stereoselectivity in the formation of the intermediates **i** and **iii** in the first step of the reaction (aldol condensation), from which, by a water trans-elimination, the *E*-, **ii** (Scheme 1), and *Z*-, **iv**, isomers are formed leading, under ring closure, to the formation of the coumarin-3-phosphonate **7** and the 1,2-oxaphosphorine **8** respectively. It is clear that the intermediate **iii** suffers a much stronger steric interaction between the bulky phosphonate group and the aromatic ring, staying gauche to each other, in respect to the intermediate **i**, where the two bulky groups accept an *anti*-disposition.

Table 2. Products and Yields obtained from the Reaction of **5a–d** and **6a–d** under Various Experimental Conditions

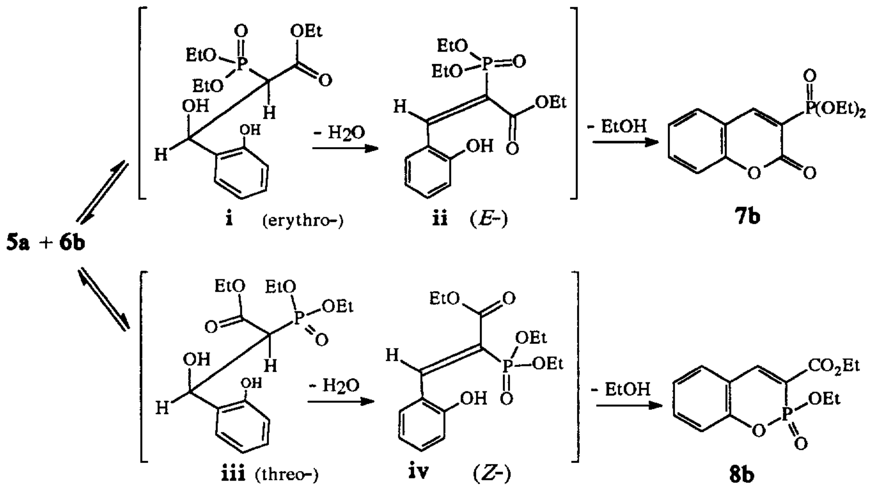
Starting compounds 5		6				Yield of Products (%)				
R	X	Y	7/8	Method	Overall yield (%)	7	8	9	11 (12)	7 : 8[a]
Me	COOEt	H	a	A	51	33	11		7	1.8 : 1
				A_1	56	27	21		8	0.9 : 1
				B	20	20	0			20 -
Et	COOEt	H	b	A	87	70	9		7 (1)	4.1 : 1
				A_1	98	84	14			6.0 : 1
				B	50	50	0			50 -
				C	74	66	8		8 (2)	3.6 : 1
Et	$COOSi(Me)_3$	H	c[b]	A	59	47	8	4		3.8 : 1
				C	28	20	2	6		2.5 : 1
				D	73	57	9	7		3.6 : 1
Et	CN	H	d[c]	A	69	45	24			1.8 : 1
				A_1	52	17	35			0.5 : 1
				B	49	49	0			49 -
				C	55	47	8			5.9 : 1
				D	60	42	18			2.3 : 1
Et	COOEt	6-Br	e	A	98	77	19		2	3.7 : 1
				B	81	81	0			81 -
				C	50	40	4		6	4.0 : 1
Et	COOEt	6-Cl	f	A	78	65	9		4	5.0 : 1
				B	71	71	0			71 -
				C	67	41	20		6	1.6 : 1
Et	COOEt	$7\text{-}NEt_2$	g	A	81	64	17			3.8 : 1
				B	3	3	0			3 -
				C	86	71	15			4.7 : 1

[a] In the yields of **8** used for calculation the **7**:**8** ratios are also included the corresponding yields of their transformation products **9**, **11** and **12**.

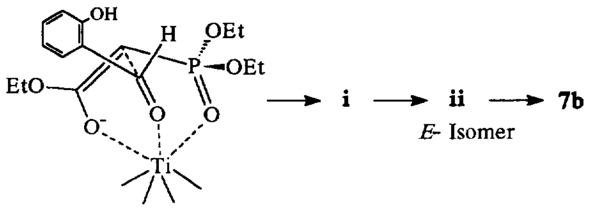
[b] Fron the reaction of **5a** and **6c** compounds **7b** and **8b** were isolated.

[c] Fron the reaction of **5a** and **6d** compounds **7b** and **8d** were isolated.

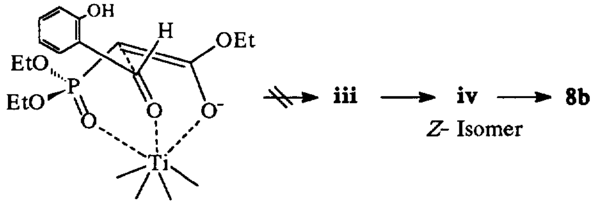
On the other hand the above reactions showed a complete regioselectivity, i.e. only the coumarin-3-phosphonates **7**, but not oxaphosphorines **8**, were isolated when carried out in the presence of titanium tetrachloride (Method B, Tables 1 and 2) or in the presence of an adsorbent (Methods E, F, G and H, Table 1). This selectivity could be explained by accepting a complexation of the phosphonates **6** with titanium as depicted in Scheme 2. In such a case the orientation of the salicylaldehyde given in **v** and leading to the intermediates **i** and **ii** and thus in **7**, is much more favoured than that given in **vi**, where there are strong steric interactions between the bulky phosphonate group and the aromatic ring. Since this steric interaction appears in the first step, as the reactants approach each other in order to react, it prevents the formation of complex **vi**, which could lead to the intermediate **iii** and hence through the *Z*-isomer **iv** to the oxaphosphorines **8**, which indeed were not isolated when the reactions were performed under the conditions mentioned above. An analogous orientation of the reactants on the surface of the adsorbent could be accepted for the reactions carried out under the conditions given in Methods E, F, G and H, where also only the coumarin-3-phosphonates **7** were isolated. It is noted that Knoevenagel condensations of aldehydes with analogous active methylene compounds, carried out in the presence of aluminium oxide, gave only the corresponding E-isomers, of the type **ii** (Schemes 1 and 2)[23,24].



Scheme 1



Scheme 2



Scheme 3

Analytical and spectral data of the compounds isolated were in agreement with the proposed structures.

Differentiation of compounds **7** and **8** was made mainly by their ^{1}H and ^{13}C NMR spectra. In particular, the main difference in the ^{1}H NMR spectra of compounds **7** and **8** was the 4-H peak, which appeared as a doublet at $\delta = 8.33$-8.53 in compounds **7**, coupled to the exocyclic phosphorus atom with a $^{3}J_{HP} = 16.5$-17.3 Hz, whereas in compounds **8**, where the endocyclic P-2 stays *trans*, the 4-H appeared as a doublet at $\delta = 7.89$-8.25, but with a $^{3}J_{HP} = 34.6$-37.6 Hz, in agreement with coupling values given in the literature[14-16] for compounds of the same structure.

Although there are some differences in the ^{13}C NMR spectra of compounds **7** and **8** concerning the shifts of certain carbon atoms, of diagnostic importance were some coupling values exhibited between the phosphorus and certain carbons of the benzopyran ring system. Thus C-3 in compounds **7** appeared as a doublet at 106-117 ppm, with a $^1J_{CP}$ = 196-201 Hz, whereas in compounds **8** C-3 appeared at 108-120 ppm, but with a $^1J_{CP}$ = 176-181 Hz. In the ^{13}C NMR spectra of compounds **7** C-4 appeared as a doublet at ~ 152-154 ppm with a $^2J_{CCP}$ = 6.2-7.6 Hz and the carbonyl carbon, C-2, gave a doublet at 157-159 ppm, with a $^2J_{CCP}$ = 14-16 Hz. There was no or a very small coupling of C-4 with P-2 in compounds **8**, where C-4 appeared at 149-154 ppm. The carbonyl carbon of the 3-carboethoxy-group appeared at 163-165 ppm, with a $^2J_{CCP}$ = 12-13 Hz. Further C-8 and C-8a in compounds **8** gave doublets at 110-119 and 151-155 ppm with $^3J_{COCP}$ = 6.7-7.8 and $^2J_{COP}$ = 7.8-8.8 Hz respectively. It is interesting to note the high field shift of C-3 of about 10-11 ppm, and the increase of the $^1J_{CP}$, of about 4 Hz, found in the 7-dimethylaminoderivatives **7g** and **8f** in respect to the corresponding values in **7b** and **8b**, which both indicate an electron charge on C-3, due to an electron delocalization caused by the electron donor 7-dimethylamino-group.

The ^{31}P shifts measured for compounds **7e** and **7f** were found at ~9.8 ppm whereas for compounds **8b**, **8e** and **8f** were found at ~4.4-5.0 ppm, in agreement with the findings given for analogous compounds in the literature[13,15,25].

Photochemical head-to-tail dimerization of oxaphosphorines **8**. The oxaphosphorines **8a,b,e,f** were not stable in solution and when exposed to sunlight and/or during the separation on the column of the reaction mixtures small amounts of the corresponding head-to-tail dimers **11** and **12** were isolated.

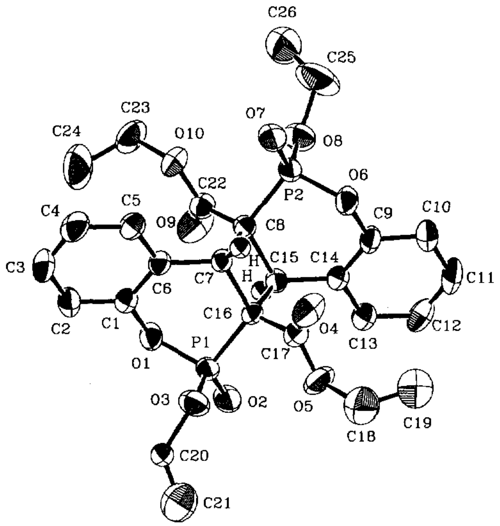
The photochemical [2+2] cyclodimerization of the mentioned oxaphosphorines **8** was confirmed by irradiating a chloroform solution of **8e** with the unfiltered light of a medium-pressure mercury vapour lamp, that yielded the dimer **11e** in good yield (60%). Photochemical dimerization of the oxaphosphorines **8b,e** was also achieved by allowing a chloroform solution of them to stay in direct sunlight. However, whereas the reaction of **8e** gave only one dimer, that with a symmetry centre, **11e**, the photodimerization of **8b** besides the symmetrical dimer **11b**, which was isolated in 82% yield, it also gave in small yield (8%) its phosphorus epimer **12b**. Compound **12b** when recrystallized from ethyl acetate was completely transformed to its symmetric phosphorus diastereomer **9b**.

The structure of dimers **11a,b,e,f** and **12b** was elucidated by their spectroscopic and analytical data and for the compounds **11b**,**e** and **12b** was confirmed by X-ray analyses.

In the ^1H NMR spectra of the symmetric dimers **11** of diagnostic importance were the peaks due to the two 6b-H and 12b-H protons (see **11** for numbering) of the oxaphosphorine rings, which appeared at δ = 5.3-5.4 with a characteristic pattern of an XX′ part of an AA′XX′ spin system as a result of their couplings with the two phosphorus atoms. Two apparent coupling values of 22.6 and 19.5 Hz were extracted from these peaks. In the non symmetric phosphorus stereoisomer **12b** however these two protons appeared at δ = 5.23 and 5.42, coupled with the phosphorus atoms with ^3J = 21.5 Hz in the first case and with ^3J = 16.5 and 22.7 in the second.

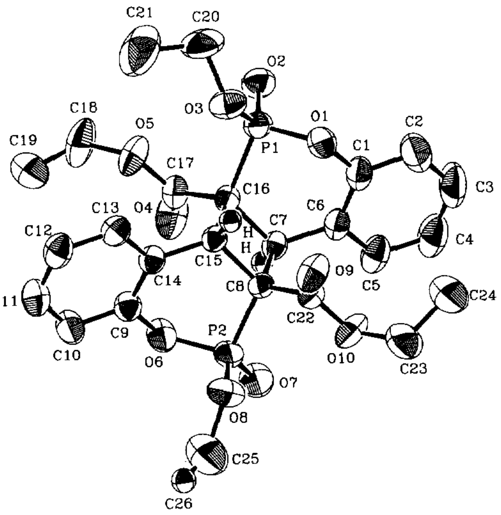
In the ^{13}C NMR spectra the two C-6b and C-12b carbons gave one triplet peak at ~42.5 ppm, coupled with both phosphorus atoms with J = 5.5 Hz, and the C-6a and C-12a carbons appeared at ~50 ppm showing coupling values of $^1J_{CP}$ = 137 and $^3J_{CCCP}$ ~5 Hz. C-6c and C-12c carbons appeared at ~122 ppm showing two $^3J_{CCCP}$ of ~14 and ~5 Hz. The non symmetric dimer **12b** showed in its ^{13}C NMR spectrum peaks for each carbon of the two benzo-oxaphosphorine rings and of the four ethoxy groups.

The X-ray structures of compounds **11b**,e and **12b** are given in Figures 1, 2, and 3. As it can be seen structures **11b** and **11e** are centrosymmetric, with the two ethoxy groups on the phosphorous atoms having an exo-disposition and the two oxygen atoms of the P=O moiety showing an endo-orientation. In **12b**



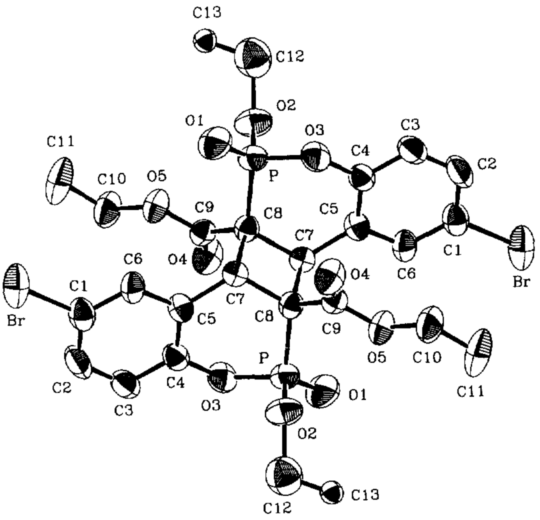
ROTATIONS: -165.0 ABOUT X, 188.0 ABOUT Y, 0.0 ABOUT Z

Figure 1. ORTEP view of compound **11b**



ROTATIONS: -10.0 ABOUT X, 8.0 ABOUT Y, 0.0 ABOUT Z

Figure 2. ORTEP view of compound **12b**



ROTATIONS: -13.0 ABOUT X, 0.0 ABOUT Y, 0.0 ABOUT Z

Figure 3. ORTEP view of compound **11e**

although the general geometry of the molecule is remained, there is no symmetry centre, since the stereochemistry of one of the phosphorus atoms is reversed in respect to **11b**, with the ethoxy group showing an endo- and the oxygen of the P=O bond an exo-orientation.

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. IR spectra were recorded with a Specord 71 IR, Perkin-Elmer 297 or Perkin-Elmer PE 983 G spectrophotometers. ^{1}H-NMR and ^{13}C-NMR spectra, reported in δ units, were obtained with a Brucker AM 300 (at 300 and 75.4 MHz respectively) or a Brucker WM 250 (at 250 and 62.9 MHz respectively) instruments. All NMR spectra were obtained by using TMS as internal standard in $CDCl_3$ or DMSO-d_6 solutions. ^{31}P-NMR spectra were recorded on a Brucker AC 200 (81.0 MHz) in $CDCl_3$ with 85% phosphoric acid as an external reference. E.I. mass spectra were obtained at 70 eV with a VG TS-250 spectrometer. Elemental analyses of C, H, P and N were carried out in the Laboratory of Elemental Analysis at the Department of Organic Chemistry of the University of Sofia. Column chromatography was carried out on silica gel (Merck 60; 0.063-0.2 mm), using *n*-hexane/EtOAc mixtures of increasing polarity as eluent. A Hanovia (UVS 500) medium-pressure mercury vapour lamp was used as light source for the irradiation of compounds **8**. The samples were placed in a cell which was thermostatically controlled at 15 °C.

Preparation of the Starting Materials. Phosphonoacetates **6a-d** were prepared by means of the Michaelis-Arbuzov reaction as described in the literature[26,27]. Salicylaldehydes **5a-d** were available commercially.

Reaction of the phosphonoacetates 6 with salicylaldehydes 5. - General Procedure. Depending on the reaction conditions (solvent, catalyst, temperature, adsorbent used) the following methods are distinguished:

Method A : To a solution of the corresponding phosphonoacetates **6** (20 mmoles) and salicylaldehyde (20 mmoles) in dry toluene (60 ml) piperidine (0.5 ml) was dropped. The solution was then refluxed under a Dean-Stark trap until the starting materials were consumed (tlc monitoring). After evaporation of the solvent under reduced pressure the residue was chromatographed on a silica gel column with *n*-hexane-ethyl acetate (of increasing polarity) as eluent.

Method A_1: The same as in method A but with 40 ml of toluene and short distance Dean-Stark apparatus.

Method A_2: The same as with A_1, but with acetic acid (2 drops) as catalyst.

Method A_3: As in A_2, but the reaction was performed in absolute ethanol (40 ml) as solvent.

Method B: It was used the method given in the literature[22]. A solution of **6** (20 mmoles) and the corresponding salicylaldehyde (20 mmoles) in tetrahydrofuran (60 ml) and in the presence of equimolecular amounts of titanium tetrachloride/pyridine was refluxed. The reaction mixture was worked up as described in the literature[22] and recrystallized from *n*-hexane/diethyl ether to give only the 3-phosphonocoumain isomer (**7**).

Method C : As in A_2 but in the presence β-alanine/piperidine acetate, as described in the literature [15].

Method D: The reaction was carried out in toluene (40 ml) under reflux for 3 hours and in the presence of piperidine and molecular shieves 4A.

Method E: As in method D but without piperidine. Refluxing for 3 hours.

Method F: A mixture of the phosphonoacetate (20 mmoles) and the corresponding salicylaldehyde (20 mmoles), in the presence of aluminium oxide (3 g), was stirred at room temperature for 1 hour. The mixture then was chromatographed in the usual manner.

Method G: As in method F, but in the presence of Na13X-zeolite (2 g) and with stirring for 10 minutes.
Method H: A mixture of **5d** (20 mmoles) and **6d** (20 mmoles) was stirred at room temperature for 48 hours and in the presence of Florisil (2 g).

Dimethyl 2-oxo-2H-1-benzopyran-3-phosphonate **(7a)**: From **5a** and **6a**: (yields and methods prepared as in Table 2), m.p. 70-71 °C (*n*-hexane). - IR ($CHCl_3$): ν = 1730, 1615, 1560, 1025 cm^{-1}. - ^{1}H-NMR ($CDCl_3$) (250 MHz): δ = 3.91 (d, J=11.3 Hz; CH_3), 7.32-7.39 (m; 2H), 7.59-7.69 (m; 2H), 8.53 (d, J=17.3 Hz; 1H, 4-H). - ^{13}C-NMR ($CDCl_3$) (62.9 MHz): δ = 53.73 (d, $^2J_{COP}$=5.7 Hz; CH_3), 116.92 (d, $^1J_{CP}$=197.2 Hz; C-3), 116.93 (C-8), 118.12 (d, $^3J_{CCCP}$=15.0 Hz; C-4a), 124.93 (C-6), 129.55 (C-5), 134.35 (C-7), 153.87 (d, $^2J_{CCP}$=6.0 Hz; C-4), 155.34 (C-8a), 158.84 (C=O). - MS: m/z (%) = 255 (53), 254 [M^+] (100), 226 (15), 223 (32), 209 (5), 196 (90), 180 (8), 165 (12), 161 (7), 149 (7), 146 (22), 145 (12), 132 (16), 131 (45), 118 (47), 115 (13), 109 (16), 93 (29), 90 (17), 89 (46).

$C_{11}H_{11}O_5P$	(254.18)	Calcd.	C 51.98	H 4.36	P 12.18.
		Found:	C 52.32	H 4.38	P 11.92.

Ethyl 2-methoxy-2-oxo-2H-1,2-benzoxaphosphorine-3-carboxylate **(8a)**: From **5a** and **6a**: (yields and methods prepared as in Table 2), m.p. 95-97 °C (*n*-hexane). - IR ($CHCl_3$): ν = 1715, 1610, 1560, 1040 cm^{-1}. - ^{1}H-NMR ($CDCl_3$) (250 MHz): δ = 1.41 (t, J=7.2 Hz; 3H, CH_3), 3.99 (d, J=12.1 Hz; 3H, CH_3), 4.29-4.51 (m; 2H, CH_2), 7.18-7.27 (m; 2H), 7.46-7.54 (m; 2H), 8.25 (d, J=37.2 Hz; 1H, 4-H). - ^{13}C-NMR ($CDCl_3$) (62.9 MHz): δ = 14.08 (CH_3), 54.76 (d, $^2J_{COP}$=5.9 Hz; CH_3), 61.84 (CH_2), 118.11 (d, $^1J_{CP}$=179.2 Hz; C-3), 118.62 (d, $^3J_{CCOP}$=6.7 Hz; C-8) 119.41 (d, $^3J_{CCCP}$=15.5 Hz; C-4a), 124.12 (C-6), 131.50 (C-5), 133.59 (C-7), 150.30 (C-8a), 152.47 (d, $^2J_{COP}$=8.6 Hz; C-4), 163.49 (d, $^2J_{CCP}$=12.3 Hz; C=O). - MS: m/z (%) = 269 (21), 268 (84) [M^+], 240 (22) 224 (17), 223 (100), 209 (23), 197 (13), 196 (99), 193 (11), 173 (18), 166 (19), 165 (16), 159 (16), 146 (23), 137 (29), 136 (11), 132 (11), 131 (30), 118 (39), 116 (17), 115 (32), 105 (8), 101 (16), 90 (20), 89 (58), 77 (11).

$C_{12}H_{13}O_5P$	(268.20)	Calcd.	C 53.74	H 4.89	P 11.55.
		Found:	C 53.54	H 4.57	P 11.15.

Diethyl 6a,6b,12a,12b-tetrahydro-exo,exo-6,12-dimethoxy-endo,endo-6,12-dioxo-6H,12H-cyclobuta[1,2-c:3,4-c']bis[1,2]benzoxaphosphorine-trans-6a,12a-dicarboxylate **(9a)**: This compound was isolated from the reaction of **5a** and **6a**: (yields and methods prepared as in Table 2), m.p. 235-237 °C (ether). - IR (nujol): ν = 1735, 1615, 1490, 1270, 1220 cm^{-1};.- ^{1}H-NMR ($CDCl_3$) (300 MHz): δ = 0.84 (t, J=7.1 Hz; 3H, CH_3), 3.72 (d, J=11.1 Hz; CH_3O), 3.70-3.87 (m; 2H, CH_2O), 5.42 (dd, J=19.5 and 22.6 Hz, 2H, 6b/12b-H), 7.08 (d, J=8.1 Hz, 2H, 4/10-H), 7.18 (dd as t, J=7.5 Hz, 2H, 2/8-H), 7.32 (dd as t, J=7.5 Hz; 2H, 3/9-H), 7.52 (dd, J= 7.6 and 1.7 Hz; 2H, 1/7-H). - ^{13}C-NMR ($CDCl_3$) (75.4 MHz): δ = 15.3 (CH_3), 42.7 (t, $^2J_{CCP}$=5.5 Hz; C-6b/C-12b), 50.6 (dd, $^1J_{CP}$=137.9, $^3J_{CCCP}$=5.2 Hz; C-6a/C-12a), 53.6 (d, $^2J_{COP}$=8.1 Hz; CH_3OP), 62.4 (CH_2O), 119.4 (C-4/C-10), 122.8 (dd, $^3J_{CCCP}$=13.6 and 5.0 Hz; C-6c/C-12c), 125.2 (C-2/C-8), 130.3 (C-3/C-9), 132.0 (C-1/C-7), 151.5 (C-4a/C-10a), 166.26 (C=O). - MS: m/z (%) = 537 (5), 536 [M^+] (8), 463 (4), 418 (6), 362 (13), 360 (15), 315 (7), 289 (27), 287 (34), 262 (58), 260 (37), 224 (21), 223 (71), 196 (100), 166 (13), 157 (31), 144(24), 118 (33), 115(25), 91(23), 89(62).

$C_{24}H_{26}O_{10}P_2$	(536.40)	Calcd.	C 53.74	H 4.89	P 11.55.
		Found:	C 53.94	H 5.05	P 11.63.

Diethyl 2-oxo-2H-1-benzopyran-3-phosphonate **(7b)**. From salicylaldehyde (**5a**) and **6b** (and from **5a** with **6c** and **6d**): (yields and methods prepared as in Table 1 and 2), m.p. 72-74 °C (*n*-hexane) (lit.[13] 65-66 °C,[14] 65 °C,[15] 92 °C). - IR ($CHCl_3$): ν = 1725, 1615, 1570, 1245, 1030 cm^{-1}. - ^1H-NMR ($CDCl_3$) (250 MHz): δ = 1.40 (t, J=7.0 Hz; 6H, CH_3), 4.18-4.40 (m; 4H, CH_2), 7.33-7.39 (m; 2H), 7.61-7.70 (m; 2H), 8.53 (d, J=17.2 Hz; 1H, 4-H). - ^{13}C-NMR ($CDCl_3$) (62.9 MHz): δ =15.72 (d, $^3J_{CCOP}$=5.8 Hz; CH_2), 62.62 (d, $^2J_{COP}$=5.8 Hz; CH_2), 116.04 (C-8), 117.21 (d, $^3J_{CCCP}$=14.0 Hz; C-4a), 117.25 (d, $^1J_{CP}$=196.8 Hz; C-3), 124.27 (C-6), 128.81 (C-5), 133.60 (C-7), 152.44 (d, $^2J_{CCP}$=6.7 Hz; C-4), 154.48 (C-8a), 157.38 (d, $^2J_{CCP}$=14.2 Hz; C=O). - MS: m/z (%) = 283 (50), 282 [M^+] (59), 254 (4), 253 (3), 237 (5), 226 (9), 210 (30), 209 (68), 198 (7), 182 (46), 175 (10), 174 (85), 173 (97), 172 (13), 153 (15), 147 (15), 146 (100), 144 (25), 133 (16), 131 (12), 118 (72), 116 (14), 113 (25), 105 (17), 90 (52), 89 (99), 77 (20).

$C_{13}H_{15}O_5P$	(282.22)	Calcd.	C 55.32	H 5.32	P 11.00.
		Found	C 55.21	H 5.26	P 11.24

Ethyl 2-ethoxy-2-oxo-2H-1,2-benzoxaphosphorine-3-carboxylate **(8b)**. From salicylaldehyde (**5a**) and **6b** (and from **5a** with **6c**): (yields and methods prepared as in Table 2), m.p. 67-68 °C (*n*-hexane). - IR ($CHCl_3$): ν = 1715, 1610, 1560, 1205, 1035 cm^{-1}. - ^1H-NMR ($CDCl_3$) (250 MHz): δ = 1.40 (t, J=7.1 Hz; 3H, CH_3), 1.41 (t, J=7.1 Hz; 3H, CH_3), 4.28-4.51 (m; 4H, CH_2), 7.17-7.24 (m; 2H), 7.45-7.53 (m; 2H), 8.24 (d, J=37.0 Hz; 1H, 4-H). - ^{13}C-NMR ($CDCl_3$) (62.9 MHz): δ = 13.89 (CH_3), 16.10 (d, $^3J_{CCOP}$=6.0 Hz; CH_2), 61.57 (CH_2), 64.46 (d, $^2J_{COP}$=6.2 Hz; CH_2), 118.18 (d, $^1J_{CP}$=176.9 Hz; C-3), 118.39 (d, $^3J_{CCOP}$=7.3 Hz; C-8) 119.26 (d, $^3J_{CCCP}$=15.8 Hz; C-4a), 123.89 (C-6), 131.34 (C-5), 133.35 (C-7), 149.98 (C-8a), 152.32 (d, $^2J_{COP}$=8.3 Hz; C-4), 163.33 (d, $^2J_{CCP}$=12.5 Hz; C=O). - ^{31}P-NMR: δ = 5.02 (dt, J=37.0 and 8.5 Hz). - MS: m/z (%) = 283 (6), 282 (33) [M^+], 255 (3), 254 (24) 237 (18), 210 (20), 209 (57), 192 (8), 183 (12), 182 (100), 173 (13), 153 (20), 146 (20), 136 (7), 128 (6), 118 (33), 105 (8), 90 (17), 89 (40).

$C_{13}H_{15}O_5P$	(282.22)	Calcd.	C 55.32	H 5.32	P 11.00.
		Found	C 55.20	H 4.92	P 11.32

Diethyl 6a,6b,12a,12b-tetrahydro-exo,exo-6,12-diethoxy-endo,endo-6,12-dioxo-6H,12H-cyclobuta[1,2-c:3,4-c']bis[1,2]benzoxaphosphorine-trans-6a,12a-dicarboxylate **(11b)**: This compound was isolated from the reaction of **5a** and **6b**: (yields and methods prepared as in Table 2), m.p. 217-219 °C (ether). - IR ($CHCl_3$): ν = 1745, 1600, 1475, 1030 cm^{-1}. - ^1H-NMR ($CDCl_3$) (300 MHz): δ = 0.83 (t, J=7,1 Hz; 6H, CH_3), 1.16 (t J=7.1 Hz; 6H, CH_3), 3.69-3.89 (m; 4H, CH_2OP), 4.04-4.24 (m; 4H, CH_2OCO), 5.42 (XX' part of an AA'XX' spin system as dd, J=19.7 and 22.5 Hz; 2H, 6b/12b-H), 7.04 (d, J=8.0 Hz; 2H, 4/10-H), 7.17 (dd as t, J=7.5 Hz; 2H, 2/8-H), 7.29 (dd as t, J=8.0 Hz; 2H, 3/9-H), 7.52 (d, J=7.2 Hz; 2H, 1/7-H). - ^{13}C-NMR ($CDCl_3$) (75.4 MHz): δ = 13.52 (CH_3), 16.16 (d, $^3J_{CCOP}$=5.8 Hz; CH_3), 42.69 (t, $^2J_{CCP}$=5.4 Hz; C-6b/C-12b), 50.70 (d, $^1J_{CP}$=137.9 Hz; C-6a/C-12a), 62.30 (CH_2), 63.67 (d, $^2J_{COP}$=8.2 Hz; CH_2OP), 119.34 (d, $^3J_{CCOP}$=5.2 Hz; C-4/C-10), 122.9 (dd, $^3J_{CCCP}$=13.9 and 5.1 Hz; C-6c/C-12c), 125.04 (C-2/C-8), 130.11 (C-3/C-9), 132.08 (C-1/C-7), 151.52 (d, $^2J_{COP}$=9.0 Hz; C-4a/C-10a), 166.24 (CO). - MS: m/z (%) = 565 (9), 564 [M^+] (42), 519 (7), 518 (8), 491 (24), 490

(20), 445 (19), 283 (46), 282 (76), 255 (14), 254 (100), 237 (87), 236 (22), 211 (62), 210 (72), 209 (73), 183 (25), 182 (72), 175 (45), 164 (14), 153 (39), 146 (49), 134 (12), 118 (73), 101 (21), 89 (53), 77 (13).

$C_{26}H_{30}O_{10}P_2$	(564.44)	Calcd.	C 55.32	H 5.32	P 11.00.	
		Found	C 55.04	H 4.83	P 10.67	

Diethyl 6a,6b,12a,12b-tetrahydro-exo,endo-6,12-diethoxy-endo,exo-6,12-dioxo-6H,12H-cyclobuta[1,2-c:3,4-c']bis[1,2]benzoxaphosphorine-trans-6a,12a-dicarboxylate **(12b)**: This compound was isolated from the reaction of **5a** and **6b**: (yields and methods prepared as in Table 2), m.p. 251-253 °C (ether). - IR (CHCl$_3$): ν = 1745, 1610 (w), 1485, 1030 cm^{-1}. - ^{1}H-NMR (CDCl$_3$) (300 MHz): δ = 0.85 (t, J=7,1 Hz; 3H, CH$_3$), 0.90 (t, J=7,1 Hz; 3H, CH$_3$), 1.15 (t J=7.0 Hz; 6H, CH$_3$), 1.55 (t J=7.1 Hz; 6H, CH$_3$), 3.65 (dq, J=7.1 and 10.7 Hz; 1H, CH2), 3.71-3.87 (m; 2H, CH$_2$OP), 3.94 (dq, J=7.1 and 10.7 Hz; 1H, CH$_2$), 4.04-4.24 (m; 2H, CH$_2$OCO), 4.38-4.75 (m; 2H, CH$_2$OCO), 5.23 (t, J=21.5 Hz; 1H) and 5.42 (dd, J=16.8 and 21.4 Hz; 1H) (6b-H/12b-H), 7.04-7.20 (m; 4H), 7.27-7.35 (m; 3H), 7.48 (d, J=7.1 Hz; 1H, 1,7-H). - ^{13}C-NMR (CDCl$_3$) (75.4 MHz): δ = 13.52, 13.53 (CH$_3$), 16.16 (d, $^3J_{CCOP}$=5.8 Hz; CH$_3$), 16.62 (d, $^3J_{CCOP}$=6.3 Hz; CH$_3$), 42.64 (t, $^2J_{CCP}$=4.7 Hz) and 43.73 (t, $^2J_{CCP}$=6.3 Hz) (C-6b/C-12b), 50.20 (dd, $^1J_{CP}$=134.2 and $^3J_{CCCP}$= 4.2 Hz) and 51.22 (dd, $^1J_{CP}$=136.8 and $^3J_{CCCP}$= 6.4 Hz) (C-6a/C-12a), 62.33, 63.34 (CH$_2$), 63.65 (d, $^2J_{COP}$=7.0 Hz; CH$_2$OP), 65.12 (d, $^2J_{COP}$=5.4 Hz; CH$_2$OP), 119.60 (d, $^3J_{CCOP}$=4.6 Hz) and 120.23 (d, $^3J_{CCOP}$=4.6 Hz) (C-4/C-10), 122.87 (dd, $^3J_{CCCP}$=14.0 and 5.6 Hz) and 123.61 (dd, $^3J_{CCCP}$=13.3 and 3.9 Hz) (C-6c/C-12c), 124.93, 125.15 (C-2/CC-8), 130.29 (C-3/C-9), 131.08, 132.08 (C-1/C-7), 150.68 (d, $^2J_{COP}$=5.4 Hz) and 151.74 (d, $^2J_{COP}$=8.5 Hz) (C-4a/C-10a), 166.23 (d, $^2J_{CCP}$=1.8 Hz; CO), 166.78 (dd, $^2J_{CCP}$=2.1 and $^4J_{CCCCP}$=1.1 Hz; CO). - MS: m/z (%) = 565 (4), 564 [M$^+$] (17), 519 (5), 491 (25), 490 (20), 417 (15), 389 (13), 284 (41), 283 (56), 282 (52), 255 (17), 254 (100), 238 (16), 237 (73), 236 (23), 210 (59), 209 (55), 192 (24), 183 (26), 182 (55), 173 (37), 164 (11), 153 (35), 146 (31), 134 (12), 118 (57), 101 (17), 90 (21), 89 (46), 77 (11).

$C_{26}H_{30}O_{10}P_2$	(564.44)	Calcd.	C 55.32	H 5.32	P 11.00.	
		Found	C 55.42	H 5.54	P 11.40	

3-Cyano-2-ethoxy-2-oxo-2H-1,2-benzoxaphosphorine **(8d)**: From salicylaldehyde (**5a**) and **6d**: (yields and methods prepared as in Tables 1 and 2), m.p. 91-93 °C (*n*-hexane). - IR (CHCl$_3$): ν = 2220, 1600, 1555, 1020 cm^{-1}. - ^{1}H-NMR (CDCl$_3$) (250 MHz): δ = 1.46 (t, J=7.1 Hz; 3H, CH$_3$), 4.34-4.48 (m; 2H, CH$_2$), 7.21-7.31 (m; 2H), 7.42 (dd, J=7.7 and 7.6 Hz; 1H), 7.51-7.58 (m; 1H), 7.89 (d, J=34.6 Hz; 1H, 4-H). - ^{13}C-NMR (CDCl$_3$) (62.9 MHz): δ = 16.32 (d, $^3J_{CCOP}$=5.9 Hz; CH$_2$), 65.47 (d, $^2J_{COP}$=5.9 Hz; CH$_2$), 119.13 (d, $^3J_{CCOP}$=7.7 Hz; C-8), 124.86 (C-6), 131.19 (C-5), 134.38 (C-7), 153.86 (C-4). - MS: m/z (%) = 236 (8), 235 (35) [M$^+$], 208 (15), 207 (100), 206 (10), 191 (11), 190 (5), 179 (3), 144 (3), 142 (13), 136 (11), 133 (8), 115 (13), 114 (7), 106 (5), 89 (7), 77 (3).

$C_{11}H_{10}O_3NP$	(235.18)	Calcd.	C 56.18	H 4.29	P 13.17	N 5.96
		Found	C 56.24	H 4.37	P 13.11	N 5.74

Diethyl 6-bromo-2-oxo-2H-1-benzopyran-3-phosphonate **(7e)**: From **5b** and **6b**: (yields and methods prepared as in Table 2), m.p. 109-110 °C (ether)) (lit.[13] 110-111 °C, [15] 103 °C). - IR (CHCl$_3$): ν = 1735, 1615, 1560, 1030 cm^{-1}. - ^{1}H-NMR (CDCl$_3$) (250 MHz): δ = 1.39 (t, J=7.3 Hz; 6H, CH$_3$), 4.17-4.39 (m; 4H, CH$_2$), 7.24-7.29 (m; 1H, 8-H), 7.69-7.74 (m; 2H), 8.42 (d, J=17.1 Hz; 4-H). - ^{13}C-NMR (CDCl$_3$) (62.9 MHz): δ = 16.39 (d,

$^{3}J_{CCOP}$=5.9 Hz; CH$_2$), 63.60 (d, $^{2}J_{COP}$=5.9 Hz; CH$_2$), 117.43 (C-6), 118.65 (C-8), 119.53 (d, $^{1}J_{CP}$=196.3 Hz; C-3), 119.54 (d, $^{3}J_{CCCP}$=14.3 Hz; C-4a), 131.45 (C-5), 136.83 (C-7), 151.70 (d, $^{2}J_{CCP}$=6.7 Hz; C-4), 154.11 (C-8a), 157.68 (C=O). - ^{31}P-NMR (81 MHz): δ 9.76 (lit.[13,25] 5.12, [15] 9.81). - MS: m/z (%) = 363 (22), 362 (32), 361 (19), 360 (37) [M$^+$], 290 (13), 289 (31), 288 (22), 287 (28), 262 (29), 260 (30), 254 (44), 253 (100) 252 (56), 251 (87), 226 (39), 224 (48), 210 (15), 198 (36), 196 (39), 169 (23), 167 (21), 144 (11), 117 (16), 115 (27), 89 (53), 88 (35),77 (16).

$C_{13}H_{14}O_5BrP$	(361.15)	Calcd.	C 43.23	H 3.90	P 8.58.
		Found	C 43.13	H 3.94	P 8.85.

Ethyl 6-bromo-2-ethoxy-2-oxo-2H-1,2-benzoxaphosphorine-3-carboxylate **(8e)**: From **5b** and **6b**: (yields and methods prepared as in Table 2), m.p. 71-73 °C dec (*n*-hexane). - IR (CHCl$_3$): ν = 1725, 1620, 1560, 1030 cm^{-1};.- ^{1}H-NMR (CDCl$_3$) (250 MHz): δ = 1.39 (t, J=7.1 Hz; 3H, CH$_3$), 1.41 (t, J=7.0 Hz; 3H, CH$_3$), 4.32-4.48 (m; 4H, CH$_2$), 7.08 (d, J=8.5 Hz; 1H, 8-H), 7.55-7.61 (m; 2H), 8.13 (d, J=36.8 Hz; 1H, 4-H). - ^{13}C-NMR (CDCl$_3$) (62.9 MHz): δ = 14.12 (CH$_3$), 16.35 (d, $^{3}J_{CCOP}$=5.7 Hz; CH$_2$), 62.10 (CH$_2$), 65.08 (d, $^{2}J_{COP}$=5.9 Hz; CH$_2$), 116.39 (C-6), 119.88 (d, $^{1}J_{CP}$=176.8 Hz; C-3), 120.48 (d, $^{3}J_{CCOP}$=7.6 Hz; C-8), 121.14 (d, $^{3}J_{CCCP}\leq$19 Hz; C-4a), 133.57 (C-5), 136.05 (C-7), 148.64 (C-4), 151.47 (d, $^{2}J_{COP}$=7.8 Hz; C-8a), 163.23 (d, $^{2}J_{CCP}$=13.0 Hz; C=O). - ^{31}P-NMR (81 MHz): δ = 4.38 (dt, J=36.8 and 8.5 Hz). - MS: m/z (%) = 363 (11), 362 (51), 361 (11), 360 (49), 334 (29), 332 (29), 317 (14), 315 (19), 289 (53), 287 (51), 272 (56), 263 (9), 262 (100), 260 (95), 253 (15) 251 (17), 233 (11), 231 (14), 226 (21), 224 (23), 198 (25), 196 (29), 169 (22), 167 (19), 117 (12), 89 (27), 88 (29).

$C_{13}H_{14}O_5BrP$	(361.15)	Calcd.	C 43.23	H 3.90	P 8.58.
		Found	C 43.34	H 3.94	P 8.86.

Diethyl 6a,6b,12a,12b-tetrahydro-2,9-dibromo-exo,exo-6,12-diethoxy-endo,endo-6,12-dioxo-6H,12H-cyclobuta[1,2-c:3,4-c']bis[1,2]benzoxaphosphorine-trans-6a,12a-dicarboxylate **(11e)**: This compound was isolated from the reaction of **5b** and **6b**: (yields and methods prepared as in Table 2), m.p. 272-274 °C (EtOAc). - IR (CHCl$_3$): ν = 1740, 1280, 1240, 1200, 1020 cm^{-1}. - ^{1}H-NMR (CDCl$_3$) (300 MHz): δ = 0.91 (t, J=7,1 Hz; 6H, CH$_3$), 1.19 (t J=7.1 Hz; 6H, CH$_3$), 3.72-3.96 (m; 4H, CH$_2$OP), 4.02-4.24 (m; 4H, CH$_2$OCO), 5.33 (XX' part of an AA'XX' spin system as dd, J=19.4 and 22.7 Hz; 2H, 6b/12b-H), 6.94 (d, J=8.6 Hz; 2H, 4/10-H), 7.43 (dd J=8.6 and 2.0 Hz; 2H, 3/9-H), 7.66 (d, J=2.0 Hz,; 2H, 1/7-H). - ^{13}C-NMR (CDCl$_3$) (75.4 MHz): δ = 15.56 (CH$_3$), 16.18 (d, $^{3}J_{CCOP}$=5.8 Hz; CH$_3$), 42.35 (t, $^{2}J_{CCP}$=5.5 Hz; C-6b/C-12b), 50.25 (dd, $^{1}J_{CP}$=137.2 and $^{3}J_{CCCP}$= 5.2 Hz; C-6a/C-12a), 62.65 (CH$_2$), 64.18 (d, $^{2}J_{COP}$=7.8 Hz; CH$_2$OP), 117.82 (C-2/C-8), 121.10 (d, $^{3}J_{CCOP}$=5.0 Hz; C-4/C-10), 124.82 (dd, $^{3}J_{CCCP}$=14.1 and 4.4 Hz; C-6c/C-12c), 133.25 (C-3/C-9), 134.44 (C-1/C-7), 150.55 (d, $^{2}J_{COP}$=9.0 Hz; C-4a/C-10a), 165.88 (CO). - MS: m/z (%) = 722 (3), 720 (M$^+$) (4), 719 (2), 646/644 (2), 546/544 (1.5), 390/388 (1), 362/360 (15), 317/315 (5), 290 (15), 289 (80), 288 (13), 287 (82), 262 (100), 260 (98), 253/251 (17), 233/231 (19), 208 (11), 198 (36), 196 (49), 169 (25), 169 (22), 144 (20), 117 (22), 91 (47), 89 (47), 88 (32), 84 (29), 77 (28).

$C_{26}H_{28}O_{10}Br_2P_2$	(722.28)	Calcd.	C 43.24	H 3.91	P 8.58.
		Found	C 43.08	H 3.65	P 8.87.

***Diethyl 6-chloro-2-oxo-2H-1-benzopyran-3-phosphonate* (7f)**: From **5c** and **6b**: (yields and methods prepared as in Table 2), m.p. 109-111 °C (ether) (lit.^{13} 70-75 °C). - IR (CHCl$_3$): ν = 1740, 1615, 1560, 1015 cm^{-1}. - ^{1}H-NMR (CDCl$_3$) (250 MHz): δ = 1.39 (t, J=7.0 Hz; 6H, CH$_3$), 4.17-4.39 (m; 4H, CH$_2$), 7.29-7.33 (m; 1H), 7.56-7.61 (m; 2H), 8.43 (d, J=17.2 Hz; 1H, 4-H). - ^{13}C-NMR (CDCl$_3$) (62.9 MHz): δ = 16.32 (d, $^3J_{CCOP}$=5.6 Hz; CH$_2$), 63.48 (d, $^2J_{COP}$=5.7 Hz; CH$_2$), 118.30 (C-8), 118.87 (d, $^3J_{CCCP}$=14.8 Hz; C-4a), 119.43 (d, $^1J_{CP}$=196.3 Hz; C-3), 128.02 (C-5), 130.04 (C-6), 133.93 (C-7), 151.72 (d, $^2J_{CCP}$=6.1 Hz; C-4), 153.53 (C-8a), 157.51 (d, $^2J_{CCP}$=14.2 Hz; C=O). - ^{31}P-NMR (81 MHz): δ 9.77 (m, ΣJ=49.2 Hz) (lit.^{13} 10.26). - MS: m/z (%) = 318 (11), 317 (10), 316 (33) [M$^+$], 288 (3), 287 (3), 246 (7), 245 (13), 244 (20), 243 (32), 218 (8), 216 (26), 209 (36), 208 (52), 207 (100), 182 (15), 180 (42), 168 (10), 166 (8), 154 (9), 152 (26), 125 (10), 123 (30), 115 (6), 89 (17), 75 (5).

$C_{13}H_{14}O_5ClP$ (316.68) Calcd. C 49.31 H 4.46 P 9.78
Found C 49.51 H 4.48 P 9.73

***Ethyl 6-chloro-2-ethoxy-2-oxo-2H-1,2-benzoxaphosphorine-3-carboxylate* (8f)**: From **5c** and **6b**: (yields and methods prepared as in Table 2), m.p. 75-77 °C (*n*-hexane). - IR (CHCl$_3$): ν = 1720, 1615, 1560, 1030 cm^{-1};.- ^{1}H-NMR (CDCl$_3$) (250 MHz): δ = 1.40 (t, J=7.2 Hz; 3H, CH$_3$), 1.42 (t, J=7.0 Hz; 3H, CH$_3$), 4.29-4.49 (m; 4H, CH$_2$), 7.15 (d, J=9.0 Hz; 1H, 8-H), 7.41-7.46 (m; 2H), 8.14 (d, J=36.8 Hz; 1H, 4-H). - ^{13}C-NMR (CDCl$_3$) (62.9 MHz): δ = 14.08 (CH$_3$), 16.32 (d, $^3J_{CCOP}$=5.9 Hz; CH$_2$), 62.06 (CH$_2$), 65.03 (d, $^2J_{COP}$=5.9 Hz; CH$_2$), 119.91 (d, $^1J_{CP}$=177.2 Hz; C-3), 120.15 (d, $^3J_{CCOP}$=7.7 Hz; C-8), 120.58 (d, $^3J_{CCCP}$=15.7 Hz; C-4a), 129.19 (C-6), 130.52 (C-5), 133.13 (C-7), 148.67 (C-4), 150.93 (d, $^2J_{COP}$=8.8 Hz; C-8a), 163.22 (d, $^2J_{CCP}$=12.9 Hz; C=O). - ^{31}P-NMR (81 MHz): δ 4.53 (dt, J=36.8 and 8.6 Hz). - MS: m/z (%) = 318 (15), 317 (81), 316 (61) [M$^+$], 290 (7), 288 (25), 273 (5), 271 (16), 246 (5), 245 (18), 244 (18), 243 (53), 219 (17), 218 (38), 217 (14), 216 (100), 209 (9), 207 (21), 187 (16), 182 (6), 180 (21), 154 (12), 152 (35), 130 (10), 128 (26), 116 (17), 115 (26), 105 (27), 91 (17), 89 (22), 77 (16).

$C_{13}H_{14}O_5ClP$ (316.68) Calcd. C 49.31 H 4.46 P 9.78
Found C 49.79 H 4.56 P 9.30

***Diethyl 6a,6b,12a,12b-tetrahydro-2,9-dichloro-exo,exo-6,12-diethoxy-endo,endo-6,12-dioxo-6H,12H-cyclobuta[1,2-c:3,4-c']bis[1,2]benzoxaphosphorine-trans-6a,12a-dicarboxylate* (11f)**: This compound was isolated from the reaction of **5c** and **6b**: (yields and methods prepared as in Table 2), m.p. 238-240 °C (ether). - IR (nujol): ν = 1740, 1490, 1280, 1235, 1220, 1030 cm^{-1}. - ^{1}H-NMR (CDCl$_3$) (300 MHz): δ = 0.91 (t, J=7,1 Hz; 6H, CH$_3$), 1.19 (t J=7.1 Hz; 6H, CH$_3$), 3.79-3.92 (m; 4H, CH$_2$OP), 4.12-4.21 (m; 4H, CH$_2$OCO), 5.22 (XX' part of an AA'XX' spin system as dd, J=19.5 and 22.6 Hz; 2H, 6b/12b-H), 7.00 (d, J=8.7 Hz; 2H, 4/10-H), 7.28 (dd J=8.7 and 2.5 Hz; 2H, 3/9-H), 7.52 (d, J=2.5 Hz; 2H, 1/7-H). - ^{13}C-NMR (CDCl$_3$) (75.4 MHz): δ = 15.53 (CH$_3$), 16.19 (d, $^3J_{CCOP}$=5.4 Hz; CH$_3$), 42.51 (t, $^2J_{CCP}$=5.4 Hz; C-6b/C-12b), 50.22 (dd, $^1J_{CP}$=137.0 and $^3J_{CCCP}$= 5.3 Hz; C-6a/C-12a), 62.62 (CH$_2$), 64.17 (d, $^2J_{COP}$=8.4 Hz; CH$_2$OP), 120.75 (d, $^3J_{CCOP}$=5.0 Hz; C-4/C-10), 124.45 (dd, $^3J_{CCCP}$=14.1 and 4.5 Hz; C-6c/C-12c), 130.26 (C-3/C-9), 130.42 (C-2/C-8), 131.61 (C-1/C-7), 150.04 (d, $^2J_{COP}$=8.8 Hz; C-4a/C-10a), 165.90 (CO). - MS: m/z (%) = 318/316 (100), 304/302 (4), 290/288 (33), 273/271 (31), 345 (27), 244 (33), 243 (83), 218 (35), 217 (14), 216 (90), 207 (23), 187 (120, 180 (28), 154/152 (42), 125 (10), 123 (22), 89 (26), 75 (6).

$C_{26}H_{28}O_{10}Cl_2P_2$	(633.36)	Calcd.	C 49.31	H 4.46	Cl 11.20	
		Found	C 49.00	H 4.26	Cl 11.61	

Diethyl 7-N,N-diethylamino-2-oxo-2H-1-benzopyran-3-phosphonate (**7g**): From **5d** and **6b**: (yields and methods prepared as in Table 2), m.p. 93-95 °C (ether). - IR ($CHCl_3$): ν = 1720, 1620, 1590, 1020 cm^{-1}. - ^{1}H-NMR ($CDCl_3$) (250 MHz): δ = 1.24 (t, J= 7.1 Hz; 6H, CH_3), 1.37 (t, J=7.1 Hz; 6H, CH_3), 3.46 (q, J=7.1 Hz; 4H), 4.11-4.33 (m; 4H, CH_2), 6.46 (d, J=2.3 Hz; 1H, 8-H), 6.61 (dd, J=2.3 and 9.0 Hz; 1H, 6-H), 7.33 (d, J=9.0 Hz; 1H, 5-H), 8.33 (d, J=16.5 Hz; 1H, 4-H). - ^{13}C-NMR ($CDCl_3$) (62.9 MHz): δ =.76 (CH_3), 15.73 (d, $^{3}J_{CCOP}$=6.4 Hz; CH_3), 44.39 (CH_2), 62.08 (d, $^{2}J_{COP}$=5.5 Hz; CH_2), 96.03 (C-8), 106.15 (d, $^{1}J_{CP}$=201.5 Hz; C-3), 106.99 (d, $^{3}J_{CCCP}$=14.1 Hz; C-4a), 108.83 (C-6), 130.15 (C-5), 152.08 (C-8a), 152.60 (d, $^{2}J_{CCP}$=7.4 Hz; C-4), 157.74 (C-7), 158.92 (d, $^{2}J_{CCP}$=15.6 Hz; C=O). - MS: m/z (%) = 353 (100) [M^{+}].

$C_{17}H_{24}O_5NP$	(353.35)	Calcd.	C 57.79	H 6.85	P 8.77	
		Found	C 57.84	H 6.53	P 8.65	

Ethyl 7-N,N-diethylamino-2-ethoxy-2-oxo-2H-1,2-benzoxaphosphorine-3-carboxylate (**8g**): From salicylaldehyde **5d** and **6b**: (yields and methods prepared as in Table 2), m.p. 71-73 °C (*n*-hexane/ether). - IR ($CHCl_3$): ν = 1705, 1630, 1585, 1030 cm^{-1}. - ^{1}H-NMR ($CDCl_3$) (250 MHz): δ = 1.20 (t, J= 7.1 Hz; 6H, CH_3), 1.37 (t, J=7.1 Hz; 3H, CH_3), 1.39 (t, J=7.1 Hz; 3H, CH_3), 3.45 (q, J=7.1 Hz; 4H), 4.22-4.47 (m; 4H, CH_2), 6.34 (d, J=2.4 Hz; 1H, 8-H), 6.44 (dd, J=2.4 and 8.8 Hz; 1H, 6-H), 7.15 (d, J=8.8 Hz; 1H, 5-H), 8.13 (d, J=36.9 Hz; 1H, 4-H). - ^{13}C-NMR ($CDCl_3$) (62.9 MHz): δ = 12.51 (CH_3), 13.34 (CH_3), 16.43 (d, $^{3}J_{CCOP}$=5.9 Hz; CH_2), 44.88 (CH_2), 61.55 (CH_2), 64.09 (d, $^{2}J_{COP}$=6.7 Hz; CH_2), 99.80 (d, $^{3}J_{CCOP}$=7.8 Hz; C-8), 107.64 (C-6), 108.16 (d, $^{3}J_{CCCP}$=15.7 Hz; C-4a), 108.57 (d, $^{1}J_{CP}$=180.8 Hz; C-3), 133.18 (C-5), 150.96 (d, $^{2}J_{CCP}$=3.2 Hz; C-4), 152.22 (7), 155.50 (d, $^{2}J_{COP}$=7.9 Hz; C-8a), 164.82 (d, $^{2}J_{CCP}$=12.9 Hz; C=O). - MS: m/z (%) = 354 (23), 353 (100) [M^{+}], 339 (20), 338 (97), 325 (5), 310 (34), 308 (34), 280 (11), 264 (25), 236 (20), 180 (4), 174 (8), 116 (4), 89 (3).

$C_{17}H_{24}O_5NP$	(353.35)	Calcd.	C 57.79	H 6.85	P 8.77	N 3.96
		Found	C 57.36	H 7.17	P 8.22	N 3.90

2-Ethoxy-2-oxo-2H-1,2-benzoxaphosphorine-3-carboxylic acid (**9**): This compound was obtained from the reaction of salicylaldehyde (**5a**) and **6c**: (yields and methods prepared as in Table 2), m.p. 186-189 °C (EtOAc). - IR ($CHCl_3$): ν 1725, 1625, 1570, 1030 cm^{-1}. - ^{1}H-NMR ($CDCl_3$/DMSO-d_6) (250 MHz): δ 1.38 (t, J=7.1 Hz; 3H, CH_3), 4.25-4.38 (m; 2H), 7.17-7.26 (m; 2H), 7.48-7.55 (m; 2H), 8.24 (d, J=37.6 Hz; 1H, 4-H). - ^{13}C-NMR ($CDCl_3$/DMSO-d_6) (62.9 MHz): δ 14.73 (d, $^{3}J_{CCOP}$=6.0 Hz; CH_2), 62.92 (d, $^{2}J_{COP}$=5.9 Hz; CH_2), 116.86 (d, $^{3}J_{CCOP}$=7.4 Hz; C-8), 117.77 (d, $^{1}J_{CP}$=174.0 Hz; C-3), 118.11 (d, $^{3}J_{CCP}$=15.9 Hz; C-4a), 122.80 (C-6), 130.44 (C-5), 132.14 (C-7), 148.52 (d, $^{2}J_{CCP}$=2.7 Hz; C-4), 150.84 (d, $^{2}J_{COP}$=8.1 Hz; C8a), 163.29 (d, $^{2}J_{CCP}$=13.8 Hz; C=O). - MS: m/z (%) =(15), 255 (91), 254 (12) [M^{+}], 237 (82), 236 (34), 211 (20), 210 (52), 209 (21), 183 (14), 182 (100), 136 (6), 128 (12), 118 (60), 105 (7), 90 (13), 89 (53).

$C_{11}H_{11}O_5P$	(254.18)	Calcd.	C 51.98	H 4.36	Cl 12.19	
		Found	C 52.36	H 4.54	Cl 12.58	

Photochemical transformation of 8e. - Preparation of 11e: A solution of **8e** (0.030 g) in 23 ml chloroform and 2 ml abs. EtOH (2,2.10^{-3}M) was irradiated with polychromatic light for 4 hours. The solvent was removed and the residue was chromatographed on a silica gel column (*n*-hexane/chloroform 9:1 as eluent) to give 0.019 g (63%) of **11e**, m.p. 271-273 °C, with spectral characteristics identical to those given above.

Photochemical transformation of 8b. - Preparation of 11b and 12b: A solution of **8b** (0,50 g) in 100 ml chloroform was allowed to stay at room temperature and under direct sunlight for 8 hours. The solvent was removed and the residue was chromatographed on a silica gel column (*n*-hexane/chloroform 9:1 as eluent) to give: firstly **11b**, 0.41 g, (82%), m.p. 217-219 °C and secondly **12b**, 0.04 g (8%), m.p. 250-251 °C, both showing analytical and spectral data identical to those given above.

X-ray analysis of 11b, 11e and 12b. Colourless prismatic crystals for **11b**, **11e** and **12b** crystallized from ether-p. ether. A crystal was mounted in air with approximate dimensions: 0.10x0.10x0.50 (**11b**),

Table 3. Summary of Crystal, Intensity Collection and Refinement Data for Compounds **11b**, **12b** and **11e**.

	11b	**12b**	**11e**
Formula	$C_{26}H_{30}O_{10}P_2$	$C_{26}H_{30}O_{10}P_2$	$C_{26}H_{28}O_{10}P_2Br_2$
Formula weight	564.44	564.44	722.28
Temperature, K	298	298	293
Wavelength	Mo Ka 0.71073	Mo Ka 0.71070	Mo Ka 0.71070
Space group	$Pca2_1$	P-1	Pccn
a (Å)	19.033(8)	8.6635(9)	16.9103(12)
b (Å)	9.611(4)	11.7595(12)	17.9274(12)
c (Å)	15.1516)	15.486(2)	9.9569(8)
V, (Å^3)	2775(2)	1399.1(3)	3018.5(4)
z	4	2	4
Dcalcd/Dmeasd (Mg m^{-3})	1.351/1.34	1.340/1.32	1.589/1.56
abc coeff(m), mm^{-1}	0.211	0.209	2.844
Scan mode/speed (deg/min)	θ-2θ/1.8	θ-2θ/3.0	θ-2θ/4.5
Scan range (deg)	2.5+ $\alpha_1\alpha_2$ separation	2.5+ $\alpha_1\alpha_2$ separation	2.5+ $\alpha_1\alpha_2$ separation
θ range (deg)	2.1 to 24.99	1.4 to 25.5	1.66 t0 25.49
Reflections collected	4565	5416	2979
Independent reflections	4387[R(int)=0.01171]	5211R(int)=0.0234]	2613
Range of h,k,l	0→22, -11→0, -18→16	-9→10, -14→14, -18→ 0	0→19, 0→21, 0→12
F (000)	1184	592	1456
$[\Delta/\sigma]_{max.}$	0.002	0.012	0.001
W^a	a=0.0542 b=0.4658	a=0.0663 b=0.7043	a=0.0242 b=6.4032
$[\Delta\rho]_{max.}/[\Delta\rho]_{min}$ (e/Å^3)	0.384 and -0.284	0.361 and -0.281	0.503 and -0.382
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2	Full-matrix least squares on F^2
Data/restrains/parameters	4381 / 1 /403	5194 / 0 / 425	2613 /0 / 185
Goodness-of-fit on F^2	1.083	1.051	1.072
R indices^b	R1=0.0400, wR2=0.1007^c	R1=0.0466, wR2=0.1264^d	R1=0.0505, wR2=0.1015^e
R indices (all data)	R1=0.0560, wR2=0.1147	R1=0.0743, wR2=0.1608	R1=0.0.1726, wR2=0.1486

[a] $W=1/[\sigma^2(Fo^2)+(a*P)^2+b*P]$ and $P_2=(Max\ (Fo^2,0)+2*Fc^2)/3$

[b] R1 based on F's, wP2 based on F^2 [c] [3642 refs I>2σ (I)] [d] [3683 refs I> 2σ (I)] [e] [1142 refs I>2σ (I)]

0.15x0.25x0.45 (**12b**) and 0.42x0.24x0.10 (**11e**). Diffraction measurements were made on a P2 Nicolet diffractometer upgraded by crystal Logic using a Zr-filtered Mo radiation (**11e** and **12b**) or on a Crystal Logic Dual Goniometer, using graphite monochromated Mo-radiation (**11b**). Unit cell dimensions were determined and refined by using the angular settings of 24 automatically centred reflections in the range $11^{\circ}<2\theta<23^{\circ}$ (for 11b, 12b) and $11^{\circ}<2\theta<24^{\circ}$ (for 11e) and they appear in Table 3. Intensity data were recorded using a θ-2θ scan to 2θ(max) and scan speeds and scan ranges as given in Table 3. Three standard reflection monitored every 97 reflections showed less than 3% variation and no decay. Lorenz, polarisation corrections were applied using Crystal Logic software. The structures were solved by direct methods using SHELXS-86 program[28] and refined by full-matrix least-squares techniques on F^2 with SHELXL-93 program[29]. Reflections collected and used, as well as the final values for R, Rw and GOF for observed data are given in Table 3. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre and are available on request.

Acknowledgement.

This work was financially supported by the Bulgarian National Fund for Scientific Investigation.

REFERENCES AND NOTES

1. Bojilova, A.; Ivanov, C. *Synthesis* **1976**, 267-268.
2. Bojilova, A.; Kostantinova, T.; Ivanov, C. *Synth. Commun.* **1989**, *19*, 2963-2975.
3. Bojilova, A.; Kostantinova, T.; Ivanov, C. *Liebigs Ann. Chem.* **1989**, 1041-1043.
4. Bojilova, A.; Trentafilova, A.; Ivanov, C.; Rodios, N. A. *Tetrahedron* **1993**, *49*, 2275-2286.
5. Rodios, N. A.; Bojilova, A.; Terzis, A.; Raptopoulou, C. P. *J. Heterocyclic Chem.* **1994**, *31*, 1129-1133.
6. Ivanov, C.; Bojilova, A. *Chem. Ber.* **1978**, *111*, 3755-3763.
7. Bojilova, A.; Ivanov, C. *Indian J. Chem.* **1978**, *26B*, 731-735.
8. Bojilova, A.; Ivanov, C. *Synthesis* **1986**, 415-416.
9. Bojilova, A.; Rodios, N. A.; Nikolova, R.; Ivanov, C. *Liebigs Ann. Chem.* **1991**, 1279-1284.
10. Bojilova, A.; Rodios, N. A.; Nikolova, R.; Ivanov, C. *Synth. Commun.* **1992**, *22*, 741-754.
11. Bojilova, A.; Ivanov, C. Balkan Chemistry Days, Varna, Bulgaria, 1983. Abstracts of papers, p 1.13.
12. Robinson, C. N.; Addison, J. F. *J. Org. Chem.* **1966**, *31*, 4325-4326.
13. Singh, R. K.; Rogers, M. D. *J. Heterocyclic Chem.* **1985**, *22*, 1713-1714.
14. Bouyssou, P.; Chenault, J. *Tetrahedron Lett.* **1991**, *32*, 5341-5344.
15. Falsone, G.; Cateni, F.; De Nardo, M. M.; Darai, M. M. *Z. Naturforsch.* **1993**, *48b*, 1391-1397.
16. Chen, C. H.; Fox J. L.; Lippert, J. L. *J. Heterocyclic Chem.* **1987**, *24*, 931-932.
17. Schenck, G. H.; van Wiluski, I.; Krauch, C. H. *Chem. Ber.* **1962**, *95*, 1409 .
18. Hammond, G. S.; Stout, C. A.; Lamola, A. A. *J. Am. Chem. Soc.* **1964**, *86*, 3103 .
19. Abdou, W. M.; Mahran, M. R.; Sidky, M. M.; Wamhoft, H. *Phosphorus and Sulfur* **1988**, *39*, 199 .
20. Compound **10** was in some cases isolated, but it was not possible to purify it enough as to obtain its physical, analytical and spectral data.
21. Lehnert, W. *Tetrahedron Lett.* **1970**, *54*, 4723.
22. Lehnert, W. *Tetrahedron* **1974**, *30*, 301 .
23. F. Texier-Boullet, F.; Foucaud, A. *Tetrahedron Lett.* **1982**, *23*, 4927-4928.
24. Texier-Boullet, F.; Villemin, D.; Ricard, M.; Moison, H.; Foucaud, A. *Tetrahedron* **1985**, *41*, 1259-1266.
25. In the ^{31}P spectra of compound **7b**[16] the authors gave shifts for the phosphorus atom equal to 5.0 ppm; to our opinion the sample from which the ^{31}P NMR spectrum was recorded most probably it was not the **7b** but that of **8b**, which was missed by the authors.
26. Kosolapoff, G. M. *Organophosphorus Compounds*, J.Wiley and Sons, Inc., New York, N. Y.: 1950; chap. 7.
27. Dawson, N. D.; Burger, A. *J. Am. Chem. Soc.* **1952**, *74*, 5312-5314.
28. Sheldrick, G. M. SHELXS-86: Stucture Solving Program. University of Göttingen, Germany, **1986**.
29. Sheldrick, G. M. SHELXS-93: Crystal Stucture Refinement. University of Göttingen, Germany, **1986**.

(*Received in UK* 4 *July* 1996; *revised* 8 *August* 1996; *accepted* 15 *August* 1996)