

(CDCl<sub>3</sub>) showed a sharp singlet at 2.75 (CH<sub>3</sub>, 3 H) and two doublets of an AB quartet centered at 6.99 and 7.28 ppm (aromatic, 2 H,  $J_{AB} = 9.0$  cps).

*Anal.* Calcd for C<sub>9</sub>H<sub>8</sub>O<sub>4</sub>S: C, 51.4; H, 2.9; S, 15.3. Found: C, 51.6; H, 2.9; S, 15.6.

The filtrate was combined with the washings and heated on a steam bath. After 1 hr of heating, no change was detected by tlc. Only upon prolonged heating (3 hr) did a reaction occur. The mixture was poured into 500 ml of water, and the precipitate was collected and recrystallized from ethanol-water to give 1.5 g (11%) of yellow needles, mp 209–210°. This material was identified by nmr spectroscopy as the 7-acetyl isomer. Its nmr spectrum (DMSO-*d*<sub>6</sub>) showed a sharp singlet at 2.64 (CH<sub>3</sub>, 3 H) and two doublets of an AB quartet centered at 7.21 and 7.42 ppm (aromatic, 2 H,  $J_{AB} = 2.5$  cps).

*Anal.* Calcd for C<sub>9</sub>H<sub>8</sub>O<sub>4</sub>S: C, 51.4; H, 2.9; S, 15.3. Found: C, 51.5; H, 2.7; S, 15.3.

The product ratio of the crude mixture was analyzed by nmr spectroscopy and vpc to be 83% 4-acetyl isomer and 17% 7-acetyl isomer.

**Registry No.**—4,7-Dimethyl-5-hydroxy-2-imino-1,3-benzoxathiole hydrochloride, 17630-80-7; **9**, 17631-02-6; **10**, 17631-03-7; **13**, 17631-04-8; **14**, 17631-05-9; **15**, 17630-66-9; **16**, 17630-71-6; 4,7-dichloro-5-hydroxy-2-imino-1,3-benzoxathiol-2-one, 17630-72-.

**Acknowledgment.**—The authors gratefully acknowledge the assistance of Dr. T. H. Regan and Mr. R. L. Young in the preparation and interpretation of the nmr spectra.

## Base-Induced Cyclization of 2-Oximinophosphonium Salts. Synthesis and Spectroscopic Properties of 1,2,5-Oxazaphosph(V)ol-2-ines

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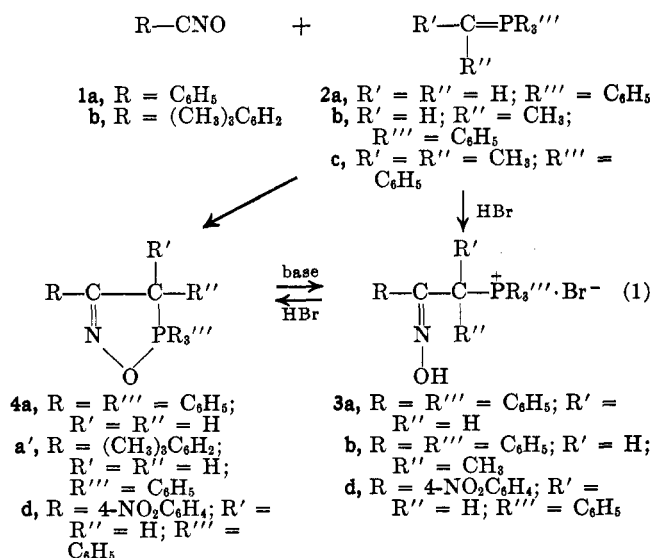
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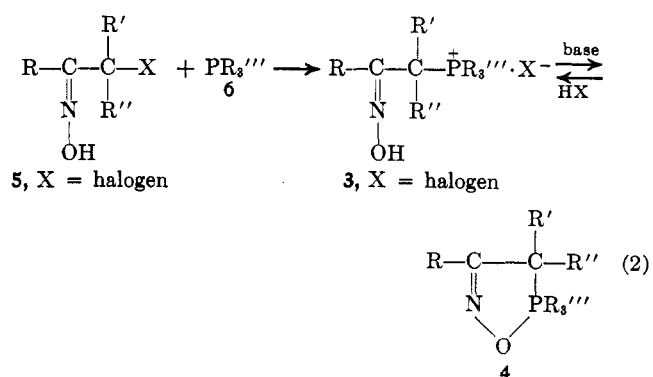
Several 1,2,5-oxazaphosph(V)ol-2-ines (**4**) have been prepared in high yield by basic treatment of 2-oximinophosphonium salts (**3**). These salts were easily obtained either by reaction of  $\alpha$  halo ketoximes with triphenyl- or tri-*n*-butylphosphine, by oximation of the corresponding 2-keto phosphonium salts, or finally by reaction of nitrile oxides with phosphonium ylides in dimethyl sulfoxide. The reaction of desyl bromide with triphenylphosphine in benzene gave a mixture of the keto (**8**) and enol phosphonium (**8a**) salts. Treatment of **8** with hydroxylamine gave the corresponding ylide (**9**) instead of the expected oxime. The ring of 1,2,5-oxazaphosph(V)ol-2-ines can be opened by treatment with acids in the cold, affording the corresponding 2-oximinophosphonium salts. Thermal decomposition of 3-(4-bromophenyl)-5,5,5-triphenyl-1,2,5-oxazaphosph(V)ol-2-ine (**4d**) gave 2H-3-(4-bromophenyl)azirine (**10**) together with triphenylphosphine oxide. The comparison of the mass spectra of 1,2,5-oxazaphosph(V)ol-2-ines with the spectra of the corresponding phosphonium salts confirmed the cyclic structure of the former. <sup>1</sup>H nmr spectra of the title compounds and of the corresponding salts (**3**) were measured in several solvents and discussed. From the chemical-shift and coupling-constant values it can be deduced that the P–O bond in the cycles (**4**) has high covalent character. The effect of substituents on chemical shifts and coupling constants are discussed.

In a recent paper<sup>2</sup> two of us reported the reaction between benzonitrile oxide (**1a**) and a few phosphonium ylides (**2**). The reaction of **1a** with triphenylphosphonium methylide (**2a**) and ethylide (**2b**) in dimethyl sulfoxide (DMSO), after the work-up in acidic medium, gave the 2-oximinophosphonium salts **3a** and **3b** (eq 1). We also reported the successful trans-

formation of **3a** into the corresponding cyclic compound **4a** by means of base, and the reverse reaction which leads from **4a** to **3a** with hydrobromic acid. We pointed out that such a cyclization could be the final step of an easy route to 1,2,5-oxazaphosph(V)ol-2-ines (**4**), starting from  $\alpha$ -halo oximes (**5**) and phosphines (**6**), through the phosphonium salts (**3**) (eq 2).



(1) In alphabetical order.



The only members of this class of cyclic compounds **4** so far known are **4a** and its mesityl analog **4a'** obtained by Huisgen and Wulff<sup>3</sup> directly from **1a** and **1b**, respec-

(2) A. Umani-Ronchi, M. Acampora, G. Gaudiano, and A. Selva, *Chim. Ind. (Milan)*, **49**, 388 (1967).

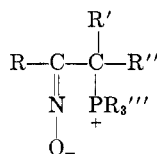
(3) R. Huisgen and J. Wulff, *Tetrahedron Lett.*, 917 (1967).

TABLE I  
 2-OXIMINOPHOSPHONIUM SALTS (3)

Compd no.	Formula	Method of preparation <sup>b</sup>	Yield, <sup>a</sup> %	Reaction conditions			Mp, °C
				Solvent	Temp, °C	Time, hr	
3a	C <sub>6</sub> H <sub>5</sub> C(NO <sub>2</sub> )CH <sub>2</sub> P <sup>+</sup> (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ·Br <sup>-</sup> <sup>c,d</sup>	A	40				231
3a'	C <sub>6</sub> H <sub>5</sub> C(NO <sub>2</sub> )CH <sub>2</sub> P <sup>+</sup> (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ·Cl <sup>-</sup>	B	100	CHCl <sub>3</sub>	Reflux	2	215
3b	C <sub>6</sub> H <sub>5</sub> C(NO <sub>2</sub> )CH(CH <sub>3</sub> )P <sup>+</sup> (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ·Br <sup>-</sup> <sup>e</sup>	A	65				157
3c	C <sub>6</sub> H <sub>5</sub> C(NO <sub>2</sub> )CH( <i>n</i> -C <sub>3</sub> H <sub>7</sub> )P <sup>+</sup> (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ·Br <sup>-</sup>	A	45				191
3d	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub> C(NO <sub>2</sub> )CH <sub>2</sub> P <sup>+</sup> (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ·Br <sup>-</sup>	B	51	EtOH	20	72	219
3e	β-C <sub>10</sub> H <sub>7</sub> C(NO <sub>2</sub> )CH <sub>2</sub> P <sup>+</sup> (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ·Br <sup>-</sup> <sup>e</sup>	B'	81	Aq. MeOH	Reflux	30	226
3f	CH <sub>3</sub> C(NO <sub>2</sub> )CH <sub>2</sub> P <sup>+</sup> (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ·Cl <sup>-</sup>	B	57	CHCl <sub>3</sub>	20	72	223
		B'	56	Aq. EtOH	Reflux	10	
3g	(CH <sub>2</sub> ) <sub>4</sub> C(NO <sub>2</sub> )CHP <sup>+</sup> (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ·Cl <sup>-</sup>	B	55	Ether	20	72	198
3h	C <sub>6</sub> H <sub>5</sub> C(NO <sub>2</sub> )CH <sub>2</sub> P <sup>+</sup> ( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> ·Cl <sup>-</sup>	B	87	Ether	20	46	197
3i	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub> C(NO <sub>2</sub> )CH <sub>2</sub> P <sup>+</sup> ( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> ·Br <sup>-</sup>	B	85	Ether	20	48	168

<sup>a</sup> No systematic attempt was made to improve yields by modification of the reaction conditions. <sup>b</sup> A, from the corresponding nitrile oxide<sup>2</sup>; B, from the α-halo oxime; B', from the corresponding 2-oxophosphonium salt by oximation. <sup>c</sup> See ref 2. <sup>d</sup> An attempt to synthesize 3a by method B, using the oxime obtained from ω-bromoacetophenone and hydroxylamine hydrochloride, according to H. Korten and R. Schöll [Ber., 34, 1901 (1901)], resulted in a mixture of 3a and 3a' (revealed by the mass spectrum). Evidently, according to the observation of Masaki,<sup>5</sup> the oximation of ω-bromoacetophenone by NH<sub>2</sub>OH·HCl affords a mixture of the ω-bromo- and ω-chloroacetophenone oximes by halogen exchange. <sup>e</sup> C<sub>10</sub>H<sub>7</sub> = naphthyl.

tively, and 2a in benzene.<sup>4</sup> In addition, in a more recent paper, Masaki, *et al.*, reported the basic cyclization of 3a and 3d to 4a and 4d.<sup>5</sup> They stated that the <sup>1</sup>H nmr and the analytical data of the dehydrohalogenated compounds could also suggest an open betainic structure (7a and 7d) analogous to that (7c) proposed by Bestmann and Kunstmann<sup>6</sup> for the product obtained from 1a and 2c. On the other hand Huisgen and Wulff discarded the betainic structures 7a and 7a' for their products on the basis of the chemical-shift value in the <sup>31</sup>P nmr spectra. In this paper we report the synthesis



- 7a, R = R''' = C<sub>6</sub>H<sub>5</sub>; R' = R'' = H  
 a', R = (CH<sub>2</sub>)<sub>3</sub>C<sub>6</sub>H<sub>5</sub>; R' = R'' = H; R''' = C<sub>6</sub>H<sub>5</sub>  
 c, R = R''' = C<sub>6</sub>H<sub>5</sub>; R' = R'' = CH<sub>3</sub>  
 d, R = 4-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>; R' = R'' = H; R''' = C<sub>6</sub>H<sub>5</sub>

of several members of this new class of heterocycles (4) by the methods outlined in eq 1 (method A, through the phosphonium salts) and eq 2 (method B), and discuss the nmr and mass spectra of these compounds which support the cyclic covalent structures shown. We also report the synthesis and spectral data of the corresponding 2-oximinophosphonium salts (3), none of which was known before our earlier report.<sup>5</sup>

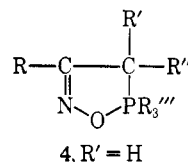
**Method A.**—This method (eq 1) was only used in three cases by running the reaction in DMSO. The salts obtained (see Table I) were cyclized as indicated under method B. Actually the use of nitrile oxides for the synthesis of such heterocycles, even if useful in some cases, offers a more limited route of synthesis, when compared with the reaction depicted in eq 2. This is because of the limited availability of nitrile ox-

(4) A few species of 1,2,5-oxazaphosph(V)olidines, the dihydro derivatives of the title compounds, have been recently synthesized by the same authors [J. Wulff and R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, 6, 457 (1967)].

(5) In this paper, M. Masaki, K. Fukuni, and M. Ohta, *J. Org. Chem.*, 32, 3564 (1967), the preparation of four 2-oximinophosphonium salts (3) is reported. The cyclization of two of these salts (3a and 4a) was performed by the authors by basic treatment, as already reported by us.<sup>2</sup> Evidently, because of the close timing, the authors did not notice our earlier paper on this subject.

(6) H. J. Bestmann and H. Kunstmann, *Angew. Chem.*, 78, 1059 (1966).

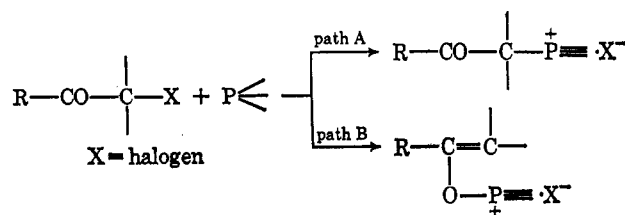
ides,<sup>7</sup> which usually are less easily obtained than α-halo oximes (5) and the evident difficulty of obtaining by this method cyclic phosphonium salts like 3g (see Table I) and the corresponding 1,2,5-oxazaphosph(V)-ol-2-ines (4g) (see Table II). Moreover the reaction requires the use of phosphonium ylides instead of simple phosphines.

 TABLE II  
 1,2,5-OXAZAPHOSPH(V)OL-2-INES FROM  
 2-OXIMINOPHOSPHONIUM SALTS


Compd no.	R	R''	R'''	Yield, %	Mp, °C
4a <sup>a</sup>	C <sub>6</sub> H <sub>5</sub>	H	C <sub>6</sub> H <sub>5</sub>	98 <sup>b</sup>	129–130
4b	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	85 <sup>b</sup>	100
4c	C <sub>6</sub> H <sub>5</sub>	<i>n</i> -C <sub>3</sub> H <sub>7</sub>	C <sub>6</sub> H <sub>5</sub>	70, <sup>b</sup> 98 <sup>c</sup>	96
4d	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>	H	C <sub>6</sub> H <sub>5</sub>	91, <sup>b</sup> 100 <sup>c</sup>	157
4e	β-C <sub>10</sub> H <sub>7</sub> <sup>d</sup>	H	C <sub>6</sub> H <sub>5</sub>	90 <sup>b</sup>	142
4f	CH <sub>3</sub>	H	C <sub>6</sub> H <sub>5</sub>	74 <sup>c</sup>	116
4g	(CH <sub>2</sub> ) <sub>4</sub>	(CH <sub>2</sub> ) <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	53 <sup>b</sup>	102
4h	C <sub>6</sub> H <sub>5</sub>	H	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	80 <sup>b</sup>	<sup>e</sup>
4i	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>	H	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	85 <sup>b</sup>	96

<sup>a</sup> See ref 2 and 3. <sup>b</sup> By the resin method. <sup>c</sup> By NaOH or KOH. <sup>d</sup> C<sub>10</sub>H<sub>7</sub> = naphthyl. <sup>e</sup> Liquid.

**Method B.**—When an α-halo carbonyl compound reacts with phosphines either a 2-oxophosphonium salt or an enol phosphonium salt (or both) can be formed,

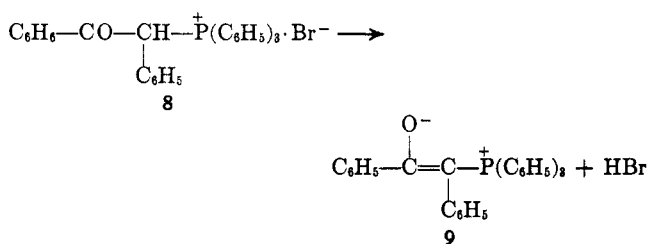


(7) A. Quilico in "The Chemistry of Heterocyclic Compounds," Interscience Publishers, New York, N. Y., 1962; C. Grundmann in Houben-Weyl's "Methoden der organischen Chemie," Vol. 10/3, G. Thieme Verlag, Stuttgart, 1965.

depending on the nature of the  $\alpha$ -halo carbonyl compound, the phosphine, and the solvent.<sup>8</sup>

It has been found that when the reaction is run in a protic solvent the formation of the enol salt is favored. Since a similar behavior might be expected for the reaction of the  $\alpha$ -halo oximes with phosphines, in order to obtain the quaternary C salts (path A), we choose an aprotic solvent.<sup>9</sup> Actually when an  $\alpha$ -halo oxime reacts with triphenyl- or tributylphosphine in ether or chloroform in the cold or at reflux, the quaternization of the phosphine takes place smoothly, giving a good yield of 2-oximinophosphonium salt.<sup>10</sup>

An alternative route to the phosphonium salts (3) based on the oximation of the corresponding 2-oxophosphonium salts can also be used and is recommended when the  $\alpha$ -halo oxime is not easily obtained or its reaction with phosphine gives unsatisfactory yields. The oximation of the 2-oxophosphonium salts is usually performed by using hydroxylamine in a slightly acidic medium to avoid the formation of the ylide corresponding to the salt. Under these conditions, however, the oximation requires many hours at water-bath temperature, and in some cases, does not occur at all. An attempt at oximation of the phosphonium salt (8)<sup>11</sup> by hydroxylamine hydrochloride failed even after 6 days at 80°, and attempts with free or partially free hydroxylamine resulted in the formation of the ylide (9).



The phosphonium salts that we have obtained by these two methods are listed in Table I.

The cyclization of the 2-oximinophosphonium salts (3) to the corresponding 1,2,5-oxazaphosph(V)ol-2-ines (4) can be best performed by percolating an alcoholic solution of the salt through a basic ion exchange resin, whereby the cycle is obtained in high yield and purity. Alternatively, the cyclization can be accomplished by using cold aqueous NaOH or KOH. The use of cold pyridine as base is not adequate for the cyclization. In fact the nmr spectra of the salts can be measured in pyridine. The cycles obtained by basic treatment of the corresponding salts are listed in Table II.

1,2,5-Oxazaphosph(V)ol-2-ines (4) are in general crystalline solids with melting points rather lower than the corresponding salts. When R and R''' are aromatic they are scarcely soluble in the common organic

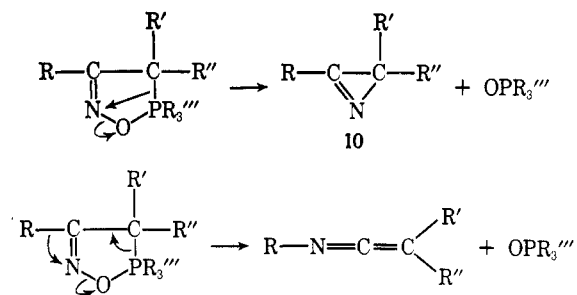
(8) For a recent review on this subject, see A. J. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorus," Elsevier Publishing Co., 1967, p 117; see also I. J. Borowitz and H. Parnes, *J. Org. Chem.*, **32**, 3560 (1967).

(9) With the only exception of compound 8d.

(10) The reaction of some 2-bromoacetophenone oximes with P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> in acetonitrile has been recently investigated by Masaki.<sup>5</sup>

(11) This salt, according to the report of H. Hoffmann and H. J. Diehr [*Angew. Chem.*, **76**, 944 (1964)], based on unpublished results (Hoffmann and Beller), can be obtained in high yield from desyl bromide and triphenylphosphine in benzene. Actually in our hands the reaction afforded essentially the corresponding enol salt (8a), C<sub>6</sub>H<sub>5</sub>C(=CHC<sub>6</sub>H<sub>5</sub>)OP<sup>+</sup>(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Br<sup>-</sup>, together with a minor amount of the keto salt 8. In fact the mixture of the salts obtained from desyl bromide and P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>, after treatment with water, gave a large amount of PO(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> and desoxybenzoin, both compounds being indicative of the formation of the enol salt<sup>5</sup> (see Experimental Section).

solvents. These compounds are opened by acid treatment in the cold, affording the corresponding salts by the P-O bond fission<sup>2,5</sup> (eq 2). They are thermally unstable giving an azirine and/or ketenimine, by loss of OPR<sub>3</sub>''.<sup>3,6</sup> Accordingly, from 4d, by thermal decom-



position, we isolated a solid azirine (10, R = *p*-BrC<sub>6</sub>H<sub>4</sub>; R' = R'' = H): ir (Nujol) 1730 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>),  $\delta$  1.80 (s).

**Nmr Spectra.**—Since few nmr data concerning pentavalent phosphorus-containing molecules are available,<sup>12,13</sup> we will discuss here in some detail the <sup>1</sup>H nmr spectra of this class of new compounds, the 1,2,5-oxazaphosph(V)ol-2-ines (4), together with their corresponding oximinophosphonium salts (3).

Huisgen<sup>3,4</sup> has shown the phosphorus atom to be pentavalent in 4a and 4a' and in some 1,2,5-oxazaphosph(V)olidines, because of the positive chemical shift value of <sup>31</sup>P signals. Comparing the <sup>1</sup>H nmr parameters of 1,2,5-oxazaphosph(V)ol-2-ines and the corresponding oximinophosphonium salts, we have found some interesting features.

First it is noteworthy that even from the <sup>1</sup>H chemical shifts and coupling constants it can be deduced that the P-O bond in 1,2,5-oxazaphosph(V)ol-2-ines has a high covalent character.

The two hydrogens at C<sub>4</sub> are magnetically equivalent in both salts and cyclic compounds; indeed the latter have a plane of symmetry identified with the plane of the heterocyclic ring, assuming rapid flipping of this ring and free rotation of the phenyl groups. The spectra are not temperature dependent over a range from +30 to -50°. <sup>14</sup>

**Chemical Shifts.**—Comparing the chemical-shift values of cyclic compounds with that of the corresponding oximinophosphonium salts,<sup>15</sup> a marked difference in the  $\delta$  value of the protons on C<sub>4</sub> can be observed; the localized positive charge on the P atom in the salts produces a strong deshielding on these protons which appear at a lower field than the corresponding 1,2,5-oxazaphosph(V)ol-2-ines [ $\Delta\delta = -(1.3-1.7)$ ]<sup>16</sup>.

It is interesting to note that such an effect in the salts is exerted through three, four, and even five bonds. For example the CH<sub>3</sub> signals (three bonds away) in the 3b-4b pair show  $\Delta\delta = -0.14$ ;<sup>16</sup> the CH<sub>3</sub> signals (five bonds away) of the 3c-4c pair give  $\Delta\delta = -0.10$ ; and

(12) G. Mavel in "Progress in Nmr Spectroscopy," J. W. Emsley, J. Feeney, L. H. Sutcliffe, Ed., Pergamon Press Ltd., Oxford, 1966.

(13) See, for example, F. Ramirez, A. V. Patwardhan, and C. P. Smith, *J. Org. Chem.*, **31**, 3159 (1966); R. Burgada, D. Houlla, and R. Wolf, *C. R. Acad. Sci., Paris, Ser. C*, **264**, 356 (1967); F. Ramirez, K. Tasaka, N. B. Desai, and C. P. Smith, *J. Amer. Chem. Soc.*, **90**, 751 (1968).

(14) This measurement was performed on 4i in CDCl<sub>3</sub> solution.

(15) No effect of halide ion on either chemical shift or J was observed in the salts.

(16)  $\Delta\delta = \delta_{\text{cycle}} - \delta_{\text{salt}}$ ; chemical shifts are compared in CDCl<sub>3</sub>.

TABLE III  
 NMR SPECTRAL DATA FOR 2-OXIMINOPHOSPHONIUM SALTS<sup>a</sup>

$$\begin{array}{c} \text{R}' \\ | \\ \text{R}-\text{C}-\text{CH}-\text{P}^+\text{R}_3'' \cdot \text{X}^- \\ || \\ \text{NOH} \end{array}$$

Compd	R	R'	R''	J, cps			Grouping	Chemical shifts, $\delta$ , ppm		
				CDCl <sub>3</sub>	DMSO-d <sub>6</sub>	Pyridine-d <sub>5</sub>		CDCl <sub>3</sub>	DMSO-d <sub>6</sub>	Pyridine-d <sub>5</sub>
3a	C <sub>6</sub> H <sub>5</sub>	H	C <sub>6</sub> H <sub>5</sub>	<sup>2</sup> J <sub>P,H</sub>	16.8 <sup>b</sup>	15.0 <sup>c</sup>	CH <sub>2</sub> P <sup>+</sup>	5.16 (d) <sup>b</sup>	5.37 (d) <sup>c</sup>	
3d	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>	H	C <sub>6</sub> H <sub>5</sub>	<sup>2</sup> J <sub>P,H</sub>	16.5	14.7 <sup>c</sup>	OH	12.16 (s) <sup>b</sup>	<i>d</i>	
							CH <sub>2</sub> P <sup>+</sup>	5.20 (d)	5.23 (d) <sup>c</sup>	
3e	2-C <sub>10</sub> H <sub>7</sub> <sup>e</sup>	H	C <sub>6</sub> H <sub>5</sub>	<sup>2</sup> J <sub>P,H</sub>	16.5	15.5 <sup>c</sup>	OH	12.40 (s)	<i>d</i>	
							CH <sub>2</sub> P <sup>+</sup>	5.27 (d)	5.72 (d) <sup>c</sup>	
3f	CH <sub>3</sub>	H	C <sub>6</sub> H <sub>5</sub>	<sup>2</sup> J <sub>P,H</sub>	14.0	13.5 <sup>f</sup>	OH	12.33 (s)	<i>d</i>	
							CH <sub>2</sub> P <sup>+</sup>	4.99 (d)	5.76 (d) <sup>f</sup>	
							CH <sub>3</sub>	1.84 (s)	2.29 (s)	
							OH	11.05 (s)	<i>d</i>	
3h	C <sub>6</sub> H <sub>5</sub>	H	(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	<sup>2</sup> J <sub>P,H</sub>	16.7	16.9	16.8	CH <sub>2</sub> P <sup>+</sup>	4.20 (d)	4.80 (d)
								CH <sub>2</sub> <sup>g</sup>	1.9-2.5	1.8-2.5
								CH <sub>3</sub> <sup>h</sup>	0.82 <sup>i</sup>	0.82 <sup>i</sup>
								OH	12.56 (s)	12.63 (s)
								OH	12.71 (s)	12.65 (s)
3i	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>	H	(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	<sup>2</sup> J <sub>P,H</sub>	16.7	16.8	CH <sub>2</sub> P <sup>+</sup>	4.21 (d)	4.04 (d)	
							CH <sub>2</sub> <sup>g</sup>	1.8-2.5	1.7-2.5	
							CH <sub>3</sub> <sup>h</sup>	0.85 <sup>i</sup>	0.83 <sup>i</sup>	
							BrC <sub>6</sub> H <sub>4</sub> <sup>j</sup>	7.44, 7.73	7.65, 7.83	
3b	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	<sup>2</sup> J <sub>P,H</sub>	13.5	13.5 <sup>b</sup>	10.5-10.8	OH	12.71 (s)	12.65 (s)
								CHP <sup>+</sup>	4.91 (qd)	5.16 (qd) <sup>b</sup>
								CH <sub>3</sub>	1.80 (dd)	1.83 (dd) <sup>b</sup>
								OH	12.50 (s) <sup>b</sup>	<i>d</i>
3c	C <sub>6</sub> H <sub>5</sub>	CH <sub>2</sub> <sup>A</sup> -CH <sub>2</sub> <sup>B</sup> -CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	<sup>2</sup> J <sub>P,H</sub>	12.5-13.0	13.0	<i>m</i>	CHP <sup>+</sup>	5.01 <sup>i</sup>	5.21 <sup>i</sup>
								CH <sub>2</sub> <sup>A</sup>	2.41, 1.84 <sup>n</sup>	1.8-2.6
								CH <sub>2</sub> <sup>B</sup>	1.53 <sup>o</sup>	1.1-1.7
								CH <sub>3</sub>	0.83 (t)	0.86 (t)
								OH	12.05 (s)	12.58 (s)

<sup>a</sup> A few data are missing because of either low solubility or scarcity of some products. <sup>b</sup> See ref 2. <sup>c</sup> Concentration 0.05 M. <sup>d</sup> Together with H<sub>2</sub>O signal. <sup>e</sup> C<sub>10</sub>H<sub>7</sub> = naphthyl. <sup>f</sup> Concentration 0.1 M. <sup>g</sup> Broad, six protons (CH<sub>2</sub>P<sup>+</sup>) of butyl groups. <sup>h</sup> Three equivalent CH<sub>3</sub> of butyl groups. <sup>i</sup> Strongest transition of the A<sub>2</sub>B<sub>2</sub> pattern, part A. <sup>j</sup> A<sub>2</sub>B<sub>2</sub> pattern,  $\delta_A$  and  $\delta_B$  values are given. <sup>k</sup> Not visible. <sup>l</sup> Eight-line pattern. <sup>m</sup> Not analyzed. <sup>n</sup> Centers of broad absorptions, measured by decoupling experiments. <sup>o</sup> Quintet,  $J = 7$  cps.

even the aromatic protons *meta* to Br (five bonds away) in the 3i-4i pair show a  $\Delta\delta = -0.18$  (protons *ortho* to Br,  $\Delta\delta = +0.02$ ).<sup>17</sup> A model inspection shows that the influence of the anisotropy of phenyl groups is comparable in each salt-cycle pair, so that it can not be responsible for this effect. If fact the deshielding is also observed when phenyls on P are replaced by butyls (3i).

As for the effect of substituents at P on the  $\delta$  value of the C<sub>4</sub> protons, we have found the same behavior in both salts and cyclic compounds. Inspection of the data in Tables III and IV shows that, when butyl groups instead of phenyls are attached at the phosphorus, the methylene protons shift more than 1 ppm upfield. The effect of substitution at C<sub>3</sub>, as expected, is not so strong; on going from C<sub>6</sub>H<sub>5</sub> to C<sub>6</sub>H<sub>4</sub>Br and C<sub>10</sub>H<sub>7</sub> only a very slight deshielding is observed, whereas the presence of a CH<sub>3</sub> causes C<sub>4</sub> protons to shift upfield, as expected. This effect is a little more marked in the cyclic derivatives [ $\delta$  (4a) -  $\delta$  (4f) = +0.4] than in the salts.

**Coupling Constants.** The two-bond coupling constant <sup>2</sup>J<sub>P,H</sub> in oximinophosphonium salts<sup>15</sup> is always higher in modulus than in cyclic derivatives. The positive shift<sup>18</sup> on going from polar structures (P hybridization  $\sim$ sp<sup>3</sup>) to cyclic ones is in agreement with a view of a high contribution of pentavalent character

of the P atom in the latter compounds (hybridization  $\sim$ sp<sup>3</sup>d).<sup>12</sup> The value of <sup>2</sup>J<sub>P,H</sub> is found to be independent of substituents on the phosphorus atom in both phosphonium salts, as already observed by Griffin,<sup>19</sup> and cyclic compounds. However this geminal coupling is sensitive, as expected, to change in substituents on C<sub>4</sub>. It is interesting to note that, while the change of <sup>2</sup>J<sub>P,H</sub> upon alkylation at C<sub>4</sub> in the phosphonium salts falls in the same range as reported by Mavel<sup>12</sup> [e.g., 3a ( $J = 16.8$  cps)  $\rightarrow$  3b ( $J = 13.5$  cps)], in the cyclic compounds this change is drastic [e.g., 4a ( $J = 11.9$  cps)  $\rightarrow$  4b ( $J = 3.5$  cps)].

It has not yet been possible to determine the sign of these constants.<sup>20</sup> From the available data<sup>12</sup> we could assume that the large couplings are negative, but, concerning the small ones, no assumption can be made. In any case such a variation (positive shift) is strong and cannot adequately be explained solely in terms of a change of the s character of the bonding orbitals of carbon to phosphorus due to the effect of the electronegativity of the substituent.<sup>12</sup> This is because of the small difference in electronegativity between hydrogen and alkyl and also because in several cases reported in the literature an opposite trend has been observed.<sup>21</sup>

In the salt series, but not in cyclic compounds, <sup>2</sup>J<sub>P,H</sub> is also sensitive to change in the nature of the substituent on C<sub>3</sub>; it decreases in modulus when aryl substitu-

(17) There are only two exceptions in this trend, for the CH<sub>3</sub> signals in the 4f-3f pair ( $\Delta\delta = +0.12$  in DMSO-d<sub>6</sub>) and for the CH<sub>3</sub> signals in the 4i-3i pair ( $\Delta\delta = +0.08$ ). However, a model inspection can explain these exceptions on the basis of a shielding effect of the phenyls which can operate only in the salts, where free rotation is allowed at C<sub>3</sub>-C<sub>4</sub> and C<sub>4</sub>-P.

(18) The sign of the <sup>2</sup>J<sub>P,H</sub> for the phosphonium salts is assumed negative; see ref 12 and S. L. Manatt, G. L. Juvinal, R. I. Wagner, and D. D. Elleman, *J. Amer. Chem. Soc.*, **88**, 2689 (1966). On account of their large modulus we assume the <sup>2</sup>J<sub>P,H</sub> to be negative also in the cyclic compounds.

(19) C. E. Griffin and M. Gordon, *J. Organometal. Chem.*, **3**, 414 (1965).

(20) In a more recent decoupling experiment, made on 4b, <sup>2</sup>J<sub>P,H</sub> and <sup>3</sup>J<sub>P,H</sub> appeared to be of opposite relative sign. Further investigations are in progress.

(21) J. B. Hendrickson, M. L. Maddox, J. J. Sims, and H. D. Kaesz, *Tetrahedron*, **20**, 449 (1964); D. W. Allen, I. T. Millar, and J. C. Tebby, *Tetrahedron Lett.*, 745 (1968).

TABLE IV  
 NMR SPECTRAL DATA FOR 1,2,5-OXAZAPHOSPH(V)OL-2-INES<sup>a</sup>

Compd	R	R'	R''	<i>J</i> , cps				Group- ing	Chemical shifts, $\delta$ , ppm			
				CCl <sub>4</sub>	CDCl <sub>3</sub>	DMSO- <i>d</i> <sub>6</sub>	Pyridine- <i>d</i> <sub>5</sub>		CCl <sub>4</sub>	CDCl <sub>3</sub>	DMSO- <i>d</i> <sub>6</sub>	Pyridine- <i>d</i> <sub>5</sub>
4a	C <sub>6</sub> H <sub>5</sub>	H	C <sub>6</sub> H <sub>5</sub>	<sup>3</sup> <i>J</i> <sub>P,H</sub>	11.9 <sup>b</sup>	11.9		CH <sub>2</sub> P	3.40 <sup>b</sup>	3.88		
4d	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>	H	C <sub>6</sub> H <sub>5</sub>	<sup>3</sup> <i>J</i> <sub>P,H</sub>		12 <sup>c</sup>	11.8 <sup>d</sup>	CH <sub>2</sub> P		3.90	3.88 <sup>d</sup>	
4e	2-C <sub>10</sub> H <sub>7</sub> <sup>e</sup>	H	C <sub>6</sub> H <sub>5</sub>	<sup>3</sup> <i>J</i> <sub>P,H</sub>		11.8	11.8 <sup>d</sup>	CH <sub>2</sub> P		3.98	4.05 <sup>d</sup>	
4f	CH <sub>3</sub>	H	C <sub>6</sub> H <sub>5</sub>	<sup>3</sup> <i>J</i> <sub>P,H</sub>	11.2	11.5 <sup>f</sup>	11.5-12.0	CH <sub>2</sub> P	3.03	3.39	3.29	
4h	C <sub>6</sub> H <sub>5</sub>	H	(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	<sup>4</sup> <i>J</i> <sub>H,M<sub>e</sub></sub>	12.0	0.7		CH <sub>3</sub>	2.50			
								CH <sub>2</sub> P	1.3-1.7			
4i	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>	H	(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	<sup>3</sup> <i>J</i> <sub>P,H</sub>	11.9	12.0	12.4	CH <sub>3</sub>	0.93			
								CH <sub>2</sub> P	2.40	2.51	2.73	
4b	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	<sup>3</sup> <i>J</i> <sub>P,H</sub>	3.5	3.6	3.5	CH <sub>2</sub> P	1.2-1.7	1.2-1.8	1.2-1.8	
								CH <sub>3</sub>	0.93	0.93	0.88	
4c	C <sub>6</sub> H <sub>5</sub>	CH <sub>2</sub> <sup>A</sup> -CH <sub>2</sub> <sup>B</sup> -CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	<sup>3</sup> <i>J</i> <sub>P,H</sub>	3.5-4	4.0 <sup>k</sup>	4.0	BrC <sub>6</sub> H <sub>4</sub> <sup>i</sup>	7.38, 7.48	7.46, 7.55	7.54, 7.62	
								CHP	3.34 (qd)	3.78 (qd)	3.70 (qd)	
				<sup>3</sup> <i>J</i> <sub>H,M<sub>e</sub></sub>	7.3	7.3	7.2	CH <sub>3</sub>	1.66 (dd)	1.54 (dd)	1.67 (dd)	
				<sup>3</sup> <i>J</i> <sub>H,H<sup>A</sup></sub>	4.0 <sup>k</sup>	l	4.0	CHP	3.55 <sup>j</sup>	3.96	3.93 <sup>j</sup>	
				<sup>3</sup> <i>J</i> <sub>H,H<sup>B</sup></sub>	8.0 <sup>k</sup>		8.0	CH <sub>2</sub> <sup>A</sup>	1.8-2.4 <sup>m</sup>		2.0-2.6	
								CH <sub>2</sub> <sup>B</sup>	1.27 <sup>n</sup>		1.36 <sup>n</sup>	
								CH <sub>3</sub>	0.73 (t)	0.66	0.62 (t)	

<sup>a</sup> A few data are missing because of either low solubility or scarcity or decomposition of some products when dissolved. <sup>b</sup> See ref 3. <sup>c</sup> Very little soluble. <sup>d</sup> Concentration 0.1 M. <sup>e</sup> C<sub>10</sub>H<sub>7</sub> = naphthyl. <sup>f</sup> Partially overlapped with the H<sub>2</sub>O signal. <sup>g</sup> Six protons (CH<sub>2</sub>P) of butyl groups. <sup>h</sup> Strongest transition, A6, of the A<sub>3</sub>B<sub>3</sub> pattern, part A. <sup>i</sup> AA'BB' pattern,  $\delta_A$  and  $\delta_B$  values are given. <sup>j</sup> Five-line pattern. <sup>k</sup> The <sup>3</sup>*J*<sub>H,H<sup>A</sup></sub> of the not equivalent CH<sub>2</sub><sup>A</sup> protons were assigned by decoupling. <sup>l</sup> Not analyzed. <sup>m</sup> Broad absorption centered at  $\delta$  2.1. <sup>n</sup> Slightly broadened quintet.

 TABLE V  
 MASS SPECTRA OF COMPOUNDS 3h, 3i, 4h, AND 4i

Significant peaks								Fragmentation	Product
3h		3i		4h		4i			
<i>m/e</i>	%	<i>m/e</i>	%	<i>m/e</i>	%	<i>m/e</i>	%		
335	7	413 <sup>a</sup>	0.5					M - HX (X = Cl or Br)	a
318	6	396 <sup>a</sup>	3					a - OH	b
306	5	384 <sup>a</sup>	0.3					a - C <sub>2</sub> H <sub>5</sub>	c
290	0.5	368 <sup>a</sup>	0.5					b - C <sub>2</sub> H <sub>4</sub>	d
278	2	356 <sup>a</sup>	1					a - C <sub>4</sub> H <sub>9</sub>	e
276	1	354 <sup>a</sup>	0.5					b - C <sub>2</sub> H <sub>6</sub>	f
262	11	340 <sup>a</sup>	3					b - C <sub>4</sub> H <sub>8</sub>	g
218	6	218	4	218	7	218	4	PO(C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	h
189	30	189	36	189	37	189	26	h - C <sub>2</sub> H <sub>5</sub>	i
176	9	176	7	176	9	176	7	h - C <sub>3</sub> H <sub>6</sub>	j
162	19	162	17	162	24	162	18	h - C <sub>4</sub> H <sub>8</sub>	k
161	17	161	18	161	17	161	12	h - C <sub>4</sub> H <sub>9</sub>	l
147	20	147	18	147	22	147	18	i - C <sub>3</sub> H <sub>6</sub>	m
134	22	134	24	134	26	134	22	k - C <sub>2</sub> H <sub>4</sub>	n
120	35	120	30	120	40	120	38	k - C <sub>3</sub> H <sub>6</sub>	o
104	7	182 <sup>a</sup>	7	104	36	182 <sup>a</sup>	13	YC <sub>6</sub> H <sub>4</sub> CH=CH <sub>2</sub> (Y = H or Br)	p
92	100	92	100	92	100	92	100	Z <sup>b</sup>	q
77	73	155 <sup>a</sup>	10	77	25	155 <sup>a</sup>	5	YC <sub>6</sub> H <sub>4</sub> (Y = H or Br)	r

<sup>a</sup> Values corresponding to ions containing one <sup>79</sup>Br. <sup>b</sup> This fragment, whose structure has not been formulated, should contain part of the P(C<sub>4</sub>H<sub>9</sub>)<sub>3</sub> grouping inasmuch as it is absent in the corresponding P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> derivatives.

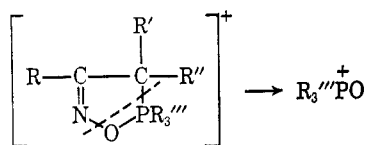
ents (*J* = 16.5-16.9 cps) are replaced by methyl (*J* = 14.0 cps). The <sup>3</sup>*J*<sub>P,M<sub>e</sub></sub> in **3b** and **4b** have the normal value expected for a three-bond coupling in a saturated fragment PCCH.

**Mass Spectra.**—Further support of the cyclic (4) against the betainic form (7) of the dehydrohalogenated compounds is found when the mass spectra of these substances are compared with the spectra of the corresponding salts (3). In fact the mass spectra of the tributylphosphine salts (**3h** and **3i**) (see Table V) exhibit the peak corresponding to the parent ion less HX, together with other peaks over *m/e* 218 [P+O-(C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>], whereas the spectra of the corresponding de-

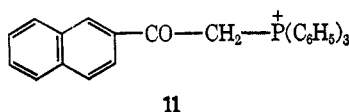
hydrohalogenated compounds (**4h** and **4i**) do not show any peak above *m/e* 218. This is indicative of the formation from the salts, before or upon electron impact, of a species (M - HX) different from the dehydrohalogenated compounds (**4h** and **4i**). Moreover, the comparison of the spectra suggests an open form for this species (M - HX) and clearly indicates a cyclic structure, with a preformed P-O bond, for **4h** and **4i**.

In the case of the triphenylphosphine salts (**3a-3g**) the spectra are often rather similar to those of the corresponding dehydrohalogenated compounds (**4a-4g**), whose dominant features are given by the peaks corresponding to the P+O(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> ion (the heaviest frag-

ment) and its fragmentation species. This is probably due, for the salts, to the easy formation, before or upon the electron impact, of the P-O bond, presumably in the same cyclic pentaatomic structure as in **4**, followed by the fragmentation



In fact, the mass spectrum of the phosphonium salt **11**,



where the formation of a P-O bond through a cyclic four-membered intermediate is much less probable, does not show any peak corresponding to  $\text{P}^+\text{O}(\text{C}_6\text{H}_5)_3$ . The evidence for a cyclic structure of the dehydrohalogenated compounds (**4a-4g**) is less straightforward than for the tributylphosphine analogous derivatives (**4h** and **4i**). However, even in this case the mass spectral data at least appear more favorable to a cyclic rather than a betainic structure.

### Experimental Section

All melting points are uncorrected. Infrared spectra were determined in Nujol, unless otherwise specified, with a Perkin-Elmer Model 137 Infracord spectrophotometer. Only prominent peaks are reported. Ultraviolet spectra (95% ethanol as solvent) were recorded on a Beckman DK2 spectrophotometer. Proton nmr spectra were recorded with Varian HA-60 and HA-100 spectrometers; decoupling experiments were performed in "frequency sweep." Chemical shifts were measured in parts per million ( $\delta$ ) from TMS as internal standard, with a Hewlett-Packard frequency counter. No appreciable variation in chemical shift and  $J$  was found within the range of concentration used (0.15-0.25 *M*), unless otherwise specified. Chemical shifts are reported either in Table III and Table IV or in the Experimental Section. Mass spectra were measured on a Hitachi-Perkin-Elmer RMU6D (single focus) spectrometer with the inlet system at 250° and an electron ionizing voltage of 70 eV (80  $\mu$  A). The values of significant peaks are reported in the General or in the Experimental Section.

**Starting Materials.**—The  $\alpha$ -halo oximes **6** were prepared by the methods reported in the literature, as indicated below under the corresponding phosphonium salts. Commercial samples of triphenylphosphine and tributylphosphine<sup>22</sup> were used in the preparation of the salts **3**; no purification was needed.

**$\beta$ -Naphthacyltriphenylphosphonium Bromide (11).**—A mixture of  $\beta$ -naphthacyl bromide (5.0 g), chloroform (40 ml), and triphenylphosphine (5.2 g) was refluxed for 30 min. The filtered solution was added to 300 ml of anhydrous ether. The precipitate was collected and crystallized from ethanol, giving 8 g (78%) of **11**: mp 251°; uv max 228 (s) ( $\epsilon$  51,100), 327 (14,000); ir 2680, 1670, 1465, 1220, 1195, 1120, 995, 940, 840, 810, 753, 748, 721, 690  $\text{cm}^{-1}$ ; nmr (DMSO- $d_6$ )  $\text{CH}_2\text{P}^+$   $\delta$  5.26 ( $J_{\text{P,H}} = 16.5$  cps); mass spectrum  $m/e$  (relative intensity) 430 (100), 429 (75), 401 (24), 303 (95), 277 (42), 228 (27), 202 (39) 201 (23).

*Anal.* Calcd for  $\text{C}_{30}\text{H}_{24}\text{BrOP}$ : C, 70.5; H, 4.7; Br, 15.7; P, 6.1. Found: C, 70.6; H, 4.5; Br, 15.7; P, 6.0.

**2-Oximinophosphonium Salts. Method A Illustrated for the Oxime of 1-Propylphenacyltriphenylphosphonium Bromide (3c).**—A solution of benzylidene-triphenylphosphorane was prepared as follows. A 50% NaH-paraffin oil mull (3.2 g) was introduced into a dry round-bottomed flask equipped with a mercury sealed stirrer, a dropping funnel, a reflux condenser, and an inlet tubing for nitrogen, to exclude oxygen during the reaction. The NaH

was washed three times in the flask with hexane, and 150 ml of DMSO (distilled over  $\text{CaH}_2$ ) was added. The mixture was then kept at 75-80° for 45 min. After cooling in an ice bath, 100 ml of dry tetrahydrofuran (THF) and 26 g of butyltriphenylphosphonium bromide<sup>23</sup> were added while stirring. In the meantime a solution of benzonitrile oxide was prepared by dissolving 10.0 g of benzohydroxamyl chloride<sup>24</sup> in 50 ml of dry THF at -20°, by adding 9.0 ml of triethylamine and filtering from the triethylamine hydrochloride. The solution was immediately added to the phosphorane, while stirring and cooling at 0°, during 5 min. The mixture was then kept for 2 hr at room temperature with continuous stirring and then poured into a cold (ice) dilute solution of HBr in water. After three washings with ether, the solution was left for a long time at room temperature. The salt **3c** began to separate after several hours, but the precipitation was complete only after 2 weeks. The salt (14.5 g, 45%) was collected, dissolved in ethanol-ether, and crystallized by cooling to -40°: mp 191° dec; uv max 262  $\mu$  (s) ( $\epsilon$  9800); ir 1470, 1450, 1105, 1100, 995, 950, 750, 725, 695  $\text{cm}^{-1}$ .

*Anal.* Calcd for  $\text{C}_{29}\text{H}_{23}\text{BrNOP}$ : C, 67.2; H, 5.6; Br, 15.4; N, 2.7; P, 6.0. Found: C, 67.1; H, 5.3; Br, 15.8; N, 2.8; P, 6.3.

**2-Oximinophosphonium Salts. Method B Illustrated for the Oxime of Phenacyltriphenylphosphonium Chloride (3a').**—A mixture of  $\omega$ -chloroacetophenone oxime<sup>25</sup> (2.0 g), triphenylphosphine (3.23 g) and chloroform (70 ml) was refluxed for 3 hr. The white precipitate (5.2 g, 100%, mp 211°) was collected and crystallized from a little ethanol. The pure salt (**3a'**) showed mp 215° dec; uv max 226 (s) ( $\epsilon$  33,300), 258 (s) (11,000); ir 1435, 1310, 1110, 960, 757, 750, 695  $\text{cm}^{-1}$ .

*Anal.* Calcd for  $\text{C}_{26}\text{H}_{23}\text{ClNOP}$ : C, 72.3; H, 5.4; Cl, 8.2; N, 3.2; P, 7.2. Found: C, 72.0; H, 5.4; Cl, 8.5; N, 3.4; P, 7.7.

The same procedure was followed for the other salts but varying the solvent, time, and temperature, according to the data reported in Table I. Other data and modifications of the standard procedure, if any, are reported below.

**The oxime of *p*-bromophenacyltriphenylphosphonium bromide (3d)** was obtained from *p*-bromophenacyl bromide oxime<sup>26</sup> and triphenylphosphine. Owing to its solubility in the reaction medium, after elimination of most of the solvent at reduced pressure, the salt **3d** was isolated by precipitation with ether. After crystallization from a little ethanol it melted at 219° dec; uv max 225 (s) ( $\epsilon$  21,600), 263 (15,100); ir 1430, 1105, 962, 748, 690  $\text{cm}^{-1}$ .

*Anal.* Calcd for  $\text{C}_{26}\text{H}_{22}\text{Br}_2\text{NOP}$ : C, 56.2; H, 3.9; Br, 28.8; N, 2.6; P, 5.6. Found: C, 56.8; H, 4.1; Br, 29.5; N, 2.5; P, 5.6.

**2-Oximinopropyltriphenylphosphonium chloride (3f)** was obtained from chloroacetone oxime<sup>27</sup> and triphenylphosphine: white crystals from ethanol; mp 223°; yield 57%; uv max 224 (s) ( $\epsilon$  26,100), 269 (3200), 277 (2600); ir 3500, 1110, 820, 755, 720, 690  $\text{cm}^{-1}$ .

*Anal.* Calcd for  $\text{C}_{21}\text{H}_{21}\text{ClNOP}$ : C, 68.2; H, 5.7; Cl, 9.6; N, 3.8; P, 8.4. Found: C, 67.9; H, 5.8; Cl, 9.6; N, 3.6; P, 8.5.

**2-Oximinocyclohexyltriphenylphosphonium chloride (3g)** was obtained from 2-chlorocyclohexanone oxime<sup>28</sup> and triphenylphosphine: mp 198° (from ethanol-ether); yield 55%; uv max 225 (s) ( $\epsilon$  20,000), 269 (3000), 277 (2400); ir 3400, 1465, 1110, 1005, 998, 750, 728, 698  $\text{cm}^{-1}$ .

*Anal.* Calcd for  $\text{C}_{24}\text{H}_{25}\text{ClNOP}$ : Cl, 8.6; N, 3.4; P, 7.6. Found: Cl, 8.5; N, 3.5; P, 7.5.

**The oxime of phenacyltri-*n*-butylphosphonium chloride (3h)** was obtained from  $\omega$ -chloroacetophenone oxime<sup>26</sup> and tri-*n*-butylphosphine: mp 197° (from ethanol); yield 87%; uv max 248  $\mu$  ( $\epsilon$  10,500); ir 2950, 1470, 1405, 1300, 1045, 965, 802, 748, 705  $\text{cm}^{-1}$ .

**The oxime of *p*-bromophenacyltri-*n*-butylphosphonium bromide (3i)** was obtained from *p*-bromophenacyl bromide oxime<sup>26</sup> and tri-*n*-butylphosphine: mp 168° (from ethanol); yield

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(28) We thank Dr. A. Nenz (Istituto G. Donegani, Novara) for the kind gift of this compound.

(22) Fluka AG, Buchs SG, Switzerland.

85%; uv max 259  $m\mu$  ( $\epsilon$  15,500); ir 1460, 1400, 1300, 1045, 960, 920, 845, 725  $cm^{-1}$ .

Anal. Calcd for  $C_{20}H_{24}Br_2NOP$ : Br, 32.3; N, 2.8; P, 6.3. Found: Br, 32.5; N, 2.9; P, 6.5.

**2-Oximinophosphonium Salts. Method C Illustrated for the Oxime of  $\beta$ -Naphthacyltriphenylphosphonium Bromide (3e).**—To a solution of 11 (6.0 g) in methanol (60 ml) was added 10 g of  $NH_2OH \cdot HCl$  dissolved in the minimum amount of water. The mixture was refluxed for 30 hr and then poured into water; The precipitate was collected and crystallized from ethanol-water, giving 5.0 g (81%) of 3e: mp 226°; uv max 230  $m\mu$  ( $\epsilon$  46,000), 277 (13,000), 287 (11,600), 297 (10,400); ir 3000, 1430, 1300, 1105, 975, 925, 820, 742, 692  $cm^{-1}$ .

Anal. Calcd for  $C_{30}H_{25}BrNOP$ : C, 68.4; H, 4.7; Br, 15.2; N, 2.6; P, 5.9. Found: C, 68.6; H, 4.5; Br, 14.6; N, 2.6; P, 5.9.

**2-Oximinopropyltriphenylphosphonium chloride (3f)** was prepared by the same procedure from 2-oxopropyltriphenylphosphonium chloride,<sup>29</sup> using ethanol instead of methanol; reflux time was 10 hr; yield was 56%.

**1-Benzoylbenzyltriphenylphosphonium Bromide (8).**<sup>11</sup>—Desyl bromide<sup>30</sup> (9.0 g, 32.7 mmol) dissolved in 100 ml of dry benzene was refluxed for 5 hr together with 8.6 g (32.7 mmol) of triphenylphosphine. After cooling, the whole mixture was shaken with water. The undissolved solid, collected and crystallized from ethanol, gave 2.9 g (5.4 mmol, 17%) of 8: mp 237–239°; uv max 268  $m\mu$  ( $\epsilon$  11,000); ir 1675, 1445, 1220, 1115, 997, 760, 708  $cm^{-1}$ .

Anal. Calcd for  $C_{32}H_{26}BrOP$ : P, 5.8; Br, 14.9. Found: P, 6.1; Br, 15.4.

The benzene solution, after elimination of the solvent, gave a solid residue which was triturated with ether. The undissolved portion (6.8 g, 24.5 mmol, 75%) was shown to be essentially pure  $OP(C_6H_5)_3$  from its ir and tlc comparison with an authentic sample. From the ethereal solution were obtained 5.1 g (26.0 mmol, 80%) of desoxybenzoin, identified by its ir spectrum and by tlc comparison with an authentic sample. Only traces of unreacted triphenylphosphine were detected by tlc.

**Attempt at Oximation of 1-Benzoylbenzyltriphenylphosphonium Bromide. 1-Benzoylbenzyltriphenylphosphonium Benzylide (9).** A.—A mixture of 0.61 g of 8 and 1.0 g of  $NH_2OH \cdot HCl$  in 95% ethanol was refluxed for 6 days. After dilution with water the filtered solid showed an ir spectrum identical with that of the starting material.

B. A mixture of 1.1 g (2 mmol) of 8, 0.7 g (10 mmol) of  $NH_2OH \cdot HCl$  and 0.8 g (8 mmol) of potassium acetate was refluxed in an aqueous alcoholic solution for 1.5 hr. After dilution with water the filtered solid (0.88 g, 93%) was identified as the ylide 9, mp 188–190° (lit.<sup>31</sup> mp 191–192°); in fact its mass spectrum showed an intense peak at 456  $m/e$  ( $M^+$ ) and no peaks corresponding to  $Br^+$  or  $(HBr)^+$ . The ir spectrum showed bands at 1510, 1480, 1430, 1380, 1250 1105, 970, 848, 725, 705  $cm^{-1}$ .

**1,2,5-Oxazaphosph(V)ol-2-ines (4).** A. **By Ion-Exchange Resin.**—The appropriate 2-oximinophosphonium salt (1 mmol) was dissolved in about 30 ml of ethanol and the solution was slowly percolated through a few grams of a basic ion-exchange resin<sup>32</sup> previously treated with 2 *N* KOH, then with water, and finally with ethanol. The less soluble 1,2,5-oxazaphosph(V)ol-2-ines (4) precipitated in pure form from the eluates and could be collected by filtration. For the more soluble 4 concentration under reduced pressure in the cold was necessary. Owing to the thermal instability of these compounds, the crystallization, when necessary, was performed most effectively by dissolving the compound in the appropriate solvent at room temperature and then cooling to about  $-30^\circ$ . This general procedure was used for the following compounds.

**3,5,5,5-Tetraphenyl-4-methyl-1,2,5-oxazaphosph(V)ol-2-ine (4b)** showed the following characteristics: mp 100° (from benzene-hexane); yield 85%; uv max 269  $m\mu$  ( $\epsilon$  11,900); ir 1460, 1080, 970, 830, 773, 760, 740, 722, 698  $cm^{-1}$ .

Anal. Calcd for  $C_{27}H_{24}NOP$ : C, 78.3; H, 5.9; N, 3.4; P, 7.7. Found: C, 78.6; H, 6.0; N, 3.5; P, 8.0.

**3,5,5,5-Tetraphenyl-4-*n*-propyl-1,2,5-oxazaphosph(V)ol-2-ine (4c)** showed the following characteristics: mp 96° (from benzene-hexane); yield 70%; uv max 223 (s) ( $\epsilon$  29,000), 259 (s) (8400); ir 1455, 1430, 1080, 980, 765, 755, 743, 725, 700  $cm^{-1}$ .

Anal. Calcd for  $C_{29}H_{28}NOP$ : C, 79.6; H, 6.4; N, 3.2; P, 7.1. Found: C, 79.4; H, 6.4; N, 3.3; P, 7.3.

**3-*p*-Bromophenyl-5,5,5-triphenyl-1,2,5-oxazaphosph(V)ol-2-ine (4d)** showed the following characteristics: mp 157° (from hot ethyl acetate); yield 91%; uv max 261  $m\mu$  ( $\epsilon$  12,900); ir 1475, 1425, 1080, 1040, 985, 805, 745, 692  $cm^{-1}$ .

Anal. Calcd for  $C_{28}H_{21}BrNOP$ : C, 65.8; H, 4.5; Br, 16.9; N, 2.9; P, 6.5. Found: C, 66.3; H, 4.7; Br, 16.6; N, 2.7; P, 6.5.

**3- $\beta$ -Naphthyl-5,5,5-triphenyl-1,2,5-oxazaphosph(V)ol-2-ine (4e)** showed the following characteristics: mp 142° (from warm benzene); yield 90%; uv max 229 ( $\epsilon$  37,700), 287 (10,300), 298 (9800); ir 1435, 1080, 1045, 985, 945, 810, 760, 742, 700  $cm^{-1}$ .

Anal. Calcd for  $C_{30}H_{24}NOP$ : C, 80.9; H, 5.4; N, 3.1; P, 7.0. Found: C, 80.5; H, 5.4; N, 3.2; P, 7.2.

**3,4-Tetramethylene-5,5,5-triphenyl-1,2,5-oxazaphosph(V)ol-2-ine (4g)** showed the following characteristics: mp 102°; yield 53%; uv max 263 ( $\epsilon$  2800), 269 (2800), 276 (2100); ir 1480, 1430, 1080, 990, 952, 760, 737, 720, 696  $cm^{-1}$ .

Anal. Calcd for  $C_{24}H_{24}NOP$ : C, 77.2; H, 6.5; N, 3.7; P, 8.8. Found: C, 76.8; H, 6.4; N, 3.8; P, 8.7.

**3-Phenyl-5,5,5-tri-*n*-butyl-1,2,5-oxazaphosph(V)ol-2-ine (4h)** showed the following characteristics: liquid; yield 80%; uv max 249  $m\mu$  ( $\epsilon$  9500); ir (neat) 2950, 1460, 1085, 1055, 1010, 990, 918, 760, 698  $cm^{-1}$ .

Anal. Calcd for  $C_{26}H_{34}NOP$ : N, 4.2; P, 9.2. Found: N, 4.1; P, 9.0.

**3-*p*-Bromophenyl-5,5,5-tri-*n*-butyl-1,2,5-oxazaphosph(V)ol-2-ine (4i)** showed the following characteristics: mp 70° (from petroleum ether, bp 30–60°); yield 85%; uv max 259  $m\mu$  ( $\epsilon$  11,700); ir 2950, 1530, 1465, 1400, 1075, 1005, 918, 810  $cm^{-1}$ .

Anal. Calcd for  $C_{26}H_{33}BrNOP$ : C, 58.0; H, 8.0; Br, 19.3; N, 3.4; P, 7.5. Found: C, 58.1; H, 7.9; Br, 19.4; N, 3.3; P, 7.6.

**B. By Treatment with Aqueous Alkali. 3,5,5,5-Tetraphenyl-4-*n*-propyl-1,2,5-oxazaphosph(V)ol-2-ine (4c).**—3c (1.0 g) was dissolved in 10 ml of ethanol; the solution was made alkaline by dropwise addition of a few milliliters of aqueous 1 *N* KOH at 0°. The white precipitate (0.84 g, 98%), collected and crystallized from benzene-hexane, melted at 95–96°. Its ir spectrum was identical with that of 4c prepared from 3c by the resin method.

**3-*p*-Bromophenyl-5,5,5-triphenyl-1,2,5-oxazaphosph(V)ol-2-ine (4d)** was prepared by the same procedure as 4c; yield 100%.

**3-Methyl-5,5,5-triphenyl-1,2,5-oxazaphosph(V)ol-2-ine (4f).**—3f (0.46 g) was dissolved in 50 ml of water and the solution was made slightly alkaline by the addition of the stoichiometric amount of 0.5 *M* NaOH. The solution was immediately extracted several times with ether and the extracts were dried over  $Na_2SO_4$ . After removal of the solvent under vacuum at room temperature, 0.31 g (74%) of 4f was obtained as a white solid, mp 116° dec. The compound is very unstable especially in solution even at room temperature, giving  $PO(C_6H_5)_3$ . It could not be purified by crystallization: uv max 224 (s) ( $\epsilon$  26,000), 268 (2800); ir 1430, 1080, 1025, 945, 747, 717, 698  $cm^{-1}$ .

Anal. Calcd for  $C_{21}H_{20}NOP$ : C, 75.5; H, 6.1; N, 4.2. Found: C, 76.5; H, 6.1; N, 3.9.

**Thermal Decomposition of 3-*p*-Bromophenyl-5,5,5-triphenyl-1,2,5-oxazaphosph(V)ol-2-ine (4d).** 2H-3-*p*-Bromophenylazirine (10).—4d (20 mg) was placed in a small test tube under vacuum (0.5 torr) and the bottom of the tube was gradually heated in an oil bath up to 148–150°. The azirine (10, 3 mg, 31%) condensed in the cold portion of the test tube as white crystals: mp 78°; uv max 257  $m\mu$  ( $\epsilon$  11,600); ir 1730, 1590, 1480, 1470, 1400, 1075, 1000, 832, 818  $cm^{-1}$ ; nmr ( $CDCl_3$ )  $\delta$  1.80 (s).

Anal. Calcd for  $C_8H_8BrN$ : C, 49.0; H, 3.1; Br, 40.8; N, 7.1. Found: C, 49.4; H, 3.3; Br, 41.0; N, 7.1.

**Registry No.**—3a, 14264-66-5; 3a', 14181-79-4; 3b, 15055-54-6; 3c, 17631-10-6; 3d, 17631-11-7; 3e, 17658-49-0; 3f, 17631-12-8; 3g, 17631-13-9; 3h, 17631-14-0; 3i, 17631-15-1; 4a, 14264-70-1; 4b, 17631-17-3; 4c, 17631-18-4; 4d, 17631-19-5; 4e,

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(32) Dowex 2, 8  $\times$  50–100 mesh, supplied by Fluka AG, Buchs SG, Switzerland.

(33) When the sublimation was carried out at higher temperature a mixture of 10 and  $PO(C_6H_5)_3$  was obtained.

17631-20-8; **4f**, 17631-21-9; **4g**, 17631-22-0; **4h**, 17631-23-1; **4i**, 17631-24-2; **8**, 1530-47-8; **10** (R = *p*-BrC<sub>6</sub>H<sub>4</sub>; R' = R'' = H), 17631-26-4; **11**, 2689-60-3.

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## Quinazolines and 1,4-Benzodiazepines. XLII.<sup>1</sup> Photochemistry of Some N-Oxides

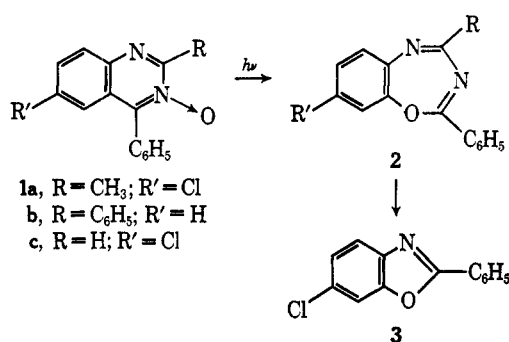
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Quinazoline 3-oxides **1** are photoisomerized to benzo[*f*]-1,3,5-oxadiazepines **2**. 6-Chloro-2-methyl-4-phenylquinazoline 1-oxide (**4**) gives 1-acetyl-5-chloro-3-phenylindazole (**6**) on irradiation. 7-Chloro-2-methylamino-5-phenyl-3H-1,4-benzodiazepine 3-oxide (**9**) gives a mixture of 9-chloro-5-methylamino-2-phenyl-4H-benzo[*g*]-1,3,6-oxadiazocine (**11**) and 1-benzoyl-7-chloro-1,2-dihydro-3-methylaminoquinoxaline (**12a**). These transformations are believed to proceed by rearrangement of the oxaziridines formed as primary isomerization products.

Aromatic N-oxides are quite generally labile to irradiation with ultraviolet light,<sup>2</sup> as illustrated by the photoisomerization of quinazoline 3-oxides **1** to benzo[*f*]-1,3,5-oxadiazepines **2**.<sup>3</sup> We wish to report two further examples of this isomerization as well as the photochemical behavior of two related N-oxides.



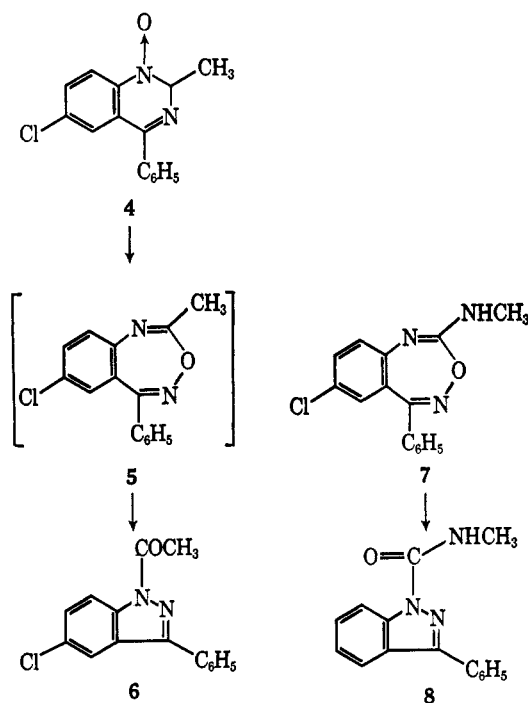
The irradiation products **2a** and **2b** were obtained in excellent yield; however, irradiation of **1c** gave only a low yield of **3**. Presumably **3** was formed from **2c** during work-up of the reaction mixture.<sup>4</sup>

In an attempt to obtain evidence for the presence of isolable intermediates in the photoisomerization of **1a**, the ultraviolet spectrum of an irradiated acetonitrile solution of **1a** was measured at intervals. These spectra showed isosbestic points at 298, 332, and 345 mμ which would indicate the absence of stable intermediates.

The quinazoline 1-oxide **4**<sup>5</sup> was also irradiated. By analogy with the quinazoline N-oxides the formation of **5** was expected.<sup>2c</sup> The product, however, displayed a prominent carbonyl band at 1720 cm<sup>-1</sup> and was readily identified as **6** by comparison with a sample obtained by acetylation of 5-chloro-3-phenylindazole. Its formation *via* **5** as an intermediate is not ruled out

since it has been shown that **7**, synthesized by non-photochemical means, gave **8** on exposure to light (Scheme I).<sup>6</sup>

SCHEME I



The photochemistry of the benzodiazepine 4-oxide **9**, which may be considered to be a homoquinazoline N-oxide, was reinvestigated. It has been reported that irradiation with sunlight gives the oxaziridine **10**<sup>7</sup> which is reconverted into **9** on heating (Scheme II). Irradiation of **10**, formed as primary product,<sup>7</sup> or more vigorous irradiation of **9** led to the formation of two new photoisomers **11** and **12a**. Direct crystallization of the reaction mixture gave **11** which was shown to be isomeric with the starting material by elemental analysis and mass spectrometry. Mild acid hydrolysis of **11** gave **13a** whose structure was proved by dechlorination to **13b**.<sup>8</sup> In addition, structure **11** was supported

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