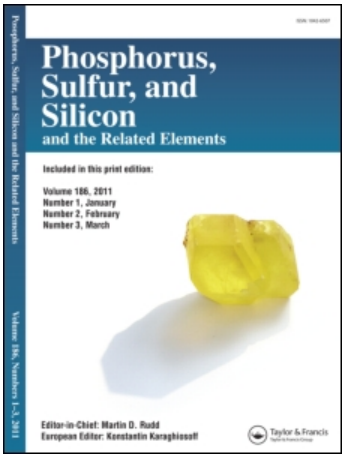

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Louis D. Quin[a]; Catherine Bourdieu[a]; Gyöngyi S. Quin[a]
[a] Department of Chemistry, University of Massachusetts, Amherst, MA

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THE GENERATION OF METAPHOSPHORAMIDATES BY FRAGMENTATION OF 2,3-OXAPHOSPHABICYCLO[2.2.2]OCTENE DERIVATIVES

LOUIS D. QUIN,* CATHERINE BOURDIEU and GYÖNGYI S. QUIN
Department of Chemistry, University of Massachusetts, Amherst, MA 01003

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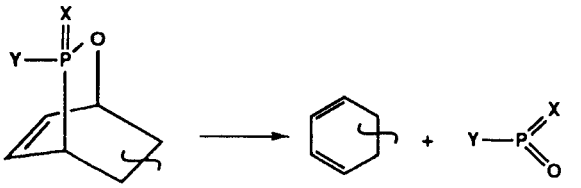
Phosphole oxides with N,N-diethylamino, N-mesitylamino and N-*tert*-butylamino substituents on phosphorus were generated in the presence of N-phenylmaleimide to give Diels-Alder adducts with the 7-phosphanorbornene framework. Products were characterized by ^{31}P and ^{13}C NMR spectroscopy, and in one case by ^{17}O NMR spectroscopy. Insertion of oxygen into a P—C bond of this strained cyclic system occurred smoothly on treatment with m-chloroperbenzoic acid. The resulting derivatives with the 2,3-oxaphosphabicyclo[2.2.2]octene ring system were characterized by ^{1}H, ^{31}P, and ^{13}C NMR spectroscopy. In the case of the N-mesityl derivative, two stable isomers were formed and separated by chromatography. The full structure of one isomer was established by X-ray diffraction analysis. The ring system was fragmented on heating in toluene (110°C, 22–48 hrs) or on irradiation (30–35°C, 254 nm, 24 hrs) with the release of the P—O bridging unit as a metaphosphoramidate ($RR'N—PO_2$). In the photolytic method, these products were effectively trapped with ethanol to give derivatives of structure RR'N—P(O)(OH)(OEt). When these phosphoramidates were formed by trapping of the thermally generated metaphosphoramidates, a second reaction occurred with the alcohol that caused displacement of the amine, possibly by an elimination-addition reaction involving ethyl metaphosphate.

Key words: Phosphole oxides; 7-phosphanorbornenes; 2,3-oxaphosphabicyclo[2.2.2]octenes; N,N-diethyl metaphosphoramidate; N-mesityl metaphosphoramidate; N-*tert*-butyl metaphosphoramidate; metaphosphates.

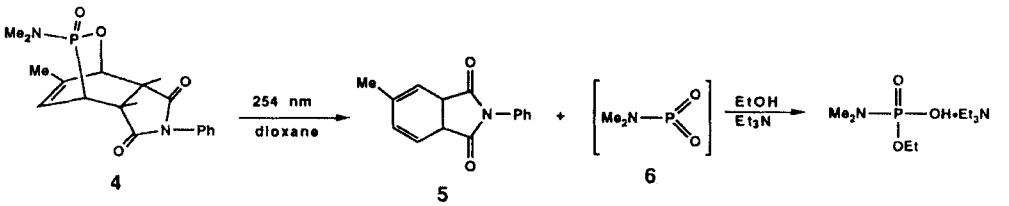
Fragmentation of compounds containing the 2,3-oxaphosphabicyclo[2.2.2]octene ring system has been shown to be a valuable technique for the generation of the family of metaphosphoric acid derivatives. Either thermal or photochemical treatment in inert solvents causes cleavage of the O—C and P—C bonds to effect the desired reaction, which has been used to generate alkyl metaphosphates (**1**),[1] alkyl metathiophosphates (**2**),[2] and N,N-dialkyl metaphosphoramidates (**3**).[3] Metaphosphoric acid derivatives are well known to be highly reactive, with the phosphorus atom acting as an electrophilic center. They undergo spontaneous self-condensation to form materials with P—O—P bonds; they are usually detected by including trapping agents in the medium in which they are generated. No successful attempts have been reported from other laboratories to stabilize metaphosphoric acid derivatives by applying the well-known[4] device of locating sterically large groups close to the reaction center of a low-coordination phosphorus compound, or to generate



	Y	X
1	RO	O
2	RO	S
3	R_2N	O

such species in solution at low temperatures where their lifetime could be appreciable. We have initiated work along such lines using the fragmentation methods mentioned above. They are well suited for such studies; a great variety of precursors is available, and the photochemical method has the potential of generating the metaphosphoric acid derivatives at low temperatures where their lifetime may be prolonged. Here we will report on the synthesis of bicyclic phosphonamides with sterically large amino substituents and on their thermal and photochemical fragmentations. Elsewhere we report on the performance of the photochemical fragmentations at low temperature (−75°C) and the successful demonstration of a finite existence for a THF-solvated form of the sterically-crowded metaphosphoramidates.[5]

The only examples of metaphosphoramidates are those that resulted from our own earlier work. N,N-Dimethylamino metaphosphoramidate (**6**) was released by photochemical fragmentation of the bicyclic phosphonamide **4** at room temperature,[3] and trapped with alcohols (in the presence of a tertiary amine to stabilize



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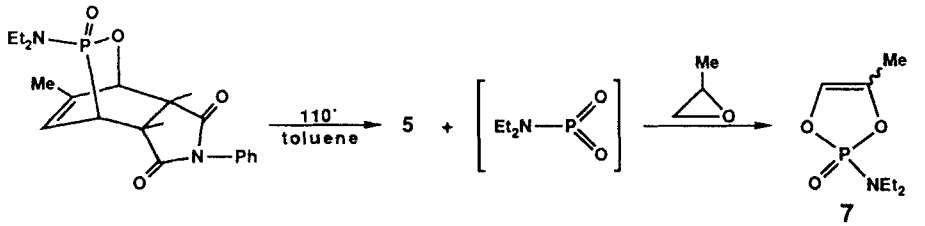
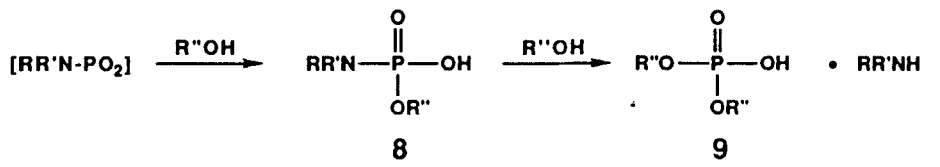
the product). We have also generated N,N-diethylamino metaphosphoramidate, employing the thermal fragmentation process with trapping by propylene oxide to form a 1,3,2-dioxaphospholane oxide (**7**).[6]



7

In the present work, we have employed alcohols as trapping agents to prove that a free metaphosphoramidate was being released. The rationale behind the use of alcohols for this purpose is discussed elsewhere[7]; we have shown in several instances by the use of kinetics measurements that trapping agents do not react with the precursor in the thermal process and only figure in the process after the free metaphosphate has been generated. The fragmentation has been characterized as a retro-cycloaddition.[7] Similarly, no role has been found for the alcohol prior to the release of the metaphosphate in the photochemical fragmentation. However, we have found that alcohols can be involved in a secondary reaction with the initially formed phosphoramidate trapping products (**8**); during the thermal process, the amino group is easily displaced by excess alcohol with the formation of O,O-dialkyl phosphates (**9**).[7] This reaction was also observed in the room-temperature photolysis of the N,N-dimethylamino derivative,[3] but as noted was prevented by the inclusion of triethylamine in the medium.



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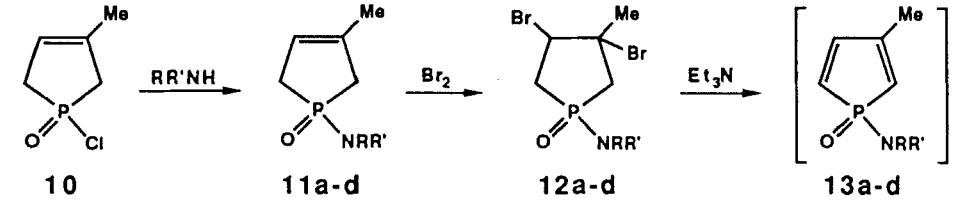
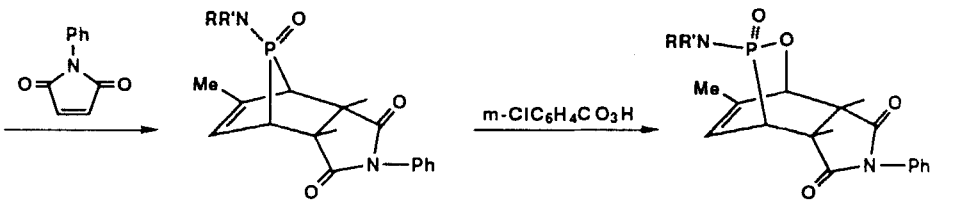
Synthesis and Stereochemistry of Phosphonamides in the 2,3-Oxaphosphabicyclo[2.2.2]octene Series

In 1986, we reported on a method for the synthesis of the first phosphonamide **4** in this bicyclic series, which had the N,N-dimethylamino substituent.[8] This method, which is outlined in Scheme 1, has been used in the present study and found to be quite valuable for the synthesis of other N-substituted compounds. In particular, we have prepared phosphonamides with N,N-diethylamino, N-mesityl, and N-*tert*-butyl substituents. We were unsuccessful in an attempt to prepare the N,N-diisopropylamino compound; the first step in the synthesis requires the displacement of chlorine in the phosphinic chloride **10** by the amino group, and the steric crowding is so great in this amine as to make this reaction impractical. Maleimide derivatives are especially effective as dienophilic partners in Diels-Alder reactions of unstabilized, highly-reactive phosphole oxides (e.g., **13**), and were selected for use here to construct the required 7-phosphanorbornene intermediates (**14**). Numerous Diels-Alder reactions of this type have been performed, and invariably give only one of several possible regio- and stereo-isomers. The ring fusion is always *endo*, and this was easily established for the amino derivatives from the large magnitude (15–16 Hz) of the 3-bond coupling of ^{31}P to ^{13}C of the carbonyl groups (Table I). This



10 11a-d 12a-d 13a-d



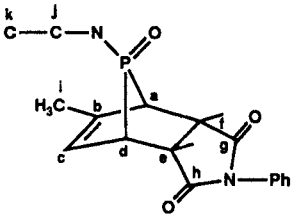
14a-d 15a-c

a, R = R' = Et
b, R = Mes, R' = H
c, R = t-Bu, R' = H
d, R = R' = Me

SCHEME I

TABLE I

^{31}P and ^{13}C NMR data for compounds **14a–c**



		^{31}P	^{13}C										
			a	b	c	d	e[a]	f[a]	g[b]	h[b]	i	j	k
14a	δ	82.9	46.2	140.6	122.4	42.9	43.7	44.7	175.8	175.4	19.6	42.6	14.6
	J		80	9.0	7.1	79.6	15.9	17.6	15.3	14.9	4.0	1.8	0
14b	δ	74.3	46.6	141.6	121.6	44.1	42.3	43.5	175.6	175.2	19.0	--[c]	
	J		77.4	8.7	6.3	78.8	17.0	20.2	16.1	15.5	4.1		
14c	δ	79.0	47.7	140.7	122.7	44.0	42.8	43.6	176.7	176.3	19.6	52.2	31.7
	J		76.6	8.8	7.1	78.3	15.7	17.9	15.7	14.9	3.8	2.2	3.8
13d[8]	δ	82.7	45.2	140.2	121.4	42.3	44.5	44.2	175.4	175.0	19.3	38.7	
	J		79.2	9.8	6.1	79.4	17.1	16.5	15.9	14.6	3.6	0	

a. Could be reversed.

b. Could be reversed.

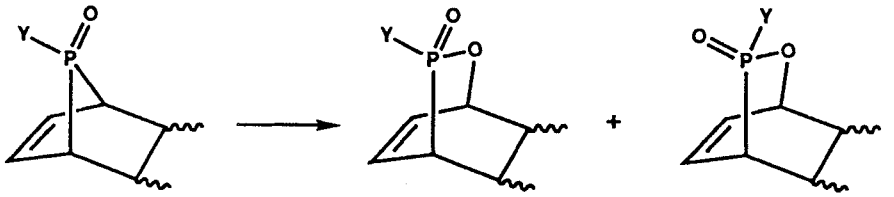
c. *ortho*-CH_3, δ 18.97(s); *para*-CH_3, δ 20.8(s).

coupling is under dihedral angle control,[9] and would be small or nil in the *exo* isomer. The amino substituents were assigned to the *syn* position relative to the ring double bond; this was established by X-ray analysis to be the preference for the N,N-dimethylamino group in a Diels-Alder dimer,[8] and was confirmed in the present case by employing natural abundance ^{17}O NMR as a diagnostic tool. We have previously established that the phosphoryl oxygen gives a signal with very

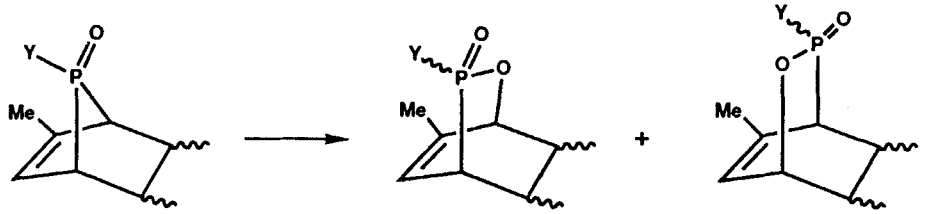
different shifts when it is *syn* or *anti* to the double bond, in both phosphonamide and phosphine oxide functionalities.[10] When *anti* to the double bond, the oxygen signals for phosphonamides based on the phosphole dimer framework occurs downfield (δ 102.7 for the dimer of **13d**), whereas the signal for the *syn* isomer is relatively far upfield (δ 48.9). For compound **14b**, the signal appeared at δ 118.7 ($^1J_{P-O}$ = 161 Hz), and this is conclusive proof of the *anti* oxygen configuration (previously confirmed in the dimer of **13d** by X-ray analysis).[8] The ^1H and ^{13}C NMR spectra of the new N-phenylmaleimide adducts **14a**, **14b** and **14c** match each other and have features resembling those previously reported[8] for the N,N-dimethylamino derivative **14d**. Accordingly, all compounds can be assigned the same stereochemical features. The data for the new compounds, as well as for **13d**, are given in Table I.

The oxygen insertion reaction with metachloroperbenzoic acid occurs with ring-strained P—C systems and takes preference to epoxidation of the double bond.[11,12] In this reaction, it is possible for two regioisomers to be formed, each with two configurational isomers at phosphorus. In none of numerous reactions of this type

a. Stereoisomers



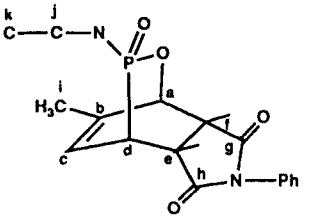
b. Regioisomers



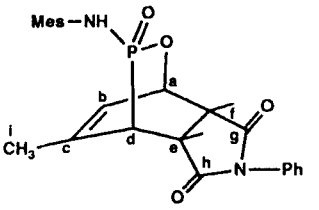
so far conducted have we ever observed more than two products. For phosphonamides **15a** and **15b**, two isomers were detected by ^{31}P NMR analysis of the crude reaction products; the two signals were close together (about 1 ppm) and in the expected region (δ 24–26) for phosphonamides. For **15a**, the minor isomer gives the upfield ^{31}P signal; it is considerably less stable than the major isomer, and is usually lost during isolation procedures. This allowed the isolation in pure form of **15a**. The phosphonamide **15c** was the single product from O-insertion into **14c**. The ^1H and ^{13}C NMR spectra of **15a** and **15c** (Table II) were very similar to those of the N,N-dimethyl derivative **4** (included in Table II for comparison), whose

TABLE II

^{31}P and ^{13}C NMR data for compounds **15a–c**



4, 15a-c



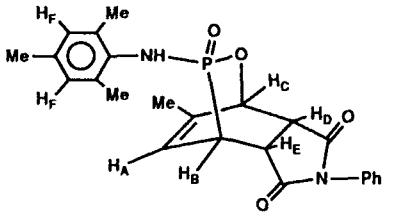
16

		^{31}P	^{13}C										
			a	b	c	d	e	f	g	h	i	j	k
15a	δ	24.5	76.9	141.1	124.2	36.2	46.1	39.5	173.2	175.6	19.7	40.7	14.7
	J		8.1	10.9	10.3	112.3	11.5	6.4	0	18.3	2.7	3.8	0
15b	δ	23.2	76.4	141.9	122.7	35.8	45.9	38.1	172.9	175.4	19.4		
	J		10.3	11.0	10.6	112.2	10.6	6.4	0	18.9	0		
16	δ	22.05	72.7	124.0	143.2	40.8	46.7	37.6	173.2	175.2	21.6		
	J		8.3	9.9	9.8	112.8	10.6	6.0	0	19	4.4		
15c	δ	25.0	76.5	140.8	123.6	36.6	46.3	38.5	174.2	176.6	19.7	51.0	31.8
	J		8.0	11.7	10.6	111.0	11.4	5.9	0	18.5	2.7	0	0
4	δ	25.0	76.7	141.1	124.0	35.0	46.0	39.0	173.0	175.3	19.5	37.6	
	J		7.7	11.0	9.9	111.3	11.9	6.6	0	18.7	2.2	4.4	

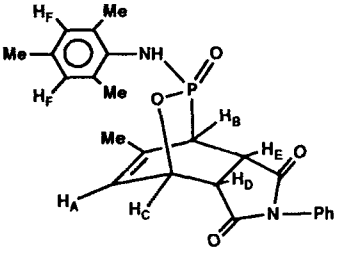
structure was determined by X-ray analysis.[8] The regio- and stereo-chemistry of the O-insertion reaction products are therefore established for the new compounds. The mechanism of the insertion reaction has been discussed elsewhere[13] and easily accounts for the observation of retention of configuration at phosphorus. However, it was observed for the insertion into the N-mesityl derivative **13b** that the two

TABLE III

^{1}H NMR spectra[a] of regioisomers **15b** and **16**



15b



16

	15b	**16**
H_A	5.89 (t with partial q, $J_{AB} \sim J_{AP} \sim 8.4$, $J_{A\text{-}Me} = 1.4$)	6.17 (m, $J_{AC} = 4.0$, $J_{A\text{-}Me} = 1.5$)
H_B	3.64 (d of d of d, $J_{BE} = 2.56$,[b] $J_{AB} = 7.2$, $J_{BP} = 12.6$)	3.92 - 4.04[c]
H_C	5.11 (d of d of d, $J_{CD} = 4.1$, $J_{CE} = 2.0$,[b] $J_{CP} = 22.7$)	5.34 (d of d of d, $J_{CA} = 4.0$, $J_{CD} = 5.3$, $J_{CP} = 23.4$)
H_D	3.97 (d of d, $J_{DC} = 4.1$, $J_{DE} = 7.96$)	3.92 - 4.04[c]
H_E	3.80 (d of t, $J_{ED} = 7.97$, $J_{EB} = 2.4$, $J_{EC} = 2.4$[b])	3.83 (d of t, $J_{ED} = 7.93$, $J_{EP} = 2.6$, $J_{EB} = 2.6$[b])
=CMe	1.71 (d of d, $J_{Me\text{-}A} = 1.4$, $J = 4.89$[d])	1.92 (t, $J_{Me\text{-}A} = 1.5$, $J_{Me\text{-}P} = 1.5$)
NH	4.21 (d, $J_{PH} = 9.6$)	3.63 (d of q, $J_{PH} = 12.8$, $J = 1.5$[e])
o-Me	2.31 (s)	2.32 (s)
p-Me	2.23 (s)	2.24 (s)
H_F	6.86 (s)	6.86 (s)

a. 200 MHz; $CDCl_3$ solutions. Coupling constants (Hz) are given in parentheses. Unless noted, ^{1}H-^{1}H couplings were confirmed by a 2-D experiment.

b. Unconfirmed.

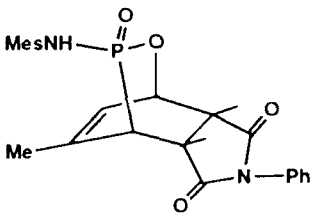
c. Overlapping of H_B and H_D.

d. Possibly $J_{Me\text{-}P}$.

e. Origin of coupling not revealed.

isomers were formed in nearly equal amount and both survived the chromatographic procedure. This presented an opportunity to determine the structure of the second isomer that is usually formed but lost, and separation of the two N-mesityl isomers was therefore performed. This proved to be easily accomplished by chromatography

on silica gel. The isomer with the downfield ^{31}P NMR signal (δ 23.2) had very similar ^{13}C NMR spectra (Table II) to those of the single isomer isolated for other amino derivatives, and is therefore assigned the usual 6-methyl structure **15b**. To place this correlation on a firmer basis, a single-crystal X-ray diffraction analysis was performed. The structure proved to be the same as found in the X-ray analysis of the analogous compound **4**; since this analysis has been reported in full detail[8] and structural parameters for **15b** are quite similar, details of the new analysis are available as Supplementary Material. The replacement of dimethylamino by the larger mesitylamino caused no significant change in bond angles at phosphorus (ring C—P—O, 98.8° in **4**, 99.1° in **15b**). The other isomer with δ ^{31}P 22.1 had pronounced differences in its ^{13}C NMR spectrum that were clearly associated with the positioning of the C-methyl group. Thus, relative to the isomer of known structure, the β-deshielding effect of methyl in **15b** is transferred from the ring carbon attached to oxygen to the ring carbon attached to phosphorus (Δ δ 5.0 ppm), with an accompanying upfield shift to the former carbon of 3.7 ppm. Another indication is provided by the coupling of ^{31}P to the ^{13}C of the methyl; no coupling is detected in the common isomer, since the nuclei have a 4-bond connection, but the methyl is a doublet (J = 4.4 Hz) from the 3-bond coupling of the regio-isomer. The ^{1}H NMR spectra of the isomers (Table III) were obtained at 200 MHz, using also the 2-D technique, which provided confirmation of the structural difference and allowed the assignment of the 5-methyl structure **16**. Especially definitive was the pronounced difference in shift and coupling constants for the olefinic proton, whose relation to a bridgehead C—H was firmly established. Thus the olefinic proton is coupled (8.4 Hz) to the bridgehead H attached to the C—P unit in **15b**,



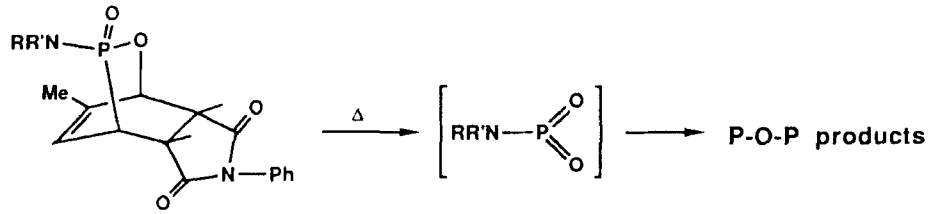
16

but in **16** the olefinic H shows no coupling to this H. Instead it is coupled to the other bridgehead H (4.0 Hz) attached to the C—O unit. These and some other useful differences are summarized in Table III. There are, however, no NMR shift or coupling differences that reveal the configuration at phosphorus in the 5-methyl isomer **16**, and difference NOE spectra proved not to be informative. Attempts to prepare cyrstals suitable for X-ray analysis have not yet been successful, and for the present we cannot assign the complete structure of this isomer.

Thermal Fragmentation of the Bicyclic Phosphonamides

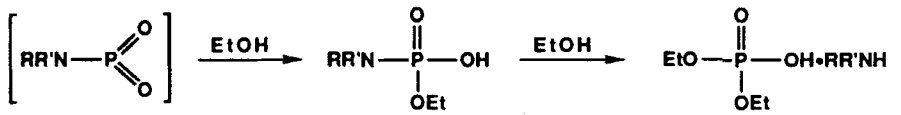
The three phosphonamides **15a**, **15b**, and **16** were fragmented by heating them in toluene solution at 110–120°C. The time period required for complete expulsion of the bridging P—O unit at 110°C was about 22 hrs for **15a**, and about 48 hrs for **15b-c**, considerably longer than is required for esters of the same framework (6–8 hrs). In another study,[7] this difference has been placed on a quantitative basis

by performing kinetics measurements on several related bridged compounds, including phosphonamide **15a**. The results confirm that the fragmentation can be described as a concerted retro-cyloaddition with formation of the metaphosphoric acid derivative as the free, monomeric species **17a–c** of fleeting existence. The course of the fragmentation of the phosphonamides **15a–c** was followed by ^{31}P NMR. At the conclusion of the process, all phosphorus was found in the form of condensed phosphates, as suggested from ^{31}P NMR signals in the approximate regions δ −9 to −12 and −20 to −25. The signals in both regions were complex, and no attempt were made to isolate individual species. Not surprisingly for these conditions, there were no signals indicative of the existence of the free metaphosphoramidates.



15a-c **17a-c**

When ethanol (usually 3 equiv.) was present in the reaction media as a trapping agent, condensed phosphate formation was almost completely avoided, and a sharp ^{31}P NMR signal appeared at around δ 0 to −1 for each compound. This signal is due to the corresponding amine salt of diethyl phosphate; had the amino group been retained on phosphorus, signals in the region of δ 6–9 would be present (confirmed with authentic samples; *vide infra*). The displacement of the amino group occurs with the trapping product and not as a preliminary reaction with the bicyclic phosphonamide, as has been confirmed in the kinetics studies.[7]



17a-c **18a-c** **19a-c**

Photochemical Fragmentation of the Bicyclic Phosphonamides

As previously observed for the N,N-dimethyl derivative,[3] irradiation of solutions of the phosphonamides **15a–c** and **16** at about 30–35°C with light provided by a medium-pressure Hanovia lamp (nominally 254 nm) caused complete expulsion of the bridging P—O unit. Solvents that were found useful for this process included acetonitrile, dioxane, and tetrahydrofuran (THF), although some photochemical degradation of all of them accompanied the main reaction. The choice of solvents is, in fact, somewhat limited for this process; common solvents that are UV-absorbers (aromatics, pyridine, ketones, di- and trichloromethane, etc.) prevented the fragmentation, and the solubility in alkanes is negligible.

When no trapping agent was present in the medium, the phosphorus-containing products were again found to be condensed phosphates, with complex ^{31}P NMR

signals in the same two upfield regions as noted for the thermal fragmentation products. No other ^{31}P NMR signals were present, and thus under these conditions the reactivity of even the hindered metaphosphoramidates is still too great to allow their detection.

The metaphosphoramidates were trapped successfully when ethanol (3 equiv.) was included in the photolysis medium. Condensed phosphate formation was avoided, and the only products were the O-ethyl phosphoramidates **18a–c**. These products gave ^{31}P NMR signals that were several ppm downfield from the alkyl phosphates; no signals for the O,O-diethyl phosphate salts (δ 0 to -1) that were formed in the thermolysis experiments were observed, and therefore these phosphoramidate trapping products are not prone to undergo the amine displacement with the ease noted for the N,N-dimethyl derivative[3] during the photolysis. However, this displacement reaction does occur for **18a–c** at higher temperatures, consistent with the observation of this reaction in the thermal fragmentation experiments. In fact, these phosphoramidates showed such instability on attempts to isolate them that this has not been successfully accomplished. Stabilization could be effected by converting them to triethylamine salts,[3] but the method used in this study was to convert them to methyl esters by reaction with diazomethane.

The resulting O,O-dialkyl phosphoramidates **20a–c** were quite stable and could be isolated by chromatography on silica gel. Distillation was also effective in the

TABLE IV

Mass spectral data[a] for O-methyl O-ethyl N-substituted phosphoramidates **20a–c**

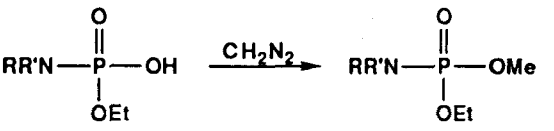
20a[b] ($C_7H_{18}NO_3P$)	**20b**[c] ($C_{12}H_{20}NO_3P$)	**20c**[d] ($C_7H_{18}NO_3P$)
195 (9.98) M^+	257 (34.0) M^+	195 (~1) M^+
180 (70.0) M^+-Me	211 (7.2) M^+-EtO-H	180 (91.0) M^+-Me
152 (100) M^+-Me-C_2H_4	197 (14.4) $MesNHPO_2^+$	152 (100) M^+-Me-C_2H_4
124 (55.5) M^+-Me-$2C_2H_4$	134 (100) $MesNH^+$	134 (20.9) $Me_3CNPO_2^+$
95 (22.9) $MeOPO(OH)^+$	95 (8.7) $MeOPO(OH)^+$	120 (26.5) $Me_2CNHPO_2^+$
72 (30.6) Et_2N^+	91 (21.9) M^+-MesNH	112 (22.2) $MeOPO(OH)_2^+$
		95 (20.2) $MeOPO(OH)^+$

a. Obtained with a Hewlett-Packard GC-Mass Selective Detector using a 30 m x 0.25 mm DB-5 column. Formulas of fragments are unconfirmed.

b. Retention time 10.08 min at 80°C for 2 min then 5°C per min increase.

c. Retention time 14.9 min at 80°C for 2 min then 10°C per min increase.

d. Retention time 6.8 min at 60°C for 1 min, then 15°C per min increase.



18a-c **20a-c**

case of **20c**. It was possible to perform the diazomethane reaction directly on the reaction mixture from the photolysis, thus allowing analysis of the mixture as well as confirmation of the phosphoramidate formula by GC-MS. We employed a GC detector system based on atomic emission, which allowed specific detection of peaks due to phosphorus compounds (186 nm). We were able to identify all P-containing compounds as arising from the reaction of the metaphosphoramidate with ethanol or traces of water; there were no compounds that could arise from reaction of the solvent (THF in these experiments) with the metaphosphoramidate, although there were numerous non-P peaks on the gas chromatogram. Data from the product analysis by NMR and by GC-MS are given in Table IV. The cause of the instability of the phosphoramidates formed in the trapping reactions is of interest, since it is possible to attribute the instability to the availability of an elimination-addition mechanism[14] that may involve a metaphosphate intermediate. We are presently exploring this possibility.

EXPERIMENTAL

General. ^{31}P NMR spectra (FT, ^{1}H-decoupled) were recorded on an IBM NR-80 spectrometer at 32.38 MHz; 85% H_3PO_4 was used as an external standard, with deuterochloroform as solvent and internal lock, unless otherwise noted. Downfield shifts are positive. ^{1}H NMR spectra were obtained on a Varian XL-200 spectrometer. GC-MS analyses were performed with a Hewlett-Packard Mass Selective Detector (70 eV).

Diels-Alder adducts of 1-amino-3-methylphosphole-1-oxides. The general procedure consisted of three steps: (1) reaction of 1-chloro-3-methyl-3-phospholene-1-oxide (**10**) with amines, (2) addition of bromine to form dibromides, (3) dehydrobromination in the presence of N-phenylmaleimide. It was preferable to perform the steps rapidly without extensive purification of the intermediates, to avoid decomposition. This was particularly a problem with the dibromides.

Step 1. The freshly-dried amine (0.9 mol) in 500 mL of dry benzene was treated dropwise with a solution of 0.3 mol of the 1-chlorophospholene 1-oxide **10** in 300 mL of benzene. The mixture was held at 0–5°C during the reaction; it was stirred for an additional hour at this temperature and then for 1 day at room temperature. The amine hydrochloride was removed by filtration, and solvent distilled from the filtrate with a rotary evaporator. The residues gave the expected ^{31}P and ^{13}C NMR spectra (Table V) and could be used directly in Step 2. Only amide **11a** has been successfully isolated and analyzed.

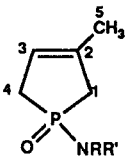
Diethylamino derivative (**11a**), 90%, bp 99–100°C (0.05 mm).
Anal. Calcd. for $C_9H_{18}NOP$: C, 57.73; H, 9.69; N, 7.48. Found: C, 57.76; H, 9.64; N, 7.58.
Mesitylamino derivative (**11b**), 70%.
t-Butylamino derivative (**11c**), 85%, bp 120–130°C (0.05 mm).

Step 2. A solution of 0.10 mol of the aminophospholene oxides **11a–c** in 250 mL of chloroform was cooled to 0°C and treated dropwise with a solution of 0.10 mol of bromine in 20 mL of chloroform. The mixture was stirred for 2 hrs at room temperture, and the solvent was removed with a rotary evaporator. The yellow solid residues gave the expected ^{31}P NMR ($CDCl_3$) spectra [**12a**, δ 57.48, 53.55 (1:1); **12b**, δ 55.8, 52.1 (1:10); **12c**, δ 53.1, 51.8 (10:1)] but were not otherwise characterized and were used directly in the next step. (*Caution*: The dibromides have some lachrymatory activity on some individuals.)

Step 3. A solution of 0.10 mol of the dibromides **12a–c** and 0.11 mol of N-phenylmaleimide in 400 mL of dry benzene was stirred in an ice bath while a solution of 0.30 mol of triethylamine in 100 mL of benzene was slowly added. The mixture was warmed to room temperature and stirred for several

TABLE V

NMR spectral data for 1-amino-3-methyl-3-phospholene-1-oxides (**11**)



R	R'	$\delta^{31}P$		C-1	C-2	C-3	C-4	C-5	C-6	C-7
6 7 -CH_2CH_3	R	66.0	δ	35.7	137.9	122.1	33.0	21.6	39.1	15.1
			J	83.8	15.3	9.7	80.4	12.0	3.7	2.8
Mes	H	62.3	δ	35.0	136.6	120.7	32.0	20.5		
			J	87.5	15.7	10.0	83.9	12.1		
6 7 -$C(CH_3)_3$	H	61.0	δ	38.2	136.4	120.6	35.2	20.6	52.0	31.9
			J	87.2	15.4	9.7	83.7	12.2	3.2	4.0

days, with occasional monitoring by ^{31}P NMR to follow consumption of the starting dibromide. The precipitate was removed by filtration and washed with a benzene-acetone (1:1) mixture. The original filtrate and the washings were evaporated to dryness in vacuo. The residues were chromatographed on a Florisil (100–200 mesh) column with elution by dichloromethane-hexane (4:1) to remove the dihydrophthalimide **5**, then dichloromethane, and finally dichloromethane-methanol (4:1) to remove the products. They were recrystallized from ethyl acetate or acetonitrile-hexane. ^{31}P and ^{13}C NMR spectra are given in Table I.

Diethylamino derivative **14a**, 52%, mp 157–158°C,[17] O NMR (CD_3CN) δ 118.7 (d, $^1J_{PO}$ = 161 Hz, P=O). Anal. Calcd. for $C_{19}H_{23}N_2O_3P$: C, 63.67; H, 6.46; N, 7.81. Found: C, 63.39, H, 6.38; N, 7.68. Mesitylamino derivative **14b**, 42%, mp 236–237°C. Anal. Calcd. for $C_{24}H_{25}N_2O_3P$: C, 68.56; H, 5.99; N, 6.66. Found: C, 68.29; H, 5.81; N, 6.55.
t-Butylamino derivative **14c**, 48%, 214–215°C. Anal. Calcd. for $C_{19}H_{23}N_2O_3P$: C, 63.67; H, 6.46; N, 7.81. Found: C, 63.54; H, 6.30; N, 7.76.

Reaction of Diels-Alder adducts **14a–c** *with m-chloroperbenzoic acid.* A solution of 0.021 mol of *m*-chloroperbenzoic acid (MCPBA), available only as a component (50%) in a mixture of water (40%) and benzoic acid (10%), in 150 mL of chloroform was prepared. The layer of water that formed was removed. Without drying, this solution was treated with 0.007 mol of the Diels-Alder adduct (**14a–c**). The solutions were stirred at room temperature and monitored by ^{31}P NMR to determine when all starting material had reacted. This usually required 1–2 days. As in other such oxidations, it was found convenient to remove the *m*-chlorobenzoic acid that was formed and the unreacted MCPBA by complexation on solid KF (0.063 mol). After 12 hrs of stirring, the solid was removed by filtration through Celite, and the filtrate then evaporated to dryness in vacuo. Products **15a–c** were isolated by column chromatography on Florisil (100–200 mesh), with elution by dichloromethane-hexane (4:1), dichloromethane, and finally dichloromethane-methanol (9:1). The products appeared in the last fractions of the elution. They were recrystallized from ethyl acetate-hexane (**15a**, **15c**) or ethyl acetate-ether (**15b**). ^{31}P and ^{13}C NMR spectra are given in Table II.

Diethylamino derivative (**15a**), 60%, mp 144–145°C. Anal. Calcd. for $C_{19}H_{23}N_2O_4P$: C, 60.95; H, 6.19; N, 7.48. Found: C, 60.77; H, 6.18; N, 7.51.

t-Butylamino derivative (**15c**), 50%, mp 86–87°C. Anal. Calcd. for $C_{19}H_{23}N_2O_4P$: C, 60.95; H, 6.19; N, 7.48. Found: C, 60.88, H, 6.16; N, 7.43.

The mesitylamino derivative, 53%, was found after Florisil chromatography to be a 1:1 mixture of two isomers **15b** and **16** by ^{31}P NMR (Table II). The mixture was separated by chromatography on silica gel (230–400 mesh) with elution by ethyl acetate and then ethyl acetate-2-propanol (100:5). The isomer (**16**) with δ ^{31}P ($CDCl_3$) 22.1 was eluted first and had mp 207–220°C dec (after recrystallization from benzene-pentane); the second isomer **15b** with δ ^{31}P ($CDCl_3$) 23.2 had mp 164–165.5°C after recrystallization from benzene-pentane. ^1H NMR spectra for both isomers are recorded in Table III. Neither isomer could be adequately freed of minor impurities for analysis. However, the crystals of **15b** were satisfactory for X-ray diffraction analysis.

Single crystal X-ray diffraction analysis of **15b**. Crystal data: $C_{24}H_{25}O_4N_2P$, *FW* = 436.45, monoclinic space group $P2_1/n$,a = 13.040(3) Å, b = 9.730(3) Å, c = 18.362(5) Å, β = 92.45(2)°, Z = 4, and D_{calc} = 1.245 g/cm^3. A total of 1593 independent reflections was measured (CAD4 diffractometer; $MoK_{\bar{\alpha}}$ radiation, λ = 0.71073 Å; θ-2θ scan mode; +h, +k, ±2°, $2\theta_{max}$ = 36°). Solution of the structure by use of direct methods was straightforward. Isotropic unit-weighted full-matrix least-squares refinement of non-hydrogen atoms gave $R(F)$ = 0.127 for 1034 observed reflections ($I \geq 3\sigma_I$).

Thermolysis of 2,3-oxaphosphabicyclo[2.2.2]-3-oxides **15a–c**. The thermolyses were conducted in sealed tubes. A solution of 50 mg of **15a–c** in 1 mL of dry toluene was heated at 110 or 120°C. The course of the reactions was followed by ^{31}P NMR spectroscopy (recorded in toluene with an external lock of $CDCl_3$); completion required 22 hrs for **15a** at 110°C, 48 hrs for **15b** at 120°C, and 48 hrs for **15c** at 120°C. Clusters of signals for P—O—P products appeared in the general regions δ −9 to δ −12 and δ −20 to δ −25 for all reaction mixtures. Ethanol (1 mmol) was used as trapping reagent in some experiments. The major signal from **15a** then occured at δ +0.03 (**19a**), from **15b** at δ −1.49 (**19b**), and from **15c** at δ −0.20 (**19c**). The mixture from **15a** also exhibited a single sharp signal at δ −11 for a presently unidentified P—O—P product. Similarly, **15c** gave a signal of δ −9.8 (about 1:1). Compound **15b** gave no such signal. When **18c** (from photolysis of **15c**) was heated in toluene at 110°C for 30 hrs, it was decomposed with the generation of the product with the signal at δ −9.8.

Photolysis of 2,3-oxaphosphabicyclo[2.2.2]-3-oxides **15a–c** *and* **16**. The photolyses were conducted in the 50-mL double-walled cylindrical quartz reactor described previously,[3] employing a 450 medium pressure Hanovia lamp. For small scale experiments, 5 mm quartz NMR tubes were used as reactors, and were fastened to the outer wall (quartz) of an Ace Glass low temperature unit. Solvents were acetonitrile, dioxane, or THF. Photolyses were conducted in the presence and absence of ethanol as a trapping agent. Some typical results for NMR tube reactors with 0.1 mmol of substrate in 1.5 mL of THF as solvent are summarized below; similar observations were made with larger scale runs. For the tube reactions, fragmentations were complete in about 2 hrs. After ^{31}P NMR determinations, the reaction products were treated with a solution of diazomethane in ether (prepared from Aldrich Diazald). ^{31}P NMR (in THF with external D_2O lock) and GC-MS measurements were made directly on the resulting solutions; results are given in Table IV. Individual observations were:

15a: Without ethanol, P—O—P signals at δ −11 and δ −22 to δ −23. With ethanol, ^{31}P at δ 9.3 for major product **18a**, δ 11.7 after methylation (**20a**). The product was isolated by silica gel chromatography; ^1H NMR ($CDCl_3$) 1.01 (t, $^3J_{HH}$ = 8.5 Hz, NCH_2CH_3), 1.31 (d of t, $^3J_{HH}$ = 7.04, $^4J_{PH}$ = 0.8 Hz, OCH_2CH_3), 2.97–3.20 (m, NCH_2), 3.66 (d, J = 11.2 Hz, OCH_3), 3.95–4.20 (m, OCH_2).

15b and **16**: Without ethanol, ^{31}P NMR signals at δ −16.0, and −16.6, and at δ −24.6 to δ −26.6 (complex). With ethanol, ^{31}P NMR at δ +6.2 for major product **18b**, which after methylation to **20b** gave ^{31}P NMR ($CDCl_3$) δ +6.0. The isomers fragmented at a similar rate.

15c: Without ethanol, ^{31}P NMR at δ −4, δ −13 to δ −15, and δ −23 to δ −25 (all complex). With ethanol, ^{31}P NMR at δ +7.2 (THF) for **18c**, giving ^{31}P δ +8.3 ($CDCl_3$) after methylation to **20c**.

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SUPPLEMENTARY MATERIAL AVAILABLE FOR X-RAY DIFFRACTION ANALYSIS OF **15b**

An ORTEP plot of the molecule; positional and isotropic thermal parameters and tables of bond lengths and angles (6 pages) have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England.

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