Syntheses of Cyclic Acyloxyphosphoranes from Phosphine Oxides: Spectroscopy, Stability, and Molecular Structure. A Stable *P*-Hydroxyphosphorane: 1-Hydroxy-1,1′-spirobi[3*H*-2,1-benzoxaphosphole]-3,3′-dione

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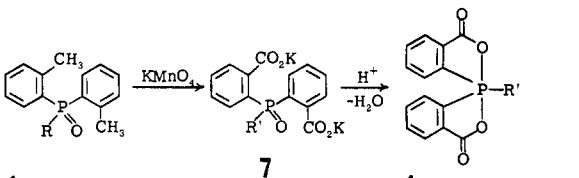
Abstract: Exceptionally stable spirocyclic acyloxyphosphoranes **4–6** are obtained by spontaneous acid catalyzed cyclodehydration of bis-*o*-carboxyphenylphosphine oxides **7** in water. 2,6-Dicarboxyphenyldiphenylphosphine oxide (**10**) gives the acyloxyphosphorane **9** upon heating with acetic anhydride. The infrared, NMR, and mass spectra and the stability of these phosphoranes are correlated with their molecular structure. X-Ray analysis of **4** reveals an almost ideal trigonal bipyramidal arrangement around phosphorus, in contrast to many five-membered spirocyclic phosphoranes of known geometry. The title compound (**14**) is obtained by trifluoroacetic acid induced intramolecular dehydration of **15**. This stable, though water-sensitive, phosphorane appears to be the first example of a hydroxyphosphorane which is long postulated as an intermediate in the hydrolysis of phosphorus esters.

Pentacoordinate oxyphosphoranes occupy a prominent position in the research front of organic chemistry.[1] The rich diversity of functional groups which can be bonded to the central phosphorus atom is reflected in the hectic activity in this field. The synthetic utility of this class of compounds has recently been reviewed,[2] but it is likely to expand immensely. Phosphoranes may be stable enough to allow isolation, purification, and characterization by chemical[3] and physical[1-4] methods. However, one of the most challenging aspects of their chemistry may well be their possible role as intermediates, or transition states, in nucleophilic substitution at tetracoordinate phosphorus,[1,5] including biologically important phosphate esters. In spite of all this, and the synthesis of acyloxyarsoranes[6] 2 decades ago, the first synthesis of stable, spirocyclic acyloxyphosphoranes had only recently been reported.[7] Moreover, these syntheses have been preceded by suggestions that cyclic acyloxyphosphoranes are intermediates in the hydrolysis of phosphoenolpyruvate esters.[8] Acyclic acyloxyphosphoranes are known as dipolar compounds, better classified as phosphonium salts.[9] Nucleophilic attack of a phosphine oxide oxygen atom on the carbonyl group of acetic anhydride, followed by formation of an unstable transient acyloxyphosphorane, has been invoked in order to explain the racemization of chiral phosphine oxides by acetic anhydride.[10] Very recently, a correlation of bonding, polarity, geometry, and carbonyl stretching frequency has been suggested for several novel cyclic acyloxysulfuranes and related compounds.[11] We now report details of our acyloxyphosphorane synthesis,[7a] a related preparation of a new acyloxyphosphorane which has a heterobicyclo[3.3.0]octane structure, a novel hydroxyphosphorane, spectral correlations, and the molecular structure of **4**, correlated with its exceptional stability.[12]

Results and Discussion

Syntheses. In search for new and convenient synthetic methods directed toward six- and seven-membered dibenzoheterocycles[13] we have prepared several *o*-tolylphosphines and the corresponding oxides,[14] such as **1–3**. We have reasoned[14] that dibenzo carbon–phosphorus heterocycles could be prepared from such simple starting materials by using a carbon–carbon bond formation reaction in the cyclization step. In exploring such routes, we have oxidized **1–3** (or their phosphine precursors)[7a] with potassium permanganate. The products obtained after the usual workup (and acidification) have been identified as the spirocyclic acyloxyphosphoranes **4–6** (Scheme I).

Scheme I

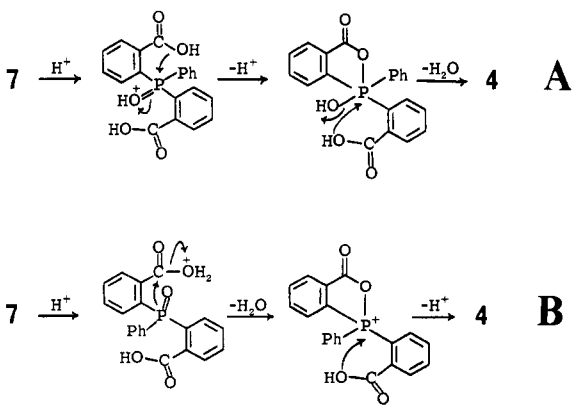


1 R = Ph
2 R = CH_3
3 R = o-$CH_3C_6H_4$
4 R′ = Ph
5 R′ = CH_3
6 R′ = o-$HO_2CC_6H_4$

Structure determination of **4–6** is supported by infrared, mass spectral, and especially ^{31}P NMR data. Moreover, the structure and trigonal bipyramidal geometry of **4** have now been confirmed by x-ray diffraction methods (vide infra).

The synthesis of **4–6** may mechanistically be visualized in two major ways, or modifications thereof, outlined in Scheme II. The major difference in these two possibilities is that the phosphine oxide oxygen is lost (as H_2O) or retained in the

Scheme II



phosphorane product in A and B, respectively. Labeling experiments (with ^{18}O) may clarify this point. The actual degree of protonation of each species is not known. Thus, CH_3COO–P bond formation may involve carboxylate anion attack in either mechanism. Moreover, it may well be that the two carboxyl groups flanking the phosphine oxide function in **7** (at least partially protonated) are involved in simultaneous formation

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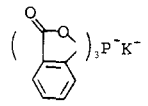
of both CH_3COO-P bonds, in analogy to the "Samson effect",[15] shown in the synthesis of a related sulfurane.

Mechanism B is similar to that suggested for the acetic anhydride induced racemization of chiral phosphine oxides.[10] Mechanism A is supported by mechanistic suggestions concerning neighboring group participation in the hydrolysis of phosphoenolpyruvate esters.[8] At this stage, it would be premature to prefer one over the other.

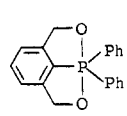
In the oxidation of **3**, **7** (R′ = *o*-$KO_2CC_6H_4$) might have been converted to a hexacoordinate phosphorus compound (**7a**). Protonation of the latter would then give **6**. This possi-



7a

bility has been ruled out by the ^{31}P NMR chemical shift of this intermediate, δ + 38.2 ppm (D_2O). This value is typical of a phosphine oxide, while hexacoordinate phosphorus compounds resonate at a much higher field.

One of the interesting features of this synthesis is the spontaneous opening of the very strong P=O bond (120–150 kcal/mol),[16] to a P-O bond. Such P=O bond formation appears to be the "driving force" in many reactions,[17] exemplified by the Arbuzov and Wittig reactions.[18] The facile transformation of tetrahedral, tetracoordinate phosphine oxides into stable, trigonal bipyramidal (TBP), pentacoordinate phosphoranes is quite remarkable.[19] A few related reactions have recently been described.[20] Unstable hydroxyphosphoranes have been shown (by trapping) as intermediates in isomerizations of phosphates[20] and phosphine oxides.[21] The first reported[22] relatively stable phosphorane which was obtained from a phosphine oxide is the thermal, or acid-catalyzed, cyclization of 2,6-bis(hydroxymethyl)phenyldiphenylphosphine oxide to the phosphorane **8**. In addition to the arsorane synthesis,[6] another related reaction is the preparation of **12** from **13** in refluxing acetic acid.[23] In all these reactions, carboxy or hydroxy groups were close enough to the phosphorus (or sulfur), thus enabling intramolecular attack to occur, which produced a five-membered ring.



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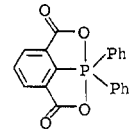

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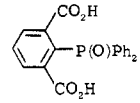

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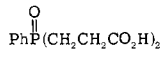

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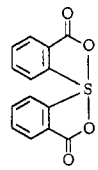
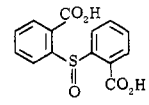


12



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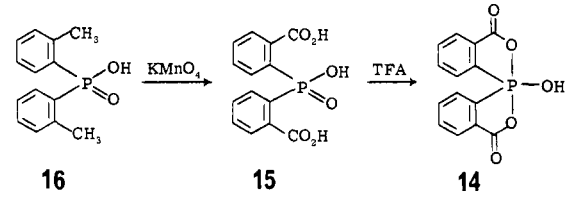
However, **10** and **11** do not spontaneously yield acyloxyphosphoranes in the presence of aqueous HCl, either at 20 or 100 °C, or upon dissolution in neat trifluoroacetic acid (TFA). So far, we have obtained **9** only by the acetic anhydride induced cyclization of **10** while as yet we have not been able to convert **11** into a phosphorane. The acetic anhydride catalyzed cyclization of **10** is reminiscent of, and has been stimulated by, reports on cyclizations of *o*-carboxyphenyl sulfoxides by this reagent,[15,24] and by the reported[10] racemization of chiral phosphine oxides mediated by acetic anhydride. Related bicyclic phosphoranes have recently been reported,[7c,22] and the analogous acyloxysulfurane has been prepared by thermolysis of a bisperester related to **10**.[25]

The exceptional stability of **4**–**6**, associated with their spirobi[3*H*-2,1-benzoxaphosphole] skeleton, the five-membered ring effect,[29] and near-ideal TBP structure, suggested that it might be possible to prepare and isolate the analogous hydroxyphosphorane **14**. This has now been achieved, as illustrated in Scheme III.

Scheme III



16 **15** **14**

Bis-*o*-tolylphosphinic acid **16** is prepared by either oxidative hydrolysis of bis-*o*-tolylphosphinous chloride or sodium hydroxide fusion with tris-*o*-tolylphosphine oxide **3** followed by acidification. Contrary to the synthesis of **4**–**6**, and in analogy to that of **9**, **14** is not spontaneously produced from **15** in the presence of aqueous hydrochloric acid. However, dissolution of **15** in TFA gives **14**, isolated as a crystalline 1:1 complex with TFA. The ^{31}P NMR chemical shift of **14** (−38.5 ppm in $CDCl_3$ and −27.5 ppm in TFA), upfield from 85% H_3PO_4 as external standard, is typical of phosphoranes.[3,7a] The low-field ^{31}P shift in TFA, as compared with $CDCl_3$, is consistent with protonation of the hydroxyl group of **14** in TFA solution. The 70-eV mass spectrum of **14** shows the molecular ion at *m/e* 288 (2%) and a much more prominent M − CO_2 ion at *m/e* 244, as could be expected (vide infra).

The successful synthesis of phosphoranes from phosphine oxides appears to be highly dependent on the stability of the products, which is mainly determined by both their spirocyclic structure and near-perfect TBP geometry. Indeed, **9** is completely decomposed by boiling 10% aqueous NaOH in 10 min, while **4** is not. These stabilizing parameters probably compensate for the rupture of the strong P=O bond. The fairly easy synthesis of arsoranes bearing no condensed aromatic rings[6] may reflect the greater dissociation energy of the P=O bond as compared with the As=O bond, rather than extra stability of the spirocyclic arsorane over the corresponding phosphorane. This view is supported by recent syntheses of nonannelated acyloxyphosphoranes starting with tervalent phosphorus compounds.[7b,c]

Spectroscopy. Contrary to acyloxysulfuranes,[11] the carbonyl stretching frequencies (ν_{CO}) of spirocyclic acyloxyphosphoranes are not very sensitive to the electronic nature of the ligand trans to an apical acyloxy group.[7] The position of the carbonyl absorption of all the known acyloxyphosphoranes is found in the rather narrow range of 1715–1740 cm^{-1}. It has been tentatively suggested[11] that this observation may reflect the covalent nature of the axial ligands in the spirocyclic acyloxyphosphoranes, while dipolar (sulfonium carboxylate) resonance forms may be much more important in representing the analogous acyloxysulfuranes.

The ν_{CO} values of 1681 and 1684 cm^{-1} of spirocyclic acyloxyarsoranes[6] may reflect both their dipolar nature[6] and the greater covalent radius of As as compared with P.[11]

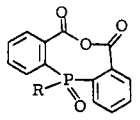
A helpful structural correlation is also provided by the two carbonyl stretching frequencies of **6**. One, derived from the aromatic carboxylic group, occurs at 1709 cm^{-1}, as could be expected for a conjugated carboxyl, leaving the other absorption at 1724 cm^{-1} to be assigned to the acyloxy carbonyl group, in a predictably higher frequency. Table I shows a gradual shift in acyloxy ν_{CO} as a function of the unsaturation

Table I. ν_{CO} and ^{31}P NMR Chemical Shifts of Cyclic Acyloxyphosphoranes as a Function of Equatorial Substituents (R)

compd	R	ν_{CO}, cm^{-1}	δ, ppm
5	CH_3	1739	−51.0
4	Ph	1730	−60.8
9	Ph	1730	−46.7
6	o-$C_6H_4CO_2H$	1724	−46.5

degree in groups equatorially bonded to phosphorus. This decrease in ν_{CO} may indicate conjugation through the P-C bond.[26]

The above infrared data could also be consistent with cyclic carboxylic anhydride structure **17**,[7a] though no band for a P=O group stretching could safely be assigned. This is not the



17

case, however, for the ^{31}P NMR data. **17** is an anhydride like **4**-**6**, but it is also a phosphine oxide and not a phosphorane. The ^{31}P chemical shift of tertiary phosphine oxides is usually observed 0-55 ppm downfield from an 85% H_3PO_4 reference.[17] Oxyphosphoranes usually exhibit ^{31}P chemical shifts upfield from the same reference.[3,27] Consequently, the ^{31}P NMR data (Table I) clearly indicate the phosphorane structure of **4**-**6** and **9**. Nevertheless, the x-ray structure analysis (vide infra) has unequivocally shown that **4** is indeed a pentacoordinate phosphorane.

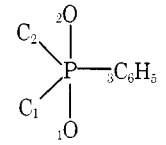
The exceptional thermal (and chemical) stability of **4** is described in the Experimental Section. Normally oxyphosphoranes are not thermally stable, including acyloxyphosphoranes.[7c] Phosphoranes containing 1,3,2-dioxaphospholen ring are decomposed above 120 °C.[3] In general, the stability of phosphoranes[3,28] and sulfuranes[29] is structure dependent as follows:

spirocyclic > monocyclic > acyclic

Thus, the exceptional stability of **4**, e.g., is probably a consequence of both its spirocyclic structure and near-ideal TBP geometry, which minimizes both steric and electronic interactions. Nevertheless, **4**-**6** and **9**, being cyclic anhydrides, are extremely unstable under electron impact,[30] and their molecular ions readily lose CO_2. The ejection of a neutral small molecule should facilitate the occurrence of this reaction, which would probably be a general and dominant mass spectral fragmentation of this class of compounds. The elimination of CO_2 is followed mainly by H (for **4** and **9**) or by the stepwise degradation of CO and R, and another CO_2 molecule for **6**, possibly from the carboxyl.

The mass spectra of o-tolylphosphines and their oxides, exemplified by **1**, are also of interest. We have concluded that the facile loss of (almost surely) an ortho hydrogen in the electron impact induced fragmentation of aromatic phosphines and their oxides is a rather general reaction of the ortho-substituted derivatives and related compounds.[31] This reaction is usually associated with the most intense metastable peak in the corresponding mass spectrum. Consequently,[31] it is probably a rearrangement reaction. It has indeed been suggested[31,32] that anchimeric assistance by a neighboring Ph, leading to a 9-phosphafluorenyl ion (or its 9-oxide analogue), could account for these observations. Similar findings and interpretations have been reported for aromatic ethers, sulfides, and sulfoxides.[33] Indeed, the mass spectra of bis-o-tolylphenylphosphine and the oxide **1** show prominent eliminations of CH_3 from their molecular ions (base peak for **1**), accompanied by very intense metastable peaks in the corresponding spectra. This reaction is quite remarkable, because it competes successfully with the well-known benzyl (or tropyl) ion production from toluene derivatives under electron impact. Other fragmentations (see Experimental Section) are typical of aromatic phosphines and their oxides.[31]

Table II. X-Ray Diffraction Bond Angles at Phosphorus for **4**



bond angle	deg	bond angle	deg
O(1)PO(2)	179.1	O(2)PC(2)	88.3
O(1)PC(1)	88.2	O(2)PC(3)	90.6
O(1)PC(2)	91.2	O(1)PC(2)	121.4
O(1)PC(3)	90.2	O(1)PC(3)	120.6
O(2)PC(1)	91.4	C(2)PC(3)	118.1

Molecular Structures.[34] The molecular structure of five-coordinate phosphorus compounds has been extensively studied.[35] Structures close to TBP[36] and square pyramidal[37] (SP) have been observed, as well as intermediate structures in between these two basic types.[4] Recently, it has been concluded that TBP structure for spirocyclic phosphoranes cannot be assumed to be preferred over a SP structure.[19] Although the difference in energy for the TBP and SP geometries may be very small, the extreme case with two electronegative and three electropositive ligands to phosphorus might be expected to lie nearer the TPB extreme. Such geometries are well described by the "hypervalent bonding" theory[38] which predicts collinearity for the two apical ligands and phosphorus.

In view of the exceptional thermal and hydrolytic stability of **4**, it appeared desirable to study its crystal and molecular structure by x-ray diffraction methods.[34] The molecular structure of **4** is almost ideal TBP with axial oxygen atoms. The angles at phosphorus are listed in Table II. These results are in accord with the polarity rules and the "hypervalent bonding" theory. The exceptional stability of **4** may imply that distortions from a TBP structure of a phosphorane would lead to a relatively less stable compound.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Infracord 137B spectrometer for $CHCl_3$ solutions, unless otherwise stated. NMR chemical shifts are reported in parts per million downfield from Me_4Si (the δ scale) for ^1H, and in parts per million downfield from 85% H_3PO_4 for ^{31}P. Unless otherwise noted, NMR spectra were obtained for $CDCl_3$ solutions. Mass spectra were obtained at 70 eV and 150-200 °C source temperature, using the direct insertion probe of a Hitachi Perkin-Elmer RMU6 and a Varian MAT 12 instrument. Solutions of products in organic solvents were dried ($MgSO_4$) and evaporated.

Bis-o-tolylphenylphosphine. A solution of phenylphosphonous dichloride (89.5 g) in benzene (200 mL) was added dropwise to a cooled, stirred solution of o-tolylmagnesium bromide, prepared from o-bromotoluene (188 g) and magnesium (26.4 g) in tetrahydrofuran (THF) (600 mL). The resulting solution was refluxed for 1 h and then half the solvent was distilled off. The cooled residue was carefully decomposed with 25% sulfuric acid (100 mL), followed by water (500 mL). The aqueous layer was extracted with benzene (100 mL) which was combined with the organic layer. Recrystallization of the crude phosphine from ethanol yielded the desired product (127 g, 88%): mp 73 °C; IR (Nujol) 1433 cm^{-1} (P-Ph); ^1H NMR δ 2.50 (6 H, d, J_{HP} = 1.5 Hz, CH_3) and 7.40 (13 H, m, ArH); MS m/e 290 (M^+, 100%), 289 (M − H, 43), 275 (M − CH_3, 91), 197 (M − H − C_7H_8, 25), 165

($C_{13}H_9^+$, 29). Anal. Calcd for $C_{20}H_{19}P$: C, 82.7; H, 6.6; P, 10.7. Found: C, 82.2; H, 6.2; P, 10.4.

Bis-*o*-tolylphenylphosphine Oxide (1). Bis-*o*-tolylphenylphosphine (120 g) was dissolved in acetic acid (400 mL) and then 30% hydrogen peroxide (60 mL) was added dropwise to the stirred solution, which reached reflux. Water (1.5 L) was added, and the crystals were filtered off and then dissolved in $CHCl_3$, dried, and recrystallized from cyclohexane (120 g, 95%): mp 136 °C; IR 1433 (P-Ph) and 1176 cm^{-1} (P=O); ^1H NMR δ 2.65 (6 H, d, J_{HP} = 1.0 Hz, CH_3) and 7.90 (13 H, m, ArH); MS *m/e* 306 (M^+, 40%), 305 (M − H, 20), 291 (M − CH_3, 100), 213 (M − H − C_7H_8, 19), 165 ($C_{13}H_9^+$, 63), and 91 ($C_7H_7^+$, 80). Anal. Calcd for $C_{20}H_{19}OP$: C, 78.4; H, 6.2; P, 10.1. Found: C, 78.7; H, 6.5; P, 9.6.

Bis-*o*-tolylmethylphosphine oxide (2), mp 120 °C (lit.[39] 120–121 °C), was similarly prepared, using methylphosphonous dichloride and *o*-tolylmagnesium bromide.

Tris-*o*-tolylphosphine, mp 124 °C (lit.[40] 125 °C), was prepared as above, using phosphorus trichloride and *o*-tolylmagnesium bromide (in 1:3 molar ratio) in THF. The solution of the crude phosphine in benzene was extracted with aqueous sodium hydroxide, thus removing some bis-*o*-tolylphosphinic acid.

Tris-*o*-tolylphosphine oxide (3), mp 153 °C (lit.[40] 153 °C), was obtained from the above phosphine upon oxidation with hydrogen peroxide, as described for **1**.

1-Phenyl-1,1′-spirobi[3*H*-2,1-benzoxaphosphole]-3,3′-dione (4). Potassium permanganate (68 g) was added in five portions (during 5–8 h), to a stirred refluxing mixture of **1** (17 g) and water (600 mL). Filtration, washing the cake with water (3 × 100 mL), and careful acidification (exothermic reaction) gave the product (immiscible in dilute sodium hydroxide) which was extracted with $CHCl_3$ (12 g, 80%): mp 225 °C (ethanol); IR 1730 cm^{-1} (C=O); ^1H NMR δ 7.45–9.05 (m, ArH); ^{31}P NMR δ −60.8 ppm (upfield from 85% H_3PO_4); MS *m/e* 348 (M^+, 0.5%), 304 (M − CO_2, 76), 303 (M − CO_2 − H, 100), 275 (M − CO_2 − H − CO, 18), 229 (M − CO_2 − C_6H_3, 27), 199 (M − CO_2 − CO − Ph, 36), 183 (M − CO_2 − PhO − CO, 24), 152 ($C_{12}H_8^+$, 54). Anal. Calcd for $C_{20}H_{13}O_4P$: C, 69.0; H, 3.7; P, 8.9. Found: C, 68.9; H, 4.0; P, 8.8.

4 was similarly prepared from bis-*o*-tolylphenylphosphine and potassium permanganate. Heating **4** at 340 °C for 30 min (atmospheric pressure) did not cause any noticeable decomposition. The phosphorane melted and partly sublimed. Equally, **4** survived refluxing for 2 h with 2 M aqueous sodium hydroxide, or refluxing for 1 h with $LiAlH_4$ or diborane in THF. However, the disodium salt analogue of **7** was obtained on heating finely divided **4** with 2 mol of powdered sodium hydroxide for 20 min at 250 °C. Dissolution of this salt in water followed by acidification gave again **4**.

1-Methyl-1,1′-spirobi[3*H*-2,1-benzoxaphosphole]-3,3′-dione (5). This *phosphorane* was prepared from **2** (7 g) and potassium permanganate (30 g) in a mixture of water (100 mL) and pyridine (40 mL) at reflux. Workup as above gave **5** (5.5 g, 63%): mp 164 °C (ethanol); IR 1739 cm^{-1} (C=O); ^1H NMR δ 2.75 (3 H, d, J_{HP} = 16.5 Hz, CH_3), 8.03 (8 H, m, ArH); ^{31}P NMR δ −51.0 ppm; MS *m/e* 242 (M − CO_2, 100%), 214 (M − CO_2 − CO, 23), 199 (M − CO_2 − CO − CH_3, 23). Anal. Calcd for $C_{15}H_{11}O_4P$: C, 62.9; H, 3.9; P, 10.8. Found: C, 63.0; H, 4.0; P, 11.0.

1-*o*-Carboxyphenyl-1,1′-spirobi[3*H*-2,1-benzoxaphosphole]-3,3′-dione (6). This *phosphorane* was prepared from **3** (5.5 g) and potassium permanganate (40 g) in water (100 mL) and pyridine (40 mL) at reflux. Workup followed by recrystallization from aqueous ethanol and drying at 150 °C (20 mmHg) gave **6** (4.2 g, 68%); mp 254–255 °C ($CHCl_3$); IR 1724 (C=O) and 1709 cm^{-1} (C=O, carboxyl); ^{31}P NMR (TFA) δ −46.5 ppm; MS *m/e* 348 (M − $2CO_2$, 16%), 304 (M − $2CO_2$, 100), 201 (91), 244 (27), 243 (39), and 152 (98). Anal. Calcd for $C_{21}H_{13}O_6P$: C, 64.3; H, 3.3; P, 7.9. Found: C, 64.7; H, 3.3; P, 8.3.

2,6-Dimethylphenyldiphenylphosphine Oxide. 2,6-Dimethyliodobenzene (20.8 g), finely divided lithium shavings (1.26 g), and dry diethyl ether (100 mL) were refluxed for 1.5 h and cooled, and then a solution of diphenylphosphinous chloride (19 g) in dry benzene (150 mL) was added during 1 h. The ether was distilled off and the mixture was then refluxed for 2 h. The organic solution was stirred and heated with 30% H_2O_2 (25 mL) and sodium hydroxide solution (30 mL, 4 M) for 1 h at 50 °C. The usual workup of the organic layer gave the desired *phosphine oxide* (13.8 g, 50%): mp 134 °C (cyclohexane); IR 1176 cm^{-1} (P=O); ^1H NMR δ 2.12 (6 H, d, $^4J_{HP}$ = 0.7 Hz, CH_3) and 6.78–7.73 (13 H, m, ArH); MS *m/e* 306 (M^+, 42%), 305 (M − H, 100), 291 (M − CH_3, 3), 166 (15), 78 (PhH^+, 37), and 77 (Ph^+, 21). Anal. Calcd for $C_{20}H_{19}OP$: C, 78.4; H, 6.2; P, 10.1. Found: C, 78.2; H, 6.4; P, 10.5.

2,6-Dicarboxyphenyldiphenylphosphine Oxide (10). 2,6-Dimethylphenyldiphenylphosphine oxide (5 g), potassium permanganate (25 g), and water (200 mL) were refluxed for 8 h. The usual workup gave the desired *acid* (4.8 g, 80%): mp 225 °C (ethanol); IR (KBr) 1690 (C=O) and 1170 cm^{-1} (P=O); ^{31}P NMR (TFA) δ +59.0 ppm. Anal. Calcd for $C_{20}H_{15}O_5P \cdot H_2O$: C, 62.5; H, 4.4; P, 8.1. Found: C, 62.8; H, 4.3; P, 8.4.

8,8-Diphenyl-2*H*,6*H*,1,2-oxaphospholo[4,3,2-*hi*][1,2]benzoxaphosphole-2,6-dione (9). *Acid* **10** (1.0 g) and acetic anhydride (15 mL) were refluxed for 5 h, cooled, and mixed with water (150 mL) and extracted with $CHCl_3$ (3 × 30 mL). Evaporation of the solvent was completed at 0.1 mmHg, giving *phosphorane* **9** (0.8 g, 85%): mp 235 °C (ethanol); IR 1730 cm^{-1} (C=O); ^{31}P NMR ($CDCl_3$) δ −46.7 ppm; MS *m/e* 348 (M^+, 1%), 304 (M − CO_2, 76), 303 (M − CO_2 − H, 100), 228 (M − CO_2 − C_6H_4, 12), 152 ($C_8H_{12}^+$, 16). Anal. Calcd for $C_{20}H_{13}O_4P$: C, 69.0; H, 3.7; P, 8.9. Found: C, 68.8; H, 3.8; P, 8.7.

1-Hydroxy-1,1′-spirobi[3*H*-2,1-benzoxaphosphole]-3,3′-dione (14). Potassium permanganate (130 g) was added in small increments (exothermic reaction) to an aqueous (800 mL) solution of sodium bis-*o*-tolylphosphinate, which was prepared from **16** (49.2 g) and sodium hydroxide (8.5 g). After all the permanganate was added, the mixture was refluxed until it was colorless, then filtered. Acidification and filtration gave *acid* **15** (43.5 g, 71%), mp 260–262 °C.

The *acid* **15** (10 g) was dissolved in TFA (60 mL) in a 200-mL flask. The clear solution was evaporated under reduced pressure and the crude **14** was recrystallized from benzene (10 g, 75%): mp 228–230 °C; ^{31}P NMR δ −38.5 and −27.5 ppm (TFA); MS *m/e* 288 (M^+, 2%), 244 (M − CO_2, 100), 199 ($C_{12}H_8OP^+$, 18), 180 ($C_{13}H_8O^+$, 54), 152 ($C_{12}H_8^+$, 53). Anal. Calcd for $C_{16}H_{10}F_3O_7P$: C, 47.8; H, 2.5; P, 7.7. Found: C, 48.1; H, 2.5; P, 8.1.

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A Study of Multiple Ring Expansion and Ring Contraction Rearrangements in Observable Cycloalkyl Cations

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Abstract: Tertiary cycloalkyl cations involving ring sizes $n = 4$ (small ring), $n = 5$–7 (common ring), $n = 8$–11 (medium ring), and $n = 12$–20 (macroring) have been prepared. These cations have been found to undergo a very general ring expansion or contraction reaction, often in a multiple or repetitive sense. These rearrangements are facile at temperatures varying between −70 and −100 °C and have activation barriers from 12 to 15.5 kcal/mol. Two regions of thermodynamic stability were found, the cyclohexyl ring and macrorings where $n > 14$ carbons. The cyclodecyl ring system sits on the energy watershed with some molecules contracting (40%) and others expanding (60%). The cyclododecyl ring system was found to be an excellent starting point for expansions to very large ring cations, involving the incorporation of up to eight carbon atoms, and some potential exists for the use of this procedure in the synthesis of large rings.

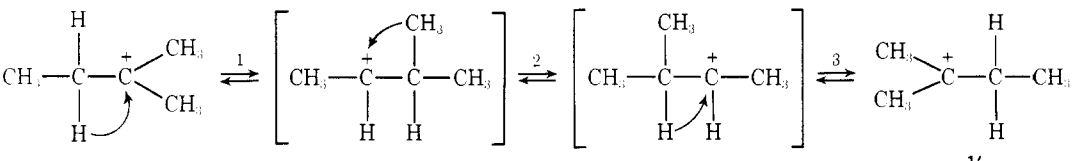
Carbocyclic ring expansion or contraction processes are a common feature of organic chemistry.[1] Many of these rearrangements occur by way of carbocation intermediates and are therefore of interest in "observable carbocation studies" where the kinetics and thermodynamics of the actual expansion or contraction step can be directly probed.

There have been a number of observable ion studies involving ring interconversions among alkyl-substituted cycloallyl cations ($C_nH_{2n-3}^+$)[2] but surprisingly few investigations involving the corresponding cycloalkyl cations ($C_nH_{2n-1}^+$).[3]

Particularly attractive targets for further study are the 1-*n*-alkylcycloalkyl cations **2**, since a plausible mechanism for interconverting these rings has been known for a number of years. In 1968, two groups[4] reported that the *tert*-amyl cation **1** undergoes a three-step degenerate rearrangement (eq 1): (1) 1,2-hydride shift to give a secondary ion, (2) 1,2-alkyl shift within the secondary ion manifold, and (3) 1,2-hydride shift to give back the tertiary ion (overall $\Delta G^{\ddagger} = 14.8$ kcal/mol).

If one now applies this sequence to tertiary cycloalkyl cations **2** (eq 1), one expects to find a *general* ring contraction–ring expansion process, where step 2 involves the actual expansion or contraction. However, even more significant, the mechanism can in principle be repeated and the ring might therefore continue stepwise to either contract or expand until a thermodynamically stable ring size is attained.

A good way of mentally visualizing such multiple rearrangements would be to think of the cycloalkyl ring as a molecular CH_2-chain lasso, with the C^+ center, together with the three-step eq 1 mechanism, functioning as a sort of "slip-knot" (see Figure 1). The incorporation of the end methyl group of the side chain into an expanding ring would be unlikely for both



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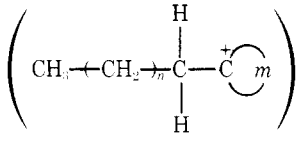
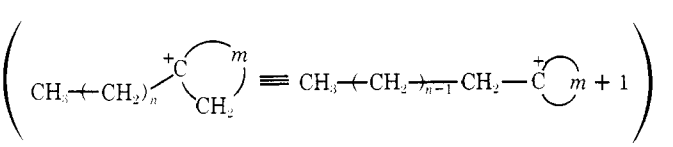


2



2′

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