For d^3, d^6, and d^8 systems, the ligand-field absorption bands occur at higher energy in the $(Me_5Cp)_2M$ compounds than in the Cp_2M derivatives. A ligand-field analysis of the spectra shows that the net ligand-field splitting is larger in the peralkylated complexes than in the unsubstituted compounds. The effect is quite substantial in the d^6 Fe(II) and Co(III) systems where Δ_1 increases by 4000–7000 cm^{-1} upon peralkylation. For the 15- and 20-electron compounds, Δ_1 is only modestly affected by peralkylation, but Δ_2 increases by 1500–3000 cm^{-1}.

All three spin-allowed d–d transitions are located in the electronic spectra of $[(Me_5Cp)_2Co]^+$ and $(Me_5Cp)_2V$. The *B* values obtained from a ligand-field analysis of the spectra are about 200 cm^{-1} greater than those determined for the unsubstituted compounds. In the case of $(Me_5Cp)_2Fe$, $(Me_5Cp)_2Ni$, and $[(Me_5Cp)_2Cr]^+$, the highest energy ligand-field band cannot be located with certainty, but the proposed range of probable energies for the transitions also yields *B* values that are moderately to significantly increased relative to the unsubstituted compounds. Electrochemical and UV–photoelectron spectral data[34e] show that the decamethylmetallocenes, as a class, are more electron rich than the corresponding metallocenes. We conclude that the increased *B* values are a result of increased electron density at the metal center in the decamethylmetallocenes.

Acknowledgment. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. W-7405-ENG-48. We wish to thank Dr. Vincent Miskowski of the California Institute of Technology for measuring the single-crystal optical spectrum of $[(Me_5Cp)_2Co]PF_6$ and for his valuable comments.

Registry No. $(Me_5Cp)_2V$, 74507-60-1; $[(Me_5Cp)_2V(NCCH_3)]PF_6$, 80679-48-7; $[(Me_5Cp)_2V(CO)_2]PF_6$, 80679-49-8; $(Me_5Cp)_2Cr$, 74507-61-2; $[(Me_5Cp)_2Cr]PF_6$, 80084-14-6; $(Me_5Cp)_2Co$, 74507-62-3; $[(Me_5Cp)_2Co]PF_6$, 79973-42-5; $(Me_5Cp)_2Ni$, 74507-63-4; $[(Me_5Cp)_2Ni]PF_6$, 80084-15-7; $[(Me_5Cp)_2Ni](PF_6)_2$, 80084-17-9; $(Me_5Cp)_2Mg$, 74507-64-5; $[(Me_5Cp)_2Fe]PF_6$, 54182-44-4; $(Me_5Cp)_2Fe$, 12126-50-0; $[(Me_5Cp)_2Ni]Cl_2$, 80679-50-1; Me_5CpNa, 40585-51-1; $[(Me_5Cp)_2Ni]BF_4$, 80679-51-2; $(Cp_2Fe)PF_6$, 11077-24-0; VCl_3·2THF, 80679-52-3; $Cr_2(OAc)_4$, 15020-15-2; $NiBr_2$·2DME, 18346-62-8; *i*-prMgCl, 1068-55-9.

Synthesis and Conformational Properties of 3,8-Phosphonanedione 1-Oxides [1]

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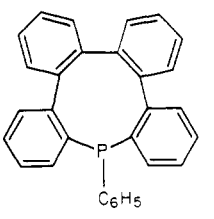
Contribution from the Gross Chemical Laboratory, Duke University, Durham, North Carolina 27706. *Received August 31, 1981*

Abstract: Ozonolysis at −78 °C of 3-phospholene derivatives with cyclohexane or substituted cyclohexanes fused at the double bond provides a useful route to derivatives of the 3,8-phosphonanedione 1-oxide system. Synthesized were the 1-methyl, 1-phenyl, 1-hydroxy, 1-phenyl-*cis*-5,6-dimethyl, 1-phenyl-*trans*-5,6-dibromo, and 1-phenyl-5,6-epoxy derivatives. Opening of the 9,10 bond of a phenanthrene fused to a 3-phospholene provided a dibenzo[*d,f*]phosphonanedione derivative. 1-Methyl-3,8-phosphonanedione 1-oxide, shown by X-ray analysis to exist in a twist chair–chair form in the solid state, undergoes rapid interconversion of conformers at room temperature, giving an averaged ^{13}C NMR spectrum. The interconversion is halted at −97 °C, where signals for two conformers are obtained (T_c = −84 °C, approximate $\Delta G^{\ddagger}$ = 9.6 kcal/mol). 1-Phenyl-5,6-dibromo-3,8-phosphonanedione 1-oxide, which X-ray analysis also showed to be in a twist chair–chair form in the solid state, however, showed nonequivalence of comparable ring carbons, implying the existence of a strongly biased equilibrium or a high barrier to ring inversion. The dibenzo[*d,f*]phosphonanedione derivative has marked rigidity, and the ^{13}C NMR spectrum reveals that comparable ring carbons are non-equivalent at room-temperature. The other phosphonanedione derivatives gave ^{13}C NMR spectra showing equivalence of comparable ring carbons, through either conformational interconversion or adoption of a symmetrical conformation.

The 9-membered phosphonin ring system is known in the literature only in specialized forms such as tetrabenzo derivatives[2] (e.g., **1**), the tetracarboxylate **2**,[3] and possibly **3**;[4] no partially or fully saturated (phosphonane) structures are known. We have devised a scheme which has led to the synthesis of a considerable number of derivatives of this ring, some of which are potential precursors of the phosphonin system in greater simplicity than is represented by structures **1–3**. Simpler structures are highly desirable for the initiation of the first studies directed to exploring the possiblity of the ten π-electron system of the phosphonins endowing these structures with "aromatic" character. This point has never before been addressed, and even in the closely related sulfur analogue (thionin) the matter is open for study. In the sulfur system, the parent monocycle remains unknown, and only dibenzo derivatives, devoid of any special properties related to the ten



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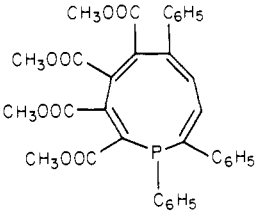

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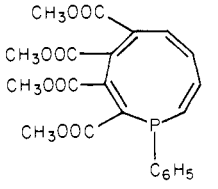

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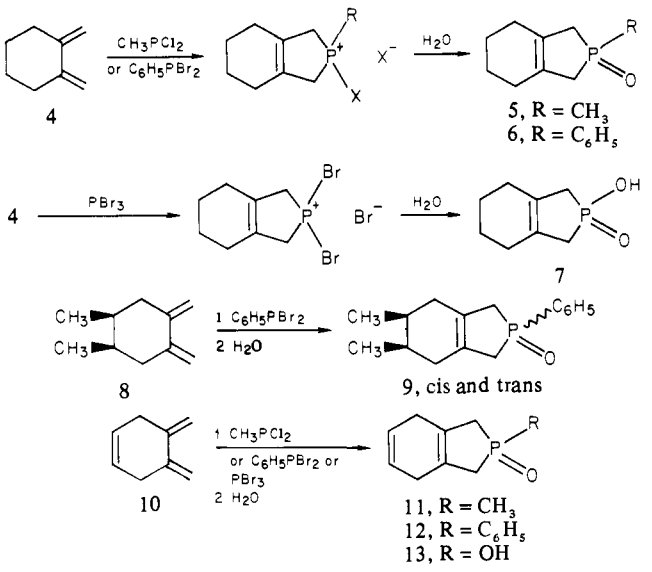
(1) Supported in part by NSF Grant CHE-7717876.
(2) (a) Wittig, G.; Maercker, H. *Chem. Ber.* **1964**, *97*, 747. (b) Hellwinkel, D. *Ibid.* **1965**, *98*, 576.
(3) Waite, N. E.; Tebby, J. C. *J. Chem. Soc. C* **1970**, 386.
(4) A substance assigned this structure was obtained in only 2.7% yield, in an experiment that could not be duplicated: Holah, D. G.; Hughes, A. N.; Kleemola, D. *J. Heterocycl. Chem.* **1978**, *15*, 1319.

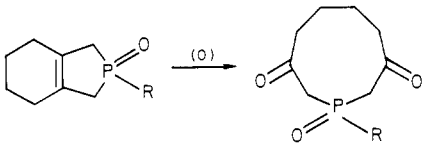
0002-7863/82/1504-1893$01.25/0

Scheme I



π-electron system, have been synthesized.[5] On the other hand, both azonines and oxonins have been prepared and, at least for some derivatives of the former, properties explainable on the basis of an aromatic system have been observed.[6] The saturated phosphonanes are also substances of great interest as they present the opportunity for the first conformational study of phosphorus rings with more than six members.

In this paper is described in detail[7a] an approach to the phosphonane system through oxidative ring opening of bicyclic phospholene derivatives, as shown in eq 1. Spectral and structural



(1)

properties established for the initially formed 3,8-phosphonanediones and some of their derivatives will be presented in this paper; observations on their chemical transformations will be reported elsewhere.[8] That this work can lead to the fully unsaturated phosphonins will be demonstrated by the synthesis of a dibenzo derivative of this ring.[7b]

Multicyclic Phospholene Derivatives. The McCormack cycloaddition provided most of the bicyclic 3-phospholene derivatives required in this study. Three different 1,2-dimethylene derivatives in the cyclohexane system were employed in this reaction with various P(III) halides, as summarized in Scheme I.

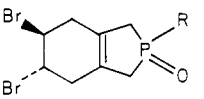
Our method for preparing dienes **4** and **10** has been reported elsewhere (ref 9 and 10, respectively) and was applied also to diene **8** (with less success). The synthesis starts with a cyclohexane(or -ene)dicarboxylic acid, which is converted in one step with $[(CH_3)_2N]_3P$ to the diamide. Reduction to the bis(dimethylamino) derivative, followed by N-oxidation and Cope pyrolysis, provides the diene. The McCormack cycloadditions were performed in the usual way at room temperature to ensure retention of the double bond in the 3-position. For the same reason, hydrolysis was performed with cold sodium bicarbonate, since the heat and acidity of uncontrolled hydrolysis can cause extensive rearrangement. Information on the cycloadditions and their products is recorded in Table I.

Table I. Data for Phospholene Derivatives[a] from McCormack Cycloaddition

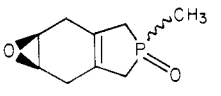
reaction			product	
compd	days	yield, %	mp, °C (solvent)	^{31}P NMR,[b] δ
5	13	82	75–78 (none)	+58.5
6	2	78	75–79 (C_6H_6, ligroin)	+50.7
7	46	61	141–144 (acetone)	+69.1
11	25	92	107–110 (none)	+58.1
12	5	85	120–121 (C_6H_6, ligroin)	+49.7
13	10	78	181–182 (C_2H_5OH)	+60.1

[a] Correct elemental analyses for C, H, and P were obtained for all products and are recorded in the supplementary material. ^1H NMR spectra were obtained on all samples but have few resolved features, except the cyclohexene olefinic H in 11–13, δ 5.71–5.77 (s). [b] In $CDCl_3$, except 13 (Me_2SO-d_6). Downfield from 85% H_3PO_4.

The series of 3-phospholenes **11–13** is not directly useful for the oxidative ring opening; they were prepared as intermediates to allow the placement of other substituents on the cyclohexane ring. Thus, reaction with bromine (1 mol) occurred specifically at the cyclohexene double bond to form the series **14–16**. Epoxidation of **11** was attempted with *m*-chloroperbenzoic acid but lacked the desired specificity. The epoxide **17** was therefore prepared by the two-step process of bromohydrin formation with *N*-bromosuccinimide and water and then dehydrobromination with base. This provided **17** as a 73:27 mixture of isomeric forms, as yet unassigned.

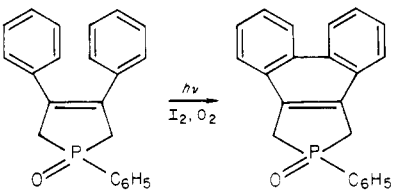


14, R = CH_3
15, R = C_6H_5
16, R = OH



17a, syn
b, anti

A different type of 3-phospholene oxide also employed in this study has the novel feature of fusion of a phenanthrene and a 3-phospholene ring, shown as **19**. This system was approached by a quite different method that makes use of a phenanthrene synthesis based on photocyclization of a stilbene moiety.[11] Phenanthrophospholene oxide **19**, the first known member of this tetracyclic system, was prepared in 56% yield as an easily purified solid by treating 1,3,4-triphenyl-3-phospholene oxide[12] (**18**) as the stilbene in the photocyclization.



18 19

Some data characterizing the new phospholene derivatives are provided in Table I.

Ozonolysis of Multicyclic 3-Phospholenes. The key step in our phosphonane synthesis has been represented by eq 1. The oxidative ring cleavage of the various bicyclic phospholene oxides has been smoothly accomplished by ozone at −78 °C in methanol. The ozonides are decomposed by addition of trimethyl phosphite at this temperature. In every case, the diketo phosphonane was recoverable as a crystalline solid. Yields were consistently in the 60–90% range. The phenanthrene ring of tetracyclic **19** required

(5) (a) Masamune, S; Takada, S.; Seidner, R. S. *J. Am. Chem. Soc.* **1969**, *91*, 7769. (b) Garratt, P. J.; Holmes, A. B.; Sondheimer, F.; Vollhardt, K. P. C. *Ibid.* **1970**, *92*, 4492.

(6) The subject has recently been reviewed: Anastassiou, A. G. In "Advances in Heterocyclic Chemistry"; Katritzky, A. R., Boulton, A. J., Eds.; Academic Press: New York, 1978; Vol. 23, pp 55–102.

(7) Preliminary communications: (a) Quin, L. D.; Middlemas, E. D. *J. Am. Chem. Soc.* **1977**, *99*, 8370. (b) Middlemas, E. D.; Quin, L. D. *Ibid.* **1980**, *102*, 4838.

(8) Quin, L. D.; Middlemas, E. D.; Rao, N. S. *J. Org. Chem.*, in press.

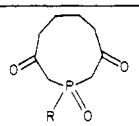
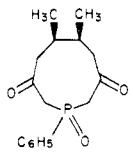
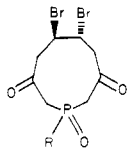
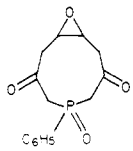
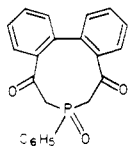
(9) Quin, L. D.; Leimert, J.; Middlemas, E. D.; Miller, R. W.; McPhail, A. T. *J. Org. Chem.* **1979**, *44*, 3496.

(10) Middlemas, E. D.; Quin, L. D. *J. Org. Chem.* **1979**, *44*, 2587.

(11) Mallory, F. B.; Wood, C. S. *Org. Synth.* **1965**, *45*, 91.

(12) Nakayama, S.; Yashifugi, M.; Okazaki, R.; Inamoto, N. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 546.

Table II. Data for 3,8-Phosphonanediones[a]

compd		yield,[b] %	mp, °C (solvent)	$\nu_{C=O}$, cm^{-1} (medium)	^{31}P NMR, δ (solvent)
	20, R = CH_3	94	130-132 (C_6H_6)	1700 ($CHCl_3$)	+32.0 ($CDCl_3$)
	21, R = C_6H_5	85[c]	129-131 (EtAc)	1680 (KBr)	+25.4 ($CDCl_3$)
	22, R = OH	84	102-104 (CH_3CN)	1690 (KBr)	+26.5 (Me_2SO-d_6)
	*syn,anti*-23	66	148-152 (acetone pentane)		40%, +23.5 60%, +25.6 ($CDCl_3$)
	24,[d] R = CH_3	86[e]	100-101 dec (EtOH)	1690 (KBr)	+33.1 (Me_2SO-d_6)
	25,[d] R = C_6H_5	89[e,f]	100-102 dec (MeOH)	1700 (KBr)	+24.3 (Me_2SO-d_6)
	26,[d] R = OH	69[e]	101-103 dec	1690 (KBr)	+25.1 (Me_2SO-d_6)
	*syn,anti*-27	88	163-188 dec (MeOH)	1690 (KBr)	27%, +22.4 73%, +24.5 (Me_2SO-d_6)
	28	58[g]	173.5-174.5 dec (acetone)	1680 ($CHCl_3$)	+25.9 ($CDCl_3$)

[a] All compounds except 26, gave correct elemental analyses for C, H and P; data are given in the supplementary material. Compound 26 decomposed during recrystallization attempts. [b] Based on use of the general procedure described for 20 in Experimental Section, except as noted. [c] This compound was partially soluble in ether; trituration of the crude dione required careful use of ice-cold ether. [d] Decomposed to a black tar on standing at room temperature for a few days. Storage in a freezer prevented decomposition. [e] Ozonolysis solvent methanol-CH_2Cl_2 (1:1). [f] Ozonolysis continued 1 h after blue color appeared. [g] See Experimental Section for procedure.

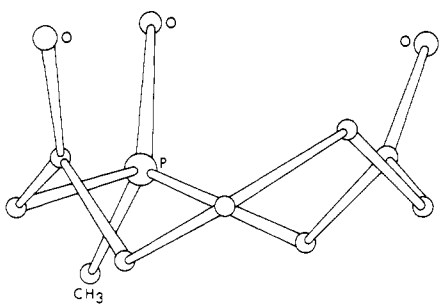


Figure 1. Structure of 1-methyl-3,8-phosphonanedione 1-oxide from X-ray analysis.

a higher reaction temperature (−40 °C) to break the aromatic double bond but nevertheless provided the diketo compound in 58% yield. Table II summarizes all of the diketo phosphonanes prepared to date. The versatility of the method is well depicted by the range of structures produced.

The structure of the ozonolysis products was easily determined spectroscopically. All possessed infrared carbonyl stretching frequencies in the range 1680–1700 cm^{-1}. The ^{31}P NMR shifts for the diketophosphonanes all fall in the narrow δ range of +22 to +32. These values resemble those reported for similarly substituted 7- and 8-membered rings,[7a] all of which are markedly upfield of the unique downfield region occupied by the 3-phospholene derivatives (e.g., δ +50 to +70 for the bicyclic derivatives of this study). The ^{13}C NMR spectra were entirely consistent with the assigned structures and are recorded in Table III. Assignment of the signals was unambiguous, except as noted. These spectra were of significance in studies of the conformations of the diketophosphonanes, as will be discussed in the next section. The ^1H NMR spectra had no unusual features except for a pronounced solvent effect in some instances; this will receive comment later in this section.

Table III. ^{13}C NMR Data for 3,8-Phosphonanediones[a]

compd	C-2,9	C-3,8	C-4,7	C-5,6
20[b,c]	46.1 (54.7)	206.0 (4.9)	44.5	23.4
21[b]	46.6 (54.7)	206.1 (4.9)	44.4	23.6
22[b]	47.4 (77.2)	205.8 (2.9)	42.5	23.0
23[b,d]	46.3 (55.7)	204.5 (4.9)	49.5	32.7
23[b,e]	47.8 (53.7)	205.5 (5.9)	49.5	33.7
25[f]	47.4 (49.8), 48.4 (54.7)	199.8 (6.8), 201.3 (3.9)	51.1	52.4
26[f]	48.6 (75.2)	200.8	51.1	53.9
27[g,h]	46.3 (56.0)	201.6 (4.2)	50.4	53.2
27[g,i]	47.2 (51.5)	194.6 (5.5)	43.1	52.3
28[b]	46.4 (57.6), 47.8 (53.7)	194.6 (~0), 194.7 (3.9)	42.2	51.1

[a] Chemical shifts (δ) downfield from Me_4Si. Values in parentheses are coupling constants (Hz) to ^{31}P, where observed. [b] Solvent: $CDCl_3$. [c] P-CH_3, δ 19.2 (72.3). [d] Major isomer; C-CH_3 δ 16.8. [e] Minor isomer; C-CH_3 δ 17.4. [f] Solvent: Me_2SO-d_6. [g] Solvent: 15% Me_2SO-d_6 in $CDCl_3$. [h] Major isomer. [i] Minor isomer.

Syn, anti isomerism can exist for the 5,6-epoxy (**27**) and *cis*-5,6-dimethyl (**23**) derivatives due to the chiral phosphorus functions. Both ^{31}P and ^{13}C NMR spectra revealed the presence of the isomers; data for both isomers are recorded in Tables II and III, but structures have not yet been assigned from these data.

Conformational Aspects. An X-ray crystal structure analysis[13]

(13) Crystal data: **20**, monoclinic, space group $P2_1$, a = 10.014 (4) Å, b = 9.639 (4) c = 5.229 (3) Å, β = 90.95 (5)°, U = 504.7 Å^3, Z = 2, d_{calcd} = 1.330 g cm^{-3}; **25**, monoclinic, space group $P2_1/c$, a = 12.793 (5) Å, b 10.329 (4) Å, c = 12.922 (5) Å, β = 113.68 (5)°, U = 1564 Å^3, Z = 4, d_{calcd} = 1.793 g cm^{-3}. Least-squares refinement of atomic positional and thermal parameters converged to R values of 0.043 and 0.073 over 893 and 1575 statistically significant reflections for **20** and **25**, respectively, measured on an Enraf-Nonius CAD-3 automated diffractomer (Ni-filtered Cu Kα radiation, λ = 5418 Å; θ–2θ scans). For further details, see ref 9.

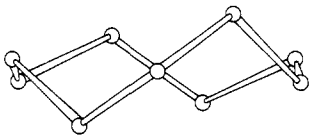
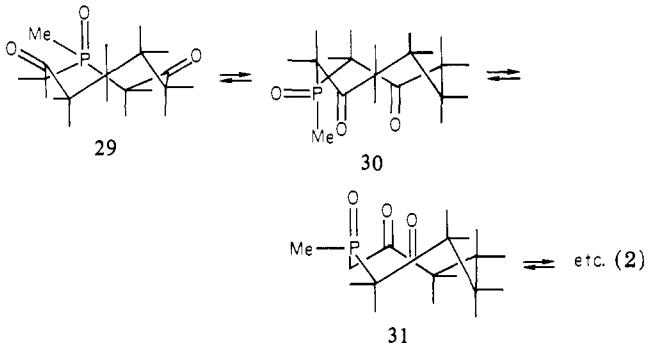


Figure 2. The twist chair–chair conformation for cyclononane.

of 1-methyl-3,8-phosphonanedione 1-oxide (**20**) demonstrated that the 9-membered ring approximates to a twist chair–chair (TCC) shape[14] in the terminology of Hendrickson[15] developed for the cycloalkanes. The angle difference at the sp^2 carbons, and longer C–P bonds, cause only moderate deviation from the idealized TCC structure for cyclononane (Figure 2). The TCC is one of three conformations with C_2 symmetry calculated for cyclononane to be of low energy, although the twist boat–chair seems generally accepted as the most stable conformation and is in fact adopted by cyclononane itself.[16] The TCC had never been observed experimentally in heterocyclic 9-membered rings[17] prior to the initiation of the studies in this department. Its adoption by **20**, as well as by the sulfone analogue of **20** (3,8-thionanedione 1,1-dioxide) also studied in this department,[9] therefore represents the first experimental demonstration of the physical reality of this proposed conformation. As seen in Figure 1, the X-ray analysis of **20** showed that in the particular invertomeric form adopted, the phosphorus atom does not lie on the C_2 axis of the TCC, and comparable carbons on either side of phosphorus are nonequivalent. Another feature of interest is that the three oxygen atoms are positioned on the same face of the ring, although other options are offered by some of the TCC invertomers.

For convenience in further discussing the shapes of the phosphonanes, an idealized representation derived from the TCC of cyclononane will be used. These structures should not be taken to imply exact positioning of atoms. Thus, **20** may be represented by **29**, and the conformational equilibrium between other TCC forms is expressed in part by eq 2. In the idealized TCC for



29 30 31

cyclononane, the ring carbons with one exception can offer a substituent a position that is crowded (pseudoaxial) by being perpendicular to the plane of the ring or tipped inward to the ring and another that is relatively uncrowded and projected away from the ring (pseudoequatorial). The exception occurs at that carbon lying directly on the C_2 axis; both positions are uncrowded and identical (isoclinal). The replacement of an sp^3 C by sp^2 C of carbonyl, and of CH_2 by P, does not alter this situation qualitatively, although distinct modifications of torsion angles and interatomic distances do occur. The approximate orientation of substituents is shown on **30** and **31**.

The ^{13}C NMR spectrum (Table III) of **20** reveals immediately that the conformation (**29**) adopted by the solid is not rigid and is not maintained in solution, since only one signal is observed for comparable carbons on either side of the phosphorus atom. This

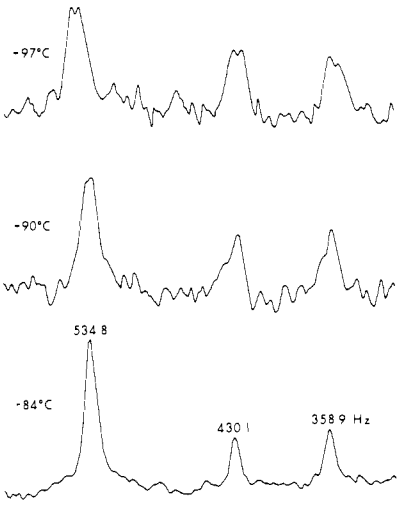


Figure 3. Upfield region of the low-temperature ^{13}C NMR spectra of **20** in CH_3OD. At −84 °C, the P-CH_3 doublet is found at 358.9 and 430.1 Hz; C-5,6 is at 534.8 Hz.

may be explained either by the ring adopting a new and symmetric conformation in solution or by rapid interconversion between the various TCC forms as expressed in eq 2 to give averaged NMR signals. Conformations other than the TCC could, of course, also be populated in solution. However, the ^{13}C NMR spectrum contains a coupling feature that supports the TCC. Thus, it is now well established[18] that the ^{31}P–^{13}C dihedral angle controls the vicinal coupling constant; for phosphine oxides, values of 0 Hz are found near 90°, with substantial coupling (10–30 Hz) at 0 and 180 °C. The absence of observable coupling in **20** between ^{31}P and C-4,7 is quite in accord with the dihedral angle of about 90° found in the TCC form.[14]

That rapid conformer interconversion does indeed occur was demonstrated by a low-temperature ^{13}C NMR experiment; at −97 °C in CH_3OD solution (the lowest temperature attainable), a new conformation of similar concentration was indicated to be present by the appearance of a second P-CH_3 doublet and C-5,6 singlet. The coupling constants for the P-CH_3 signals were essentially identical (downfield, 71.9 Hz; upfield, 71.7 Hz). Other sp^3 carbon signals were obscured by signals from the methanol, the only solvent found so far that allows attainment of the necessary low temperature while the polar phosphine oxide is kept in solution. When the temperature is raised, the signals began to move together, and by −84 °C coalescence was complete. Line positions from these spectra, shown as Figure 3, are recorded in the Experimental Section. The coupling constant for the single P-CH_3 doublet at room temperature is 71.1 Hz. There are several different environments possible in the TCC for P-CH_3 when ring inversion is stopped, and it is not known which conformers are involved in the rate process observed. Nevertheless, an approximate value for the free energy of activation ($\Delta G^{\ddagger}$) for the process observed can be derived by application of the Gutowsky–Holm equation[19] to the observed coalescence temperature and peak separation at the temperature of no exchange. This equation (see Experimental Section) applies to interconversion of conformers of equal intensity but is useful with caution in cases where unequal intensities are involved.[20] Two other approximations are involved in our treatment: that −84 °C is the coalescence temperature and that the peak separation ($\Delta\nu$) observed at the lowest temperature experimentally achieved is the maximum obtainable. The $\Delta G^{\ddagger}$ value so calculated for **20** is 9.6 kcal/mol, but it must be emphasized that refinement of the value is needed. Nevertheless, it is a reasonable value, although significantly larger than the 6 kcal/mol reported for cyclononane.[16] The demonstration of temperature-dependent phenomena for phosphonanedione **20**

(14) A detailed analysis of the structural parameters will be presented elsewhere in connection with broader studies of 9-membered ring compounds. Nonhydrogen atom fractional coordinates are provided as Table IV; other data are available as supplementary material.
(15) Hendrickson, J. B. *J. Am. Chem. Soc.* **1964**, *86*, 4854.
(16) Anet, F. A. L.; Wagner, J. J. *J. Am. Chem. Soc.* **1971**, *93*, 5266.
(17) Riddell, F. G. "The Conformational Analysis of Heterocyclic Compounds"; Academic Press: New York, 1980; pp 143–144.
(18) See: Quin, L. D.; Gallagher, M. J.; Cunkle, G. T.; Chesnut, D. B. *J. Am. Chem. Soc.* **1980**, *102*, 3136 and references cited therein.
(19) Gutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* **1965**, *42*, 3040.
(20) Shanan-Atidi, H.; Bor-Eli, K. H. *J. Phys. Chem.* **1970**, *74*, 961.

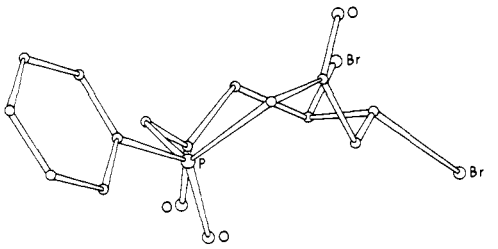


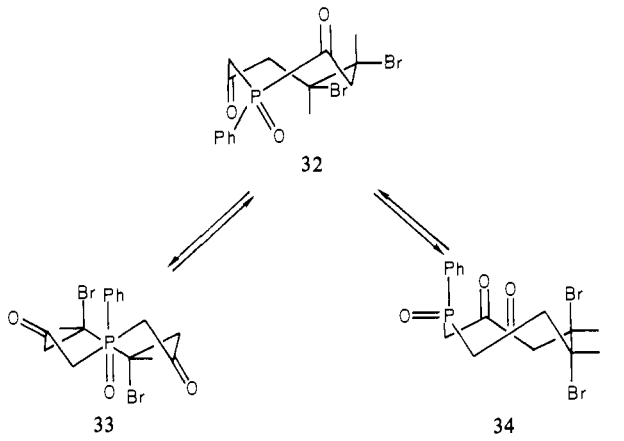
Figure 4. Structure of 1-phenyl-5,6-dibromo-3,8-phosphonane 1-oxide from X-ray analysis.

provides convincing proof that the simple spectrum obtained at room temperature is in fact the result of rapid interconversion among invertomers.

That interactions with the solvent can influence the population of the invertomeric forms, further complicating the conformational picture, is suggested by the proton NMR spectra of **20** in different solvents. The signals for protons on C-2,8 (but not at other positions) were found to be quite sensitive to solvent. In $CDCl_3$, a complex multiplet was obtained, but in Me_2SO-d_6 the multiplet collapsed to a single sharp doublet ($^2J_{PH}$ = 16 Hz) for the four protons. Simple doublets are quite characteristic of the α-CH_2 groups of 3-phospholene oxides,[21] even though these protons are diastereotopic and should show coupling. In the phosphonanedione, it appears that the highly polar Me_2SO is interacting with the polar functions in a different way than does $CDCl_3$, causing a net geometrical change in the solute. Further continued conformational studies of the phosphonane system are likely to be less complicated with the parent compound, whose synthesis is described elsewhere.[8]

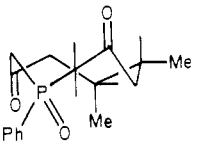
The 5,6-dibromo derivative **25** has a quite different ^{13}C NMR spectrum, one that states clearly that there is a preferred or averaged conformation in solution that lacks symmetry. Not only are there different chemical shifts for comparable carbons but also the coupling constants to ^{31}P differ. These results require that there be a distinctly different geometric relation between ^{31}P and the carbons of a comparable pair. That compound **25** also preferred the TCC conformation, at least in the solid state, was revealed by X-ray diffraction.[14] However, the invertomeric form adopted was different from that of **20**; it is shown as Figure 4 and by structure **32**, where the carbonyl oxygen atoms are seen to lie on opposite faces of the ring. This invertomer allows the two bromine atoms, as well as the phenyl group, to occupy uncrowded, pseudoequatorial positions, an energy feature of importance to larger rings just as it is in 6-membered rings.[22] The invertomer **32** lacks symmetry, and were it maintained in solution, it would give rise to different ^{13}C signals for comparable carbons. For this situation, the presence of a large energy barrier ($\Delta G^{\ddagger}$) to be surmounted between neighboring invertomers **33** and **34** (Scheme II) would have to be present, thus making the inversions slow and detectably temperature dependent. Invertomers **33** and **34** are clearly higher energy forms relative to **32** due to the presence of diaxial bromines. An attempt to determine if peak coalescence would occur with elevation of the temperature was thwarted by the decomposition of **25**. Large barriers to ring inversion in multiply substituted cyclononanes are not unknown; while the parent ring has a $\Delta G^{\ddagger}$ value of about 6 kcal/mol,[16] 1,1,4,4-tetramethylcyclononane and some derivatives are reported[23] to have barriers in the range 14–20 kcal/mol, giving NMR coalescence temperatures as high as 80 °C. Such large barriers can be attributed to the energy associated with the transannular repulsions of substituents on the ring in the pseudorotational process. These interactions can be more severe than are experienced in the better known cyclohexane ring inversion. A high $\Delta G^{\ddagger}$ value is not the only explanation for the ^{13}C NMR observations, however;

Scheme II

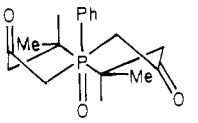


ring inversion could still be quite rapid among the various invertomers, but the position of equilibrium would favor those low-energy forms with diequatorial bromines. The averaged ^{13}C NMR spectrum for the invertomer mixture would, of course, more closely resemble that for the more stable invertomers such as 30, where nonequivalence of ring carbons is present. In this case, lowering the temperature might halt the invertomer interconversion and allow individuals to be seen. An experimental attempt to do this with **25** has so far been thwarted by failure to find a solvent that retains an adequate concentration in solution at low temperatures. These important questions of heightened barrier and conformational biasing in phosphonanes will be easier answered with more tractable derivatives than the dibromo diketones.

For the *cis*-5,6-dimethyl phosphonane derivative **23**, a different situation prevails; at each C except that on the C_2 axis, in all invertomeric TCC forms, one methyl is always pseudoaxial while the other is always pseudoequatorial. They are therefore never equivalent in any particular TCC form. To illustrate, assume that the same invertomer populated by the *trans*-dibromo compound **25** is taken up; structure **35** may then be drawn. Even when P



is on the C_2 axis, as in **36**, the methyls occupy different positions.

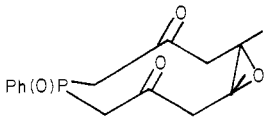


However, the ^{13}C NMR spectrum shows only one signal for both C-CH_3 groups and one signal for each pair of comparable ring carbons. This must mean that, if the TCC form is still populated by the dimethyl derivative, exchange of ring positions by pseudorotational processes is occurring rapidly at room temperature and an averaged spectrum results. That a much lower inversion barrier can exist in the *cis*-dimethyl case than in the *trans*-dibromo case may be rationalized on the basis of the quite different energies associated with the neighboring inverted forms and in the repulsions experienced in achieving them. In the dimethyl case, an inversion simply produces a new form where one methyl is crowded, the other is not; in the dibromo, as seen in Scheme II, the diequatorial invertomer is in a distinct energy valley relative to the neighboring diaxial forms.

Rigidity at the 5,6-positions, as provided by an epoxy function, leads to a ^{13}C NMR spectrum that shows only one signal for each pair of comparable ring carbons. The coplanarity of the segment C-4, C-5, C-6, and C-7 could cause the adoption of the chair–chair

(21) At the higher field of 270 MHz, more complex spectra can be observed and medium effects detected: Moedritzer, K.; Berger, P. A. *J. Org. Chem.* **1977**, *42*, 2023.
(22) Hendrickson, J. B. *J. Am. Chem. Soc.* **1967**, *89*, 7047.
(23) Borgen, G.; Dale, J. *J. Chem. Soc., Chem. Commun.* **1970**, 1105.

shape, as depicted by **37**, or the boat–chair (**38**), or twisted forms of these in rapid interconversion. Any of these situations could account for the ^{13}C spectrum.



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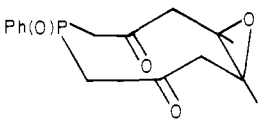

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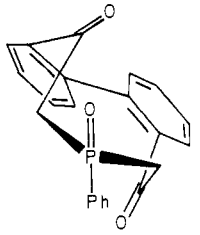
Fusion of benzo groups to the 4,5- and 6,7-positions has a profound effect on the conformation of the 3,8-phosphonanedione system. The ^{13}C NMR spectrum of **28** shows that nonequivalence is induced in ring carbons 2,9 and 3,8, since as in the dibromo case two signals with different C–P coupling constants are observed for each carbon of a pair. Rotational motion is severely restricted by the rigidity in the ring imposed by the benzo groups, and the only conformation which can be adopted is the highly twisted **39**



39

with the carbonyls *anti* to each other. Each carbonyl carbon, as well as the CH_2 groups, are therefore frozen in a different position with respect to the groups on phosphorus. To convert this form by twisting to an equivalent structure would require a prohibitively high energy, as clearly revealed by models.

Experimental Section[24]

Sources of Dienes. 4,5-Dimethylenecyclohexane (**4**)[10] and 4,5-dimethylenecyclohexene (**10**)[9] were prepared as described previously. *cis*-4,5-Dimethyl-1,2-dimethylenecyclohexane (**8**)[25] was prepared from *c*-4,*c*-5-dimethyl-*r*-1,*c*-2-cyclohexanedicarboxylic acid[26] (**40**) by the same procedures described for **4** and **10**. Acid **40** was reacted with $[(CH_3)_2N]_3P$ to form the bis(*N*,*N*-dimethylcarboxamide) as a noncrystallizing oil (34%). Reduction with $LiAlH_4$ gave the bis((dimethylamino)methyl) derivative: bp 126 °C (0.5 mm), 43%; ^1H NMR ($CDCl_3$) δ 0.83 (6 H, C-CH_3), 1.23–2.10 (12 H, C-CH_2 and CH), 2.15 (m, 12 H, N-CH_3). *N*-Oxidation with H_2O_2, followed by pyrolysis, gave the diene **8** in 9.2% crude yield, suitable for immediate use in the McCormack cycloaddition.

Preparation of 2-Substituted-2,3,4,5,6,7-hexahydro-1(*H*)-isophosphindole 2-Oxides. A general procedure for the McCormack cycloaddition with exocyclic dienes is illustrated with the 2-methyl compound (**5**). Properties of the products are given in Table I. Methylphosphonous dichloride (37.4 g, 0.32 mol) was added to a mixture of 1,2-dimethylenecyclohexane (29.3 g, 0.27 mol) and copper stearate (400 mg) in hexane (100 mL) in a widemouthed brown bottle with a Teflon-lined cap. The bottle was loosely capped until the initial exothermic reaction had subsided. As the solid cycloadduct formed, additional solvent was added (three 25-mL portions) to keep the adduct covered. The bottle was tightly sealed and allowed to stand for 13 days. The solid cycloadduct was filtered off, washed with petroleum ether (35–60 °C, three 50-mL portions), and added cautiously to an ice-cold, saturated $NaHCO_3$ solution (150 mL). The resulting solution was extracted continuously with chloroform for 48 h. The chloroform extract was dried, filtered, and concentrated to give a brown solid residue. Distillation gave 37.6 g (82%) of phospholene oxide **5** as a colorless oil, bp 106–107 °C (0.03 mm), which quickly solidified to a white, hygroscopic solid. The 100-MHz ^1H NMR spectrum ($CDCl_3$), typical of other phospholenes prepared in this study, was not well resolved and is given as an illustration of regions of absorption: δ 1.65 (d, $^2J_{PH}$ = 13 Hz, PCH_3), 1.39–1.85 (m, CH_2), 1.85–2.17 (m, allylic CH_2), 2.27–2.84 (m, PCH_2).

The 2-phenyl compound (**6**) was prepared by allowing a mixture of 24.9 g (0.23 mol) of diene **4**, 67.0 g of phenylphosphonous dibromide (0.25 mol), 300 mg of copper stearate, and ligroin (95–105 °C, 175 mL) to stand for 2 days. Heat was evolved on mixing, and ligroin was preferred over hexane. Distillation of the hydrolyzed product gave 42.3 g (78%) of phospholene oxide **6** as a colorless oil, bp 153–155 °C (0.02 mm), which solidified to a white solid, mp 75–78 °C. Recrystallization from benzene–ligroin (30–60 °C) gave white crystals, mp 75–79 °C.

Adduct formation with PBr_3 (67.5 g, 0.25 mol) and diene **4** in hexane was allowed to proceed for 46 days, although shorter periods would give acceptable yields. Solid phosphinic acid **7** was extracted from the hydrolysis product with CH_2Cl_2 and recrystallized from acetone.

5,6-Dimethyl-2-phenyl-2,3,4,5,6,7-hexahydroisophosphindole 2-Oxide. (9). In a small vial was placed 0.7 g (0.0052 mol) of diene **8**. To this was added 6 mg of copper stearate and 10 mL of ligroin, followed by careful addition of 1.4 g (0.0052 mol) of phenylphosphonous dibromide. The vial was closed tightly after a few minutes and allowed to stand for 2 days. The white solid was filtered off, washed with petroleum ether, and added cautiously to an ice-cold saturated $NaHCO_3$ solution (50 mL), forming an insoluble oil. The resulting mixture was then extracted with six 20-mL portions of chloroform. The extracts were dried ($MgSO_4$), filtered, and concentrated to give a brown noncrystallizing mixture of *cis,trans*-**9**. Only ^{31}P NMR (Table I) showed separate signals for the isomers: ^1H NMR ($CDCl_3$) δ 0.89 (d, 6 H, ^3J = 6 Hz, CH_3), 1.47–2.33 (m, 6 H, CHCH_2), 2.47–3.03 (m, 4 H, P-CH_2), 6.87–7.97 (m, 5 H, phenyl); ^{13}C NMR ($CDCl_3$) 15.7 (s, CH_3), 31.7 (s, CCH_3), 34.4 (d, $^3J_{PC}$ = 12.6 Hz, $CHCH_2$), 38.4 (d, $^1J_{PC}$ = 67.2 Hz, PCH_2), 128.3–137.5 (m, phenyl carbons). Elemental analysis was deferred to the phosphonanedione stage.

Preparation of 2-Substituted-2,3,4,7-tetrahydro-1(*H*)-isophosphindole 2-Oxides. The McCormack cycloadditions to 4,5-dimethylenecyclohexene (**10**) were carried out in ligroin, with product workup in the manner described above. Both the 2-methyl (**11**) and 2-phenyl (**12**) compounds were distilled (119–124 and 154–160 °C at 0.02 mm, respectively); the distillates readily solidified and were further purified by recrystallization. The phosphinic acid (**13**) was obtained directly as a solid. Further details and properties of the products are recorded in Table I.

Preparation of 2-Substituted-*trans*-5,6-dibromo-2,3,4,5,6,7-hexahydro-1(*H*)-isophosphindole 2-Oxides. The procedure for the 2-methyl compound (**14**) is typical: to a solution of phospholene oxide **11** (2.0 g, 0.012 mol) in methylene chloride (40 mL) at −15 °C was added a solution of bromine (1.92 g, 0.012 mol) in methylene chloride (10 mL) over a 15-min period. The resulting yellow solution was stirred at room temperature for 30 min and concentrated to give dibromide **14** as an orange oil, which could not be crystallized. Crude **14** could be precipitated as a pale yellow solid by adding ethyl acetate to a methylene chloride solution of the compound, but this solid was extremely hygroscopic and could not be purified sufficiently for analysis or melting point determination. ^1H NMR indicated, however, that complete conversion to the dibromide had taken place (absence of olefinic protons) and the crude product was used directly for ozonolysis without further purification: ^1H NMR ($CDCl_3$) δ 1.72 (br d, $^2J_{PH}$ = 13 Hz, PCH_3), 2.13–3.87 (br m, CH_2), 4.59 (br s, CH); ^{31}P NMR ($CDCl_3$)δ +59.7.

Phospholene oxide **12** (2.0 g, 8.7 mmol) and bromine (1.4 g, 8.7 mmol) in methylene chloride gave **15** as a yellow oil; chromatography on silica gel (acetone as eluant) gave a colorless oil which solidified on trituration with hexane to give 2.1 g (62%) of **15** as a white solid, mp 120–122 °C. Recrystallization from acetone-hexane gave white plates: mp 129–131 °C; ^1H NMR ($CDCl_3$) δ 2.26–3.60 (br m, CH_2), 4.60 (br s, CH), 7.26–7.98 (complex, phenyl H); ^{31}P NMR ($CDCl_3$) δ +50.0.

Anal. Calcd for $C_{14}H_{15}Br_2OP$: C, 43.11, H, 3.88; P, 7.94. Found: C, 43.36; H, 3.86; P, 7.94.

Similarly, phosphinic acid **16** (2.0 g, 11.8 mmol) in chloroform (65 mL) at 0° C was reacted with a solution of bromine (1.9 g, 11.8 mmol) in chloroform (10 mL) over a 15-min period. During the addition, the dibromide precipitated from solution as a white solid. The reaction mixture was stirred for 1 h at room temperature and was concentrated to give a white solid residue. The solid was broken up in ether, filtered,

(24) Melting points were taken on a Mel-Temp apparatus and are corrected; boiling points are uncorrected. Proton NMR spectra were obtained on a JEOL MH-100 spectrometer at 100 MHz or on either a Varian EM-360 or T-60 spectrometer at 60 MHz. Carbon-13 FT NMR spectra were taken on a JEOL FX-60 spectrometer at 15 MHz or on a Bruker HFX-10 spectrometer at 22.6 MHz, utilizing an internal deuterium lock, and are proton noise-decoupled. Proton and ^{13}C NMR chemical shifts are expressed in parts per million (δ) downfield from internal tetramethylsilane (Me_4Si). Phosphorus-31 FT NMR spectra (proton noise-decoupled) were obtained with the Bruker HFX-10 at 36.43 MHz. ^{31}P chemical shifts are expressed in parts per million relative to external 85% H_3PO_4, with positive shifts downfield and negative upfield. Infrared spectra were run on either a Perkin-Elmer 137 or 297 spectrophotometer.

(25) Bailey, W. J.; Rosenberg, J.; Young, L. J. *J. Am. Chem. Soc.* **1954**, *76*, 2251.

(26) Mann, G.; Werner, H.; Muhlstadt, M.; Engewald, W. *Tetrahedron* **1971**, *27*, 3223.

and washed with ether (three 20-mL portions) to give 3.6 g (92%) of the dibromide **16** as a fine, white solid, mp 191–193 °C. Recrystallization from methanol gave white plates: mp 193–194 °C; ^{1}H NMR (Me_2SO-d_6) δ 1.6–3.03 (complex m, CH_2), 4.72 (br s, CH), 8.02 (br s, OH); ^{31}P NMR (Me_2SO-d_6) δ +60.0.

Anal. Calcd for $C_8H_{11}Br_2O_2P$: C, 29.12; H, 3.36; P, 9.39. Found: C, 29.17; H, 3.42; P, 9.49.

5,6-Epoxy-2-phenyl-2,3,4,5,6,7-hexahydro-1(*H*)-isophosphindole 2-oxide (17). To a vigorously stirred suspension of phospholene oxide **12** (2.0 g, 8.7 mmol) in water (5 mL) was added *N*-bromosuccinimide (1.6 g, 8.7 mmol). The reaction mixture became warm (reaching 60 °C) as the suspension transformed into a cloudy solution. The reaction mixture was stirred for 30 min, after which solid NaOH (2.0 g) was added. The resulting mixture was stirred for an additional 30 min at 60 °C, whereupon an oily layer formed on the surface. The mixture was then diluted with water (5 mL) and extracted with benzene (five 20-mL portions). The benzene extract was dried ($MgSO_4$) and concentrated to give 2.0 g (93%) of *syn,anti*-**17** as a white crystalline solid, mp 131–133 °C. Recrystallization from benzene–ligroin (35–65 °C) gave feathery crystals: mp 135–137 °C; ^{1}H NMR ($CDCl_3$) δ 2.20–3.06 (m, CH,2), 3.32 (br s, CH), 7.14–7.88 (complex, phenyl H); ^{31}P NMR ($CDCl_3$) δ +49.3 (73%), +50.4 (27%).

Anal. Calcd for $C_{14}H_{15}O_2P$: C, 68.29; H, 6.14; P, 12.58. Found: C, 68.24; H, 6.20; P, 12.63.

1,3,4-Triphenyl-3-phospholene 1-Oxide (18). To a mixture of 2,3-diphenylbutadiene (31.3 g, 0.15 mol) and copper stearate (225 mg) in ligroin (95–105 °C, mL) in a small flask was added phenylphosphonous dibromide (48.2 g, 0.18 mol). The resulting mixture was stirred at 50 °C for 5 days. The solid cycloadduct which formed on the walls was filtered off and worked up as already described for McCormack adducts, yielding 16.8 g of phospholene oxide **18** as a pink solid, mp 128–135 °C. The filtrate from the cycloaddition reaction was refluxed for an additional 8 days and gave a second crop of 21.8 g of **18** as a yellow solid, mp 133–142 °C. The combined yield was 80%. Recrystallization from acetone–ligroin gave white crystals, mp 153–160 °C (lit.[12] mp 162.5–163.5 °C. Although the melting poing was substantially lower than the reported value, the ^{1}H NMR spectrum was identical with the published[2] spectrum, and the product was used directly for the subsequent photocyclization reaction.

2-Phenyldibenz[*e*,*g*]isophosphindoline 2-Oxide (19). The general procedure of Mallory[11] et al. was followed with minor modification. A solution of phospholene oxide **18** (3.3 g, 10.0 mmol) and iodine (120 mg, 0.5 mmol) in benzene (1 L) was irradiated for 5 h through a quartz insert with a Hanovia 450-W high-pressure mercury lamp. By the end of the reaction, a light deposit of an insoluble polymeric material covered the walls of the reaction vessel. The yellow reaction mixture was washed with 10% sodium thiosulfate solution (150 mL), dried ($MgSO_4$), filtered, and concentrated to give a yellow oil which quickly crystallized to a pale yellow solid. The solid was broken up in an ethyl acetate–petroleum ether solution (1:1, 15 mL), filtered, and dried under vacuum (0.1 mm) to give 1.8 g (55%) of phenanthrene **19**, mp 183–186 °C. Recrystallization from ethyl acetate–ligroin (95–105 °C) gave white plates: mp 197–198 °C; ^{1}H NMR ($CDCl_3$) δ 3.80 (d, $^2J_{PH}$ = 13 Hz, PCH_2), 7.17–8.00 (complex m, aromatic H), 8.53–8.83 (m, aromatic H); ^{13}C NMR ($CDCl_3$) δ 35.1 (d, $^1J_{PC}$ = 68.4 Hz, PCH_2), 123.2–136.8 (complex, aromatic C); ^{31}P NMR ($CDCl_3$) δ +53.9.

Anal. Calcd for $C_{22}H_{17}OP$: C, 80.47; H, 5,22; P, 9.43. Found: C, 80.71; H, 5.13; P, 9.32.

General Procedure for Ozonolysis of Bicyclic Phospholene Derivatives. The procedure is illustrated with the synthesis of the 2-methyl derivative **20**. A cold (−78 °C), dry stream of ozonized oxygen was bubbled through a solution of phospholene oxide **5** (10.9 g, 0.064. mol) in methanol (75 mL) at −78 °C until a light blue color appeared, indicating the presence of excess ozone. The excess ozone was removed by bubbling cold, dry nitrogen through the reaction mixture until the blue color disappeared. To the stirred reaction mixture, still at −78 °C, was added trimethyl phosphite (11.9 g, 0.096 mol), and the resulting solution was stirred for 5 min at −78 °C and then allowed to warm to room temperature. The reaction mixture was concentrated on a rotary evaporator at 40 °C to give a crystalline, white solid residue. Anhydrous ether (75 mL) was added to break up the solid, which was then filtered, washed with three 50-mL portions of ether, and dried under a stream of nitrogen to give 12.1 g (94%) of phosphonanedione **20** as a white crystalline solid, mp 127–131 °C. Recrystallization from dry benzene gave white plates, mp 130–132 °C. The ^{1}H NMR ($CDCl_3$) spectrum was poorly resolved: δ 1.60–2.04 (m, $CH_2CH_2C{=}O$), 1.84 (d, $^2J_{PH}$ = 13 Hz, PCH_3), 2.24–2.84 (m, $CH_2CH_2C{=}O$), 2.98–3.64 (m, PCH_2). In Me_2SO-d_6 the spectrum was the same, except that the downfield multiplet for C-2,9 collapsed to a doublet, δ 3.24 ($^2J_{PH}$ = 16 Hz); for ^{31}P NMR ($CDCl_3$) and IR spectra, see Table II, and for ^{13}C NMR spectra, see Table III. Other products prepared by this procedure are recorded in Table II, with ^{13}C NMR spectra in Table III.

Table IV. Nonhydrogen Atom Fractional Coordinates (×10^4) for 20 and 25, with Standard Deviations in Parentheses

atom	*x*	*y*	*z*
		(a) 20	
P(1)	206 (1)	5010 (...)	8467 (1)
C(2)	1166 (4)	6546 (4)	7565 (6)
C(3)	2439 (4)	6778 (4)	9110 (7)
C(4)	3782 (4)	6814 (5)	7835 (8)
C(5)	4663 (4)	5565 (6)	8551 (8)
C(6)	4719 (4)	4449 (6)	6511 (8)
C(7)	3365 (4)	3998 (5)	5491 (7)
C(8)	2433 (4)	3415 (4)	7452 (7)
C(9)	970 (3)	3555 (4)	6867 (6)
C(10)	−1370 (4)	5247 (5)	6847 (8)
O(11)	112 (3)	4826 (3)	11253 (4)
O(12)	2375 (3)	6965 (4)	11402 (5)
O(13)	2832 (3)	2861 (4)	9407 (6)
		(b) 25	
P(1)	4950 (2)	3216 (3)	−3152 (2)
C(2)	5920 (8)	4476 (10)	−3224 (8)
C(3)	6913 (8)	4824 (10)	−2138 (8)
C(4)	7728 (9)	3717 (11)	−1462 (9)
C(5)	8314 (9)	4077 (11)	−209 (9)
C(6)	7653 (11)	3678 (12)	494 (10)
C(7)	6421 (9)	4093 (10)	−39 (8)
C(8)	5660 (8)	3093 (10)	−822 (7)
C(9)	4706 (8)	3541 (10)	−1890 (8)
O(10)	5371 (6)	1894 (7)	−3198 (5)
O(11)	7089 (7)	5923 (7)	−1818 (6)
Br(12)	9805 (1)	3171 (2)	404 (2)
Br(13)	8370 (1)	4458 (2)	1998 (1)
O(14)	5787 (6)	1961 (7)	−569 (6)
C(1′)	3591 (8)	3593 (9)	−4257 (8)
C(2′)	2940 (10)	4592 (12)	−4198 (10)
C(3′)	1884 (11)	4851 (15)	−5058 (13)
C(4′)	1518 (12)	4086 (17)	−5977 (13)
C(5′)	2171 (12)	3072 (16)	−6095 (10)
C(6′)	3190 (10)	2806 (12)	−5222 (9)

5,9-Dioxo-7-phenyl-5,6,8,9-tetrahydro-7(*H*)-dibenzo[*d*,*f*]phosphonin 7-Oxide (28). A cold (−78 °C), dry stream of ozonized oxygen was vigorously bubbled through a suspension of **19** (5.1 g, 16.0 mmol) in methanol (150 mL) at −40 °C until all solids dissolved (about 90 min). Nitrogen was then bubbled through the cold reaction mixture for about 5 min to remove any excess ozone. A mixture of potassium iodide (8.0 g, 0.048 mol) and acetic acid (8.2 mL) was added, and the resulting dark mixture was allowed to stir at room temperature for 45 min. The released iodine was then reduced by the addition of a 10% sodium thiosulfate solution (200 mL), and the yellow solution was extracted with CH_2Cl_2 (five 125-mL portions). The CH_2Cl_2 extracts were combined, dried ($MgSO_4$), and concentrated to give a viscous yellow oil. The oil was dissolved in 20 mL of benzene, and the product caused to precipitate by the addition of petroleum ether (100 mL). The resulting suspension was allowed to stand overnight and then filtered to give 3.3 g (58%) of diketone **28** as a pale yellow solid, mp 152–156 °C Recrystallization from acetone gave fine white needles: mp 173.5–174.5 °C; ^{1}H NMR ($CDCl_3$) δ 3.04–3.96 (m, CH_2), 6.94–8.16 (complex m, aromatic H); analysis and ^{31}P NMR and IR spectra, Table II; ^{13}C NMR spectra, Table III.

Low-Temperature ^{13}C NMR Spectra of 20. A JEOL FX-90Q FT spectrometer was employed for recording the spectra of a 1 M solution of **20** in CH_3OD. The temperature was reduced to −97 °C (lower temperatures caused solid formation); after a 15-min equilibration period, the upfield region of the spectrum was recorded: *P-CH*$_3$, doublets at 15.5 and 18.7 ppm ($^1J_{PC}$ = 71.7 Hz) and 16.2 and 19.4 ppm ($^1J_{PC}$ = 71.9 Hz), Δν 15.6 Hz (upfield signals) and 15.8 Hz (downfield signals); *C-5,6*, singlets at δ 23.5 and 24.2, Δν = 3.5 Hz. The temperature was raised to −90 °C and after 15 min the spectrum was recorded: *P-CH*$_3$, δ 15.8 and 19.0 (^1J = 70.7 Hz) and 16.2 and 19.3 (^1J = 71.0 Hz), Δν 7.2 Hz (upfield) and 7.5 Hz (downfield); *C-5,6*, singlets at δ 23.7 and 24.1, Δν = 7.7 Hz. At −84 °C the spectrum was recorded: *P-CH*$_3$, one doublet at 15.9 and 19.1 ppm ($^1J_{PC}$ = 71.2 Hz; cf. to 71.1 Hz at room temperature). Employing a coalescence temperature of 189 K in the Gutowsky–Holm expression[19]

$$\Delta G^{\ddagger}_{T_c} = T_c[45.67 + 4.58 \log (T_c/\Delta\nu)]$$

gave $\Delta G^{\ddagger} = 9.6$ kcal/mol. The assumption that $\Delta\nu$ at −97 °C represents maximum peak separation introduces some uncertainty in this value, but a significantly increased value of $\Delta\nu$ would lower $\Delta G^{\ddagger}$ by only as much as several tenths of 1 kcal.

X-ray Crystallographic Analyses of 20 and 25. Crystal data are provided in ref 13. Nonhydrogen atom fractional coordinates are recorded in Table IV. Thermal parameters are available as supplementary material.

Registry No. 4, 2819-48-9; **5**, 65482-10-2; **6**, 80754-56-9; **7**, 65482-11-3; **8**, 80754-57-0; **9**, isomer I, 80754-58-1; **10**, 54290-41-4; **11**, 70179-64-5; **12**, 70179-63-4; **13**, 70179-65-6; **14**, 75401-33-1; **15**, 75401-34-2; **16**, 75401-35-3; **17**, isomer I, 80754-59-2; **17**, isomer II, 80794-93-0; **18**, 55781-96-9; **19**, 74078-07-2; **20**, 65114-88-7; **21**, 80754-60-5; **22**, 65114-89-8; **23**, isomer I, 80754-61-6; **23**, isomer II, 80794-94-1; **24**, 75401-36-4; **25**, 75531-99-6; **26**, 80461-86-5; **27**, isomer I, 80794-95-2; **27**, isomer II, 80794-96-3; **28**, 74078-08-3; **40**, 33383-70-9; **40** diamide, 80754-62-7; **40** diamine, 80754-63-8; methylphosphonous dichloride, 676-83-5; phenylphosphonous dibromide, 1073-47-8; phosphorus tribromide, 7789-60-8; 2,3-diphenylbutadiene, 2548-47-2; **9**, isomer II, 80794-97-4.

Supplementary Material Available: Tables of anisotropic thermal parameters for **20** and **25**, hydrogen atom fractional coordinates and isotropic thermal parameters for **20**, hydrogen atom fractional coordinates for **25**, and elemental analyses for compounds **5–7**, **11–13**, and **20–28** (5 pages). Ordering information is given on any current masthead page.

Synthesis of Aromatic Carbonyl Compounds via Thallation–Carbonylation of Arenes

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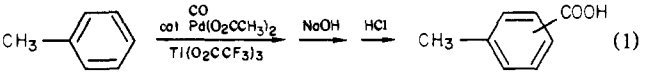
Abstract: Simple arenes, substituted benzylic and β-phenethyl alcohols, benzoic acid, phenylacetic acid, benzamide, acetanilide, phenylurea, and benzophenone have been thallated under a variety of reaction conditions with thallium(III) trifluoroacetate and subsequently carbonylated with 10% $PdCl_2$, 2 equiv of LiCl, and MgO in either methanol or tetrahydrofuran under 1 atm of carbon monoxide to give aromatic esters, substituted phthalides and 3,4-dihydroisocoumarins, phthalic and homophthalic anhydride, phthalimide, and the ortho-substituted methyl esters of acetanilide, phenylurea, and benzophenone, respectively. The scope and limitations of this approach to aromatic carbonyl compounds are examined.

Organothallium compounds have recently proven to be valuable intermediates in organic synthesis.[1-3] The highly regiospecific electrophilic thallation of arenes[4,5] and many novel methods by which the thallium moiety can be substituted by a variety of functional groups of great importance to the organic chemist have provided a number of important new routes to substituted arenes. Our own interests in the carbonylation of organomercurials[6-8] have encouraged us to look at similar applications of the closely related organothallium compounds. We herein report that the successful thallation and subsequent carbonylation of a variety of substituted arenes provides a highly convenient new route to simple aromatic esters, phthalides, 3,4-dihydroisocoumarins, anhydrides, and imides.[9]

While the direct carbonylation of arylthallium compounds has been studied, it requires high temperatures and pressures, and the yields are generally poor.[10] Since organomercurial carbonylation reactions are greatly facilitated by addition of palladium salts,[6,7] we have examined the possibility that arylthallium compounds might be carbonylated at room temperature and atmospheric pressure by addition of palladium chloride. The transmetalation of arylthallium compounds by palladium chloride has previously been communicated.[11,12] During our investigations, Van Venrooy patented a similar approach to aromatic carboxylic acids using excess benzene or toluene, thallium trifluoroacetate (TTFA), 0.1–10% palladium acetate, and 4–7 atm of carbon monoxide (eq 1).[13] Good yields of carboxylic acids were obtained based on



(1)

thallium reagent, but in order to be useful the aromatic starting material must either be cheap or recyclable. The elevated pressures and product mixtures further detract from the procedure. Our own work has concentrated on developing a simple atmospheric-pressure, room-temperature method of catalytically carbonylating arenes which provides excellent yields of the carbonyl product without using an excess of starting arene and which takes advantage of the high regioselectivity of electrophilic aromatic

Table I. Carbonylation of Phenylthallium Bis(trifluoroacetate)[a]

entry	added salt(s), equiv	% yield of methyl benzoate (% biphenyl)[b] −78 °C → 25 °C	0 °C	25 °C
1	$PdCl_2$, 1	28 (11)	53	13 (24)
2	$PdCl_2$, 1; LiCl, 2	57	39 (3)	54
3	$PdCl_2$, 1; LiCl, 2; MgO, 1			57
4	$PdCl_2$, 0.1			13 (9)
5	$PdCl_2$, 0.1; LiCl, 2	25 (7)	34 (6)	57
6	$PdCl_2$, 0.1; LiCl, 2; MgO, 1	44 (7)	57	

[a] 1 mmol of $PhTl(O_2CCF_3)_2$ in 10 mL of CH_3OH. [b] GLC analysis with tetradecane as an internal standard.

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