homoconjugate product would be $CF_3CH_2O^-(HOCH_2CF_3)_x$, both of which are structurally analogous to the species of the ion-cluster steps described here.

Acknowledgments. We gratefully acknowledge support of this research from the U.S. Army Research Office (DAAG29-77-G-0142) and the National Science Foundation (Equipment Grant CHE76-80382).

Richard N. McDonald,* A. Kasem Chowdhury, D. W. Setser
Department of Chemistry, Kansas State University
Manhattan, Kansas 66506

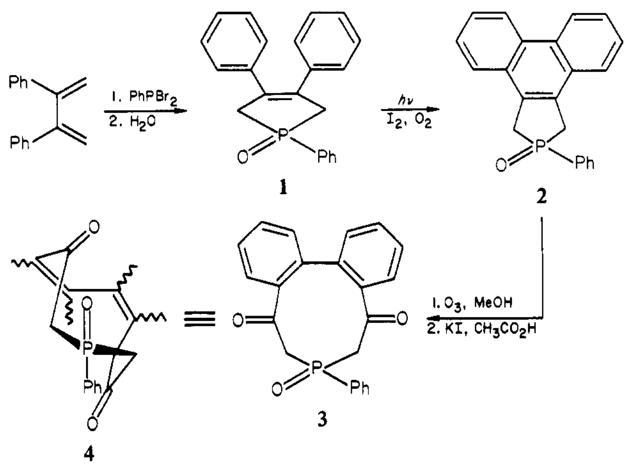
Received February 20, 1980

Synthesis of a Dibenzophosphonin

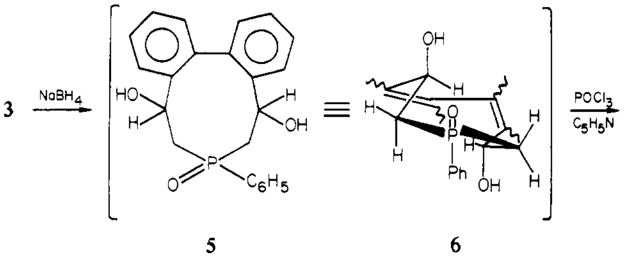
Sir:

Heterocyclic systems containing ten π electrons (heteronins) are of great theoretical interest and present a formidable synthetic challenge.[1] Of the heteronin systems prepared to date, only the nitrogen[2,3] and oxygen[4,5] compounds have been obtained in monocyclic form, while thionin is known only through annelated derivatives.[6,7] Examples of the phosphonin system have been produced in the form of tetrabenzo derivatives[8] and as the 1,6,9-triphenyl 2,3,4,5-tetracarboxylate,[9] but the heavily substituted nature of these compounds[10] vitiates their usefulness for further study as ten-π-electron systems. Of great need in the study of heteronins, therefore, is a synthetic method suitable for preparing phosphorus representatives which, in view of the results of numerous studies concerning delocalization phenomena in the π-excessive phosphole series,[11] certainly have the potential to exhibit similar effects. We now report the first stepwise synthesis of the phosphonin system, in the form of a dibenzo derivative. The nine-membered-ring intermediates in our synthesis will also be seen to be of interest from a conformational standpoint.

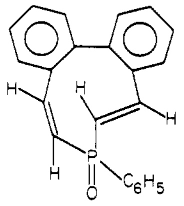
Our synthesis is based upon our previously reported method[12] for the construction of large-ring phosphorus compounds, the ring-opening ozonolysis of a phospholene oxide bearing a cycloalkano ring fused at the double bond. In the present case, the double bond is that at the 9,10 position of phenanthrene, as in **2**. This new system was prepared by photocyclization[13] of 1,3,4-triphenyl-3-phospholene oxide (**1**)[14] by irradiation through a quartz insert with a Hanovia 450-W, high-pressure mercury lamp for 5 h in benzene (56%, mp 197–198 °C).[15] Ozonolysis of **2** in methanol at −40 °C, followed by reductive workup with potassium iodide and acetic acid, afforded the diketone **3** (58%, mp 173.5–174.5 °C; δ ^{31}P +25.9 ($CDCl_3$)). In contrast to the monocyclic parent of the diketophosphonane system whose ^{13}C NMR spectrum indicates a rapid ring inversion at room temperature,[12] compound **3** was found by ^{13}C NMR to exist in an asymmetric conformation that is stable at room temperature, as revealed by the presence of two sets of signals for the carbonyl (δ 194.7 (3.9 Hz) and 194.6 (0 Hz) in $CDCl_3$) and methylene (δ 47.8 (53.7 Hz) and 46.9 (57.6 Hz)) carbons. The asymmetry arises from the chiral phosphorus atom and the inability of the puckered ring with anti carbonyls to undergo ring inversion. This process, which would interchange the carbonyls (and the methylenes also) and thereby cause their equivalence, can only take place over a very high energy barrier, due to the skeletal constraints imposed on the ring by the sites of unsaturation. A likely conformation for the diketone is shown as **4**.



1 2 3 4



5 6



7

Reduction of **3** with $NaBH_4$ in boiling ethanol gave the diol **5**$\cdot C_2H_5OH$, mp 262–263 °C, as a single isomer (one ^{31}P NMR signal, +29.9 in Me_2SO). The most likely conformation seems to be **6**, which would result from attack at similar faces of the anti carbonyls of **3**. Dehydration with $POCl_3$ in pyridine at 100 °C for 1 h gave the first phosphonin oxide (**7**, 58%) as a semihydrate, mp 166–167 °C, which is assigned the cis and trans structure from the ^1H NMR spectral data (Table I). Thus, there are two different upfield signals for the protons α to P. Each signal is split by the β protons (intermingled with the aromatic protons) but with coupling constants that are drastically different (4 and 14 Hz). The former is in the range for cis protons,[16] the latter for trans. The trans geometry in a nine-membered ring has been encountered for other heteronins[6,17] as well as in 1,2:7,8-dibenzocyclononatetraene.[18] It is notable that attempts to prepare the 1,2:3,4-dibenzocyclononatetraene[19] by dehydration of the diol

---

[1] See: (a) Anastassiou, A. G. *Adv. Heterocycl. Chem.* **1978**, *23*, 55–102; (b) *Acc. Chem. Res.* **1976**, *9*, 453; (c) *Pure Appl. Chem.* **1975**, *44*, 691; (d) *Acc. Chem. Res.* **1972**, *5*, 281.

[2] Anastassiou, A. G.; Gebrian, J. H. *J. Am. Chem. Soc.* **1969**, *91*, 4011.

[3] Masamune, S.; Hojo, K.; Takada, S. *Chem. Commun.* **1969**, 1204.

[4] Anastassiou, A. G.; Cellura, R. P. *Chem. Commun.* **1969**, 903, 1521.

[5] Masamune, S.; Takada, S.; Seidner, R. S. *J. Am. Chem. Soc.* **1969**, *91*, 7769.

[6] Bindra, A. P.; Elix, J. A.; Garratt, P. J.; Mitchell, R. H. *J. Am. Chem. Soc.* **1968**, *90*, 7372.

[7] Garratt, P. J.; Holmes, A. B.; Sondheimer, F.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1970**, *92*, 4492.

[8] (a) Wittig, G.; Maercker, H. *Chem. Ber.* **1964**, *97*, 747; (b) Hellwinkle, D. *Chem. Ber.* **1965**, *98*, 576.

[9] Waite, N. E.; Tebby, J. C. *J. Chem. Soc. C* 1970, 386.

[10] A compound obtained in 2.7% yield in a nonreproducible experiment has been tentatively identified as the 1-phenyl 2,3,4,5-tetracarboxylate: Holah, D. G.; Hughes, A. N.; Kleemola, D. *J. Heterocycl. Chem.* **1978**, *15*, 1319.

[11] Hughes, A. N.; Kleemola, D. *J Heterocycl. Chem.* **1976**, *13*, 1.

[12] Quin, L. D.; Middlemas, E. D. *J. Am. Chem. Soc.* **1977**, *99*, 8370.

[13] Mallory, F. B.; Wood, C. S. *Org. Synth.* **1965**, *45*, 91.

[14] Nakayama, S.; Yashifugi, M.; Okazaki, R.; Inamoto, N. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 546.

[15] Compounds **2–9** were fully characterized spectroscopically (Table I) and gave the correct elemental analyses. The phosphonin **8** was analyzed as its methiodide salt **9**.

[16] Emsley, J. W.; Feeney, J.; Sutcliffe, L. H. "High Resolution Nuclear Magnetic Resonance Spectroscopy"; Pergamon Press: Oxford, 1966; Vol. 2, p 711.

[17] Anastassiou, A. G.; Reichmanis, E. *J. Chem. Soc., Chem. Commun.* **1975**, 149.

[18] Rabinovitz, M.; Willner, I. *Tetrahedron Lett.* **1976**, 3335.

Table I. Spectral Characteristics of Dibenzo[*d,f*]phosphonin Derivatives

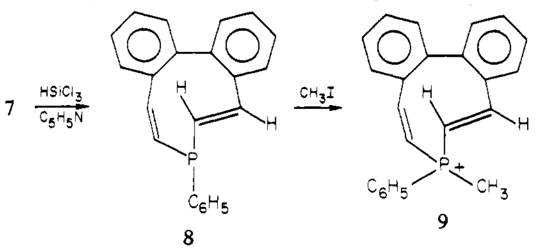
compd	^{1}H NMR^a chemical shift, δ	appearance	assignment	UV λ_{max} (EtOH)	ε	^{31}P NMR, δ^b
7	6.04	dd; $^2J_{PH}$ = 24 Hz, $^3J_{HH}$ = 14 Hz	trans PC*H*=CH	202	46 000	+17.2
	6.08	dd; $^2J_{PH}$ = 14 Hz, $^3J_{HH}$ = 4 Hz	cis PC*H*=CH	259 (sh)	7 600	
	6.64–7.88	multiplet	aromatic and PCH=C*H*			
8	5.67	dd; $^2J_{PH}$ = 35 Hz, $^3J_{HH}$ = 15 Hz	trans PC*H*=CH	202	43 500	−24.7
	5.97	dd; $^2J_{PH}$ = 11 Hz, $^3J_{HH}$ = 7 Hz	cis PC*H*=CH	255 (sh)	6 600	
	6.77–7.82	multiplet	aromatic and PCH=C*H*			
9	2.37	dd; $^2J_{PH}$ = 14 Hz	P-C*H*$_3$			+1.8
	8.15	dd; $^3J_{PH}$ = 25 Hz, ^3J_H = 13 Hz	trans PCH=C*H*	202	48 000	
	6.23–7.92	multiplet	aromatic and PC*H*=CH	259 (sh)	10 400	

[a] JEOL MH-100 spectrometer; in CDCl$_3$ solutions. [b] Chemical shifts are referenced to external 85% H$_3$PO$_4$, with downfield positive, upfield negative; proton-decoupled FT spectra obtained with a Bruker HFX-90 spectrometer on CDCl$_3$ solutions.

corresponding to **5** resulted only in transannular interaction to regenerate the phenanthrene. Perhaps because of the geometric differences associated with the presence of phosphorus, ring closure did not accompany the formation of **7**. Diol conformation **6** readily accounts for the formation of a trans double bond, since it has the proper anti arrangement of OH and H. Installation of the cis double bond would then follow. Initial cis formation is less likely since the conformation required for it, as revealed by models, has additional features of steric crowding, e.g., from severe 5-OH/4-H peripheral interaction.

The phosphonin synthesis was completed by deoxygenation (95%) of oxide **7** with HSiCl$_3$/pyridine in refluxing benzene. The product (**8**) was a stable solid, mp 68–73 °C. Spectral data are provided in Table I. The cis,trans structure was again clearly evident from ^{1}H NMR data. The ^{1}H chemical shifts are typical of those for 2-phospholenes and do not show the extra deshielding characteristic of phospholes and expected also of a delocalized heteronin. The ring, however, is severely puckered because of the cis,trans geometry and the benzo groups, and the orientation of the p orbitals is highly unfavorable for p_π–p_π overlap. The presence of severe puckering is especially revealed by the magnitude of the two $^2J_{PH}$ values; this constant, well-known[20] to be sensitive to the orientation of the lone pair on P to the coupled proton, has the large value characteristic of 2-phospholenes for one α-H (35 Hz), while the other ^2J value is only 11 Hz. Models show that the dihedral angle (φ) relating the lone pair to the α-H of the trans double bond is about 30°, in the range of that in the 2-phospholenes (φ ~ 45°), thus allowing assignment of the signal with the larger coupling to this proton. The lone pair orientation to the cis α-H is markedly different (φ ~ 120°), accounting[20] for the small size of *J*. The UV absorption is also affected in dramatic fashion by the puckering of the ring; the spectrum consists simply of an intense peak at 202 nm (ε 43 500), with weaker absorption at 255 nm (ε 6600). The characteristic styrenoid and biphenyl absorptions are absent, indicating that puckering has forced the orbitals out of alignment for conjugative interaction. The corresponding dibenzothionin is also known to show no spectral characteristics suggestive of aromaticity.

The phosphonin readily forms a methiodide (**9**, mp 208–209 °C), whose spectral data (Table I) once again reveal the cis,trans structure. The UV spectrum is virtually identical with that of the phosphine, as indeed is that also of the phosphonin oxide **7**. The general similarity of all of these spectra also rules out the presence of any special conjugative effects associated with the various phosphorus functions.



The present work has shown, therefore, that the phosphonin ring can be constructed by standard synthetic methods and that the system may prove to have reasonable stability. Highly puckered dibenzophosphonin **8** is atropic and nonaromatic, and a substance with more favorable geometry must be prepared to assess the presence of heteronin-like aromaticity in this system.

Acknowledgments. This work was supported by a grant (CHE-7717876) from the National Science Foundation.

Eric D. Middlemas, Louis D. Quin*
Gross Chemical Laboratory
Duke University, Durham, North Carolina 27706

Received November 5, 1979

---

[19] Rabinovitz, M.; Willner, I.; Gamliel, A.; Gazit, A. *Tetrahedron* **1979**, *35*, 667.

[20] Albrand, J. P.; Gagnaire, D.; Robert, J. B. *Chem. Commun.* **1968**, 1469.

Cobalt-Mediated Cyclizations of Linear Achiral Diynenes. A One-Step Construction of Complexed Chiral Polycycles

Sir:

The application of intramolecular Diels–Alder reactions ([4 + 2] cycloadditions) has provided the synthetic organic chemist with a powerful tool for the assembly of six-membered rings containing polycyclic natural products.[1] We report a novel construction of such systems based on intramolecular, cobalt-mediated [2 + 2 + 2] cycloadditions in which *three* new carbon–carbon bonds are made with regio- and (in some of the cases examined so far) stereospecificity. This method promises to be a versatile approach to the carbocyclic framework of numerous molecules of synthetic interest[2] (e.g., steroids, terpenes, alkaloids, and other medicinally important molecules). It relies on the ability

---

(1) W. Oppolzer, *Synthesis*, 793 (1978); *Angew. Chem.*, **89**, 10 (1977); *Angew. Chem., Int. Ed. Engl.*, **16**, 23 (1977); R. G. Carlson, *Annu. Rep. Med. Chem.*, **9**, 270 (1974). For some recent references, see: D. F. Taber and B. P. Gunn, *J. Am. Chem. Soc.*, **101**, 3993 (1979); F. Näf, R. Decorzant, and W. Thommer, *Helv. Chim. Acta*, **62**, 114 (1979); S. M. Weinreb, N. A. Khatri, and V. Shringarepure, *J. Am. Chem. Soc.*, **101**, 5073 (1979); S. Weinreb, R. W. Franck, and B. Nader, *ibid.*, **102**, 1154 (1980); E. J. Corey, R. L. Danheiser, S. Chandrasekaran, G. E. Keck, B. Gopalan, S. D. Larsen, P. Siret, and J. L. Gras, *ibid.*, **100**, 8034 (1978); G. Stork and D. J. Morgans, *ibid.*, **101**, 7110 (1979); J. L. Gras and M. Bertrand, *Tetrahedron Lett.*, 4549 (1979). See also: K. P. C. Vollhardt, *Acc. Chem. Res.*, **10**, 1 (1977); R. L. Funk and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, **98**, 6755 (1976); **99**, 5483 (1977); **101**, 215 (1979); *Chem. Soc. Rev.*, in press; K. P. C. Vollhardt, *Ann. N.Y. Acad. Sci.*, **333**, 241 (1980).

(2) A. A. Akrem and Yu. A. Titov, "Total Steroid Synthesis", Plenum Press, New York, 1970; R. T. Blickenstaff, A. C. Ghosh, and G. C. Wolf, "Total Synthesis of Steroids", Academic Press, New York, 1974; J. Apsimon, Ed., "The Total Synthesis of Natural Products", Vol. 2 and 3, Wiley, New York, 1973, 1977; K. Nakanishi, T. Goto, S. Itô, S. Natori, and S. Nozoe, Eds., "Natural Products Chemistry", Vol. 1 and 2, Academic Press, New York, 1974, 1975.

0002-7863/80/1502-4839$01.00/0