mp 102–104 °C); ^{1}H-NMR (CCl$_4$) δ 2.92–3.35 (complex m, 6 H), 2.70 (broad s, 2 H), 1.43 (t, 4 H, J = 1.3 Hz).

Acknowledgment. We are indebted to the National Science Foundation for a grant which supported this investigation.

Registry No.—**1,** 5603-27-0; **2,** 106-51-4; **3,** 592-57-4; **4,** 1633-14-3; **5,** 67745-70-4; **6,** 67745-71-5; **7,** 67745-72-6; **8,** 67745-73-7; **9,** 67745-74-8.

References and Notes

(1) According to IUPAC nomenclature 1,8-bishomocubane would be pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane.

(2) S. Masamune, H. Cuts, and M. G. Hagben, *Tetrahedron Lett.*, 1017 (1966).

(3) W. G. Dauben and D. L. Whalen, *Tetrahedron Lett.*, 3743 (1966).

(4) E. Sarauw, *Justus Liebigs Ann. Chem.*, **209,** 93 (1881); J. F. Bagli and P. L. Ecuyer, *Can. J. Chem.*, **39,** 1037 (1961); A. N. Grinev, V. L. Florantev, and A. P. Terentev, *Zh. Obshch. Khim.*, **30,** 2316 (1960).

(5) The use of 2,5-dibromobenzoquinone in a Diels–Alder reaction to produce 1,8-bishomocubane is modeled after the cubane synthesis of Pettit and co-workers: J. C. Barborak, L. Watts, and R. Pettit, *J. Am. Chem. Soc.*, **88,** 1328 (1966).

(6) For an analogous pseudo-Favorskii rearrangement in the generation of a highly-strained ring system, see P. E. Eaton and T. W. Cole, Jr., *J. Am. Chem. Soc.*, **86,** 3157 (1964). See also ref 5.

(7) L. M. Stock and T.-Y. Luh, *J. Am. Chem. Soc.*, **96,** 3712 (1974); E. W. Della and H. K. Patney, *Synthesis*, 251 (1976).

(8) Melting points and boiling points are uncorrected. Elemental analyses were performed by the Scandinavian Microanalytical Laboratories, Herlev, Denmark.

Carbon-13 Nuclear Magnetic Resonance Spectra of Allenic Phosphonyl Compounds and the Related 1,2-Oxaphosphol-3-enes

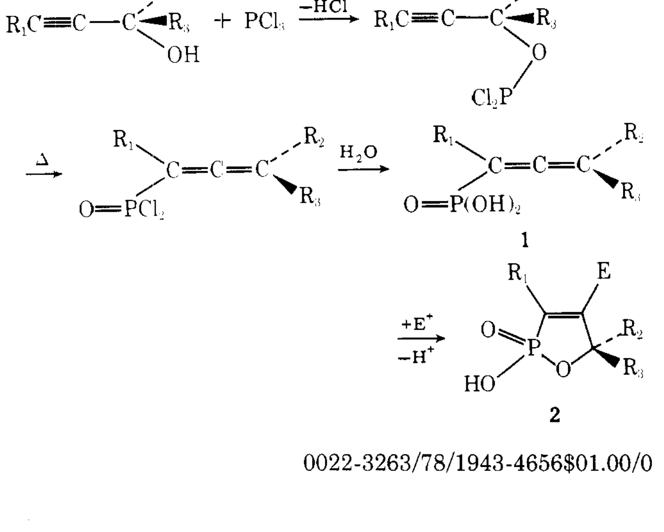
George A. Krudy and Roger S. Macomber*

Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221

Received June 27, 1978

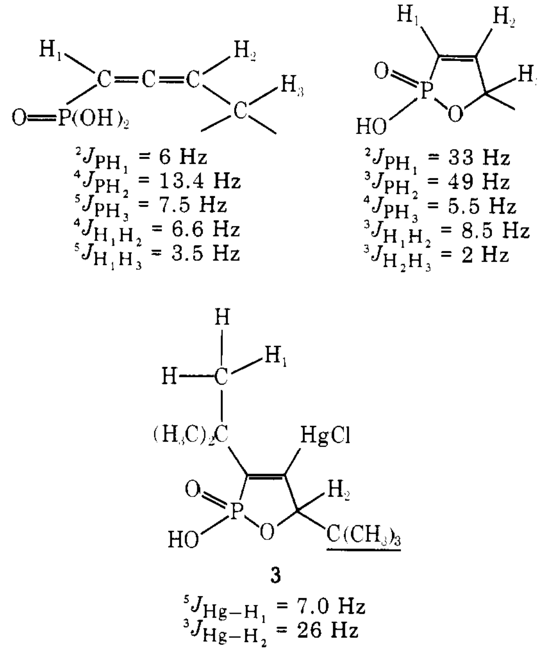
For several years we have been studying the reaction of propargyl alcohols with phosphorus trihalides under conditions which incorporate phosphorus in the products.[1-8] Of particular interest has been the reaction sequence shown in Scheme I, which leads to allenic phosphonic acids (**1**) and thence to 1,2-oxaphosphol-3-enes (**2**). Thus, a variety of allenic phosphonyl compounds have been prepared,[1,2,4] as well as oxaphospholenes with E = H,[1,2,4] Br,[5] HgX,[5] and OH (→ 4-keto-1,2-oxaphospholenes).[8] Moreover, the methyl esters of **1** and **2** are readily prepared from the free acid with diazomethane.[7]

Scheme I



The proton[1,2,4,5,8] and phosphorus[1,2,4] NMR spectra of these compounds have proven quite interesting, especially with respect to long-range heteronuclear coupling. Typical values[4] are shown with the structures in Chart I.[9a,b] Chloromercuri derivative **3** was especially noteworthy because it showed long-range ^{199}Hg couplings to protons five bonds away and an apparent effect on the rotation of the underlined *tert*-butyl group.[5] As a complement to these earlier studies, we now report the ^{13}C spectral data for some of these unique compounds. These results provide useful model data for chemical shifts and ^{13}C–^{31}P coupling constants in a wide variety of organophosphorus compounds.

Chart I[a,b]



$^2J_{\text{PH}_1}$ = 6 Hz
$^4J_{\text{PH}_2}$ = 13.4 Hz
$^5J_{\text{PH}_3}$ = 7.5 Hz
$^4J_{\text{H}_1\text{H}_2}$ = 6.6 Hz
$^5J_{\text{H}_1\text{H}_3}$ = 3.5 Hz

$^2J_{\text{PH}_1}$ = 33 Hz
$^3J_{\text{PH}_2}$ = 49 Hz
$^4J_{\text{PH}_3}$ = 5.5 Hz
$^3J_{\text{H}_1\text{H}_2}$ = 8.5 Hz
$^3J_{\text{H}_2\text{H}_3}$ = 2 Hz

$^5J_{\text{Hg-H}_1}$ = 7.0 Hz
$^3J_{\text{Hg-H}_2}$ = 26 Hz

Results

The ^{13}C chemical shifts and ^{13}C–P coupling constants for six allenic phosphonyl compounds are listed in Table I, and data for six oxaphospholene derivatives are given in Table II.

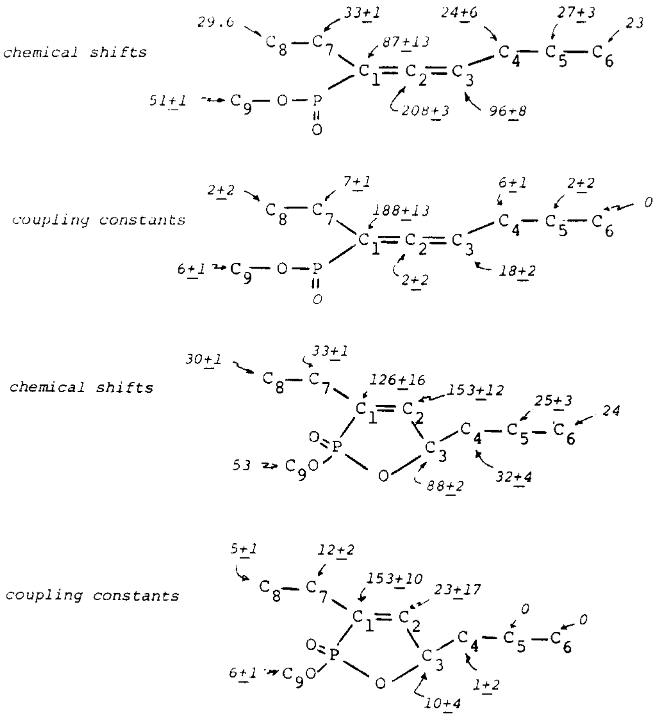
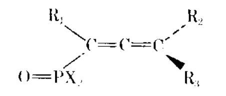
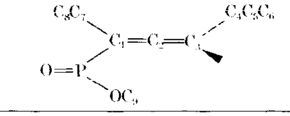


Figure 1. Average chemical shifts (parts per million downfield from Me$_4$Si) and coupling constants (hertz) for allenic phosphoryl derivatives and oxaphosphol-3-enes.

0022-3263/78/1943-4656$01.00/0

Table I. ^{13}C NMR Spectral Data for Allenic Phosphonyl Compounds[a]

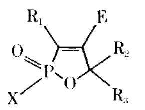


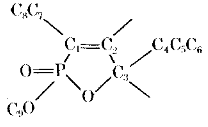


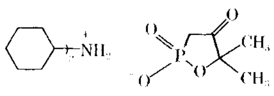
						δ_{C_i}									J_{PC_i}								
R$_1$	R$_2$	R$_3$	X	ref	registry no.	C$_1$	C$_2$	C$_3$	C$_4$	C$_5$	C$_6$	C$_7$	C$_8$	C$_9$	C$_1$	C$_2$	C$_3$	C$_4$	C$_5$	C$_6$	C$_7$	C$_8$	C$_9$
H	H	H	Cl	4	17166-36-8	90.0	212.9	80.5							166	0	22						
H	Me	Me	OH[b]	4	1831-37-4	80.8	211.3	99.8	22.2						193	0	17	5					
H	Me	Me	OMe	4, 7	4037-12-1	75.1	209.9	96.0	17.7					51.4	200	0	17	7					7
H	(CH$_2$)$_5$		OMe	4	67711-66-4	73.7	205.6	101.2	27.5	24.3	23.3			50.4	200	0	17	7	4	0			5
t-Bu	Me	Me	OMe	4	67711-67-5	100.1*	206.1	97.1	19.2			34.0	29.7	52.0	185	5	17	7			10	5	5
t-Bu	H	*t*-Bu	OMe	2	67711-68-6	104.4*	205.4	104.4	32.1[c]	29.9[c]		33.7[c]	30.1[c]	52.1[d]	187	5	17	7	0		7	0	6[c]

[a] Chemical shifts (δ) are in parts per million downfield from Me$_4$Si (CDCl$_3$ at 76.9 ppm); coupling constants (absolute values) are in hertz; the solvent was CDCl$_3$ unless otherwise noted. Asterisks indicate tentative assignment. [b] D$_2$O solvent. [c] Assigned to be consistent with relative proton chemical shifts.[2] [d] Two overlapping doublets (see text).

Table II. ^{13}C NMR Spectral Data for 1,2-Oxaphospholene Derivatives[a]





							δ									J								
R$_1$	R$_2$	R$_3$	E	X	ref	registry no.	C$_1$	C$_2$	C$_3$	C$_4$	C$_5$	C$_6$	C$_7$	C$_8$	C$_9$	C$_1$	C$_2$	C$_3$	C$_4$	C$_5$	C$_6$	C$_7$	C$_8$	C$_9$
H	Me	Me	H	OMe	4, 7	59474-17-8	114.5	156.8	85.3	27.4[b] 26.6[b]					52.8	159	15	10	0					5
H	Me	Me	H	OH	4[c]	59474-16-7	116.6	159.0	*c*	28.6						156	15	*c*	0					
t-Bu	H	*t*-Bu	HgCl	OH	5[d]	62991-78-0	146.5	160.5	90.2	35.3	26.2		32.3	31.0		137	20	15	0	0		14	5	
t-Bu	H	*t*-Bu	Br	OMe	5	67711-69-7	137.0*	133.7	89.3	36.5	27.4		33.5	28.1	53.0	155	51	5	5	0		10	4	7
H	(CH$_2$)$_5$		H	OMe	4	67711-70-0	114.5	156.2	87.2	35.8[b] 35.0[b]	21.3	24.0			52.6	159	15	10	0	0	0			7
					8[e]	65378-74-7	34.9	213.0	85.3	28.5*						124	12	0	0					

[a] See footnote *a*, Table I. [b] The two methyl(ene) groups are rendered nonequivalent by the chiral phosphorus. Similar effects were noted in the proton spectrum.[4] [c] D$_2$O solvent; quaternary carbon not found. [d] Me$_2$SO-d_6 solvent; *t*-Bu resonances assigned to be consistent with relative proton chemical shifts.[1,2,4,5] [e] Cyclohexyl resonances at δ 52.2, 25.2, 24.8, and 24.6.

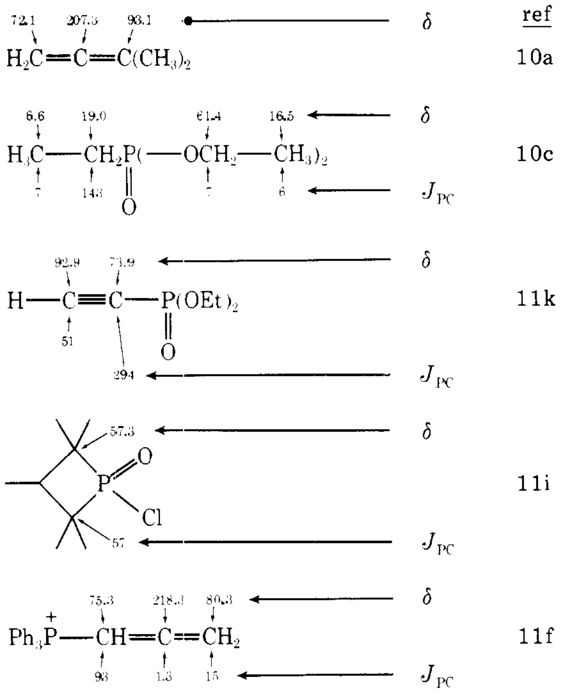
In most cases peak assignments were readily made by chemical shift and coupling constant magnitudes, and these assignments were consistent with relative peak intensities, considering nuclear Overhauser enhancements for those carbons with hydrogens directly attached.[10] Some of the quaternary carbon resonances were exceedingly weak, even with 10^5 transients; these assignments (*) should be considered tentative. Where only a single line was observed for a given carbon, the coupling constant is listed as 0, but lower limits to detection of small coupling are estimated to be 2 Hz.

Average chemical shift and coupling constant data for the allenic phosphoryl derivatives and the oxaphospholenes are summarized in Figure 1. Ranges are given as standard deviation.

Discussion

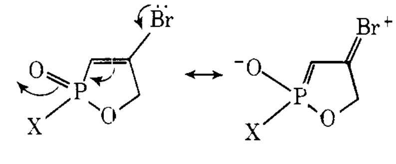
Because of the novelty of oxaphosphol-3-enes and the paucity of ^{13}C data published for allenic phosphoryl compounds, it is difficult to find exact analogies with which to compare our results. Nonetheless, from more general ^{13}C data

Chart II

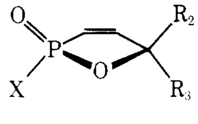


on organophosphorus compounds,[11] it is clear that the chemical shifts and coupling constants reported here occur within the regions for comparably situated carbon nuclei. Some typical data are given in Chart II.

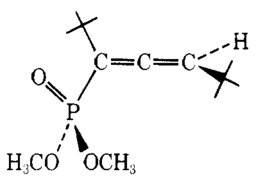
Several trends in chemical shift and coupling constants become apparent from further examination of the data in Tables I and II. Alkyl substitution at C_1 or C_3 of the allenic compounds and C_1 of the oxaphospholenes causes an ca. 20 ppm downfield shift in their resonances, as noted in model compounds.[10,11] The chemical shift of C_2 in the allenes occurs in its unique downfield position and is relatively insensitive to substitution.[10,11h] C_2 of the oxaphospholenes is not affected by substitution of HgCl for H, but E = Br causes a 25 ppm *upfield* shift. This might be ascribed to p-dπ resonance not



present when E = H or HgCl. Long-range effects of chirality on equivalence are also seen in these data. That R_2 and R_3 in the oxaphospholene *esters* are rendered diastereotopic by the



chirally substituted phosphorus can be readily seen from the first and fifth entries in Table II. This effect, previously noted by proton NMR spectroscopy,[4] is absent in the free acids and their salts. Additionally, the chirality of the 1,3-di-*tert*-butylallenyl system renders the two methoxy groups on phosphorus nonequivalent.[12]



With regard to coupling constants, the most unexpected observation was the small value observed for ^2J between P and the central allenic carbon.[11f] The coupling was in fact 0 except when R_1 = *tert*-butyl, and then only 5 Hz. Clearly the positive and negative components of the coupling constant essentially cancel one another in this arrangement. $^2J_{(P-C_2)}$ values in the oxaphospholes averaged about 17 Hz, except when E = Br (J = 51 Hz). This may be further evidence for the resonance effect described above. ^1J values for the allenes were somewhat larger than model compounds would have suggested (vide supra), but the values decreased by ca. 30 Hz to more "normal" values in the oxaphospholenes. These effects may be rationalized by changes in the s character of the C_1–P bond as R_1 substituents change and as the ring closes. A comparison of $^2J_{P-C_7}$ (allene 7 Hz, oxaphospholene 12 Hz) and $^4J_{P-C_4}$ (allene 6 Hz, oxaphospholene 1 Hz) with comparable P–H coupling constants ($^2J_{P-H}$: allene 8 Hz, oxaphospholene 33 Hz; $^4J_{P-H}$: allene 13 Hz, oxaphospholene 5 Hz)[1,2,4] shows that the former values are generally somewhat greater than predicted from differences in magnetogyric ratio alone:[13] $J_{PC}/J_{PH} \simeq \gamma_{^{13}C}/\gamma_{^1H} = 0.251$. Finally, it is interesting to note that ^3J (P–C_3) in the oxaphospholenes averages 10 Hz while the oxaphospholane (sixth entry of Table II) shows 0 coupling, even though the P–O–C (^2J) contribution is still possible. This suggests that more spin information is transmitted via the PC═CC linkage than by the P–O–C linkage.

Experimental Section

The compounds examined in this study were prepared as previously described.[1-8] ^{13}C spectra were obtained on a Varian CFT-20 spectrometer in the Fourier mode with total proton decoupling. Typical spectral parameters are the following: sweep width, 5000 Hz; transients, 8×10^4; pulse width, 8 μs; acquisition time, 0.4 s.

Acknowledgment. The authors are deeply indebted to Professor David Behnke of the University of Cincinnati Medical School for obtaining these ^{13}C spectra. The assistance of Bruce Barner, who prepared several of the compounds studied in this work, is gratefully acknowledged.

References and Notes

(1) R. S. Macomber, *J. Org. Chem.*, **36**, 2713 (1971).
(2) R. C. Elder, L. R. Florian, E. R. Kennedy, and R. S. Macomber, *J. Org. Chem.*, **38**, 4177 (1973).
(3) E. R. Kennedy and R. S. Macomber, *J. Org. Chem.*, **39**, 1952 (1974).
(4) E. R. Kennedy and R. S. Macomber, *J. Org. Chem.*, **41**, 3191 (1976).
(5) R. S. Macomber, *J. Am. Chem. Soc.*, **99**, 3072 (1977).
(6) R. S. Macomber, *J. Org. Chem.*, **42**, 3297 (1977).
(7) R. S. Macomber, *Synth. Commun.*, **7**, 405 (1977).
(8) R. S. Macomber, *J. Org. Chem.*, **43**, 1832 (1978).
(9) (a) Throughout this paper only the magnitudes of the coupling constants are given, without regard for sign. (b) The values for the allenic compounds in Chart I are especially sensitive to the substituents on phosphorus.[4] When OH is replaced by Cl, ^2J averages 28 Hz, ^4J = 17.5 Hz, and ^5J = 12 Hz.
(10) (a) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley, New York, 1972; (b) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, 1972; (c) L. F. Johnson and W. C. Jankowski, "Carbon-13 NMR Spectra", Wiley-Interscience, New York, 1972.
(11) (a) G. Szalontai, *Org. Magn. Reson.*, **10**, 63 (1977); (b) J. R. Llinas, E.-J. Vincent, and G. Peiffer, *Bull. Soc. Chim. Fr.*, 3209 (1973); (c) L. Ernst, *Org. Magn. Reson.*, **9**, 35 (1977); (d) G. A. Gray and S. E. Cremer, *J. Chem. Soc., Chem. Commun.*, 451 (1974); (e) G. W. Buchanan and F. G. Morin, *Can. J. Chem.*, **55**, 2885 (1977); (f) T. A. Albright, W. J. Freeman, and E. E. Schweizer, *J. Am. Chem. Soc.*, **97**, 2946 (1975); (g) W. G. Bentrude and H. W. Tan, *ibid.*, **98**, 1850 (1976); (h) J. K. Crandall and S. A. Sojka, *ibid.*, **94**, 5084 (1972); (i) G. A. Gray and S. E. Cremer, *J. Org. Chem.*, **37**, 3470 (1972); (j) T. A. Albright, *Org. Magn. Reson.*, **8**, 489 (1976); (k) R.-M. Lequan, M.-J. Pouet, and M.-P. Simonnin, *J. Chem. Soc., Chem. Commun.*, 475 (1974).
(12) Such long-range effects of allene chirality on nuclear equivalence have been studied previously: R. S. Macomber, *J. Org. Chem.*, **36**, 999 (1971).
(13) E. D. Becker, "High Resolution NMR", Academic Press, New York, 1969.