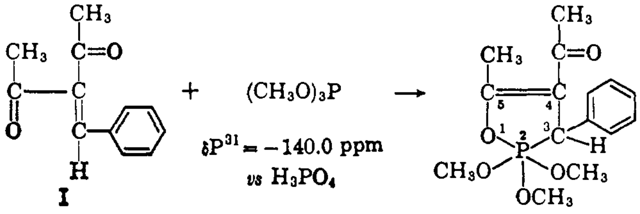
Stereoisomerism at Phosphorus in Cyclic Oxyphosphoranes. The Reaction of Phosphonite and Phosphinite Esters with 3-Benzylidene-2,4-pentanedione

Fausto Ramirez,[1] J. F. Pilot, O. P. Madan, and C. P. Smith

Contribution from the Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11790. Received October 6, 1967

Abstract: The reaction of 3-benzylidene-2,4-pentanedione with phosphonite esters, $(RO)_2PC_6H_5$, gave five-membered cyclic oxyphosphoranes, which are derivatives of the 2,2-dihydro-1,2-oxaphospholene-4 ring system. Each oxyphosphorane was obtained in two stereoisomeric forms which gave different values of the P^{31} nmr shifts in solution at 25°. Both values of the shift were positive relative to H_3PO_4. The study of the H^1 nmr spectra from -60 to $+151°$ suggested that the molecules had the geometry of trigonal bipyramids with the phospholene ring in an apical–equatorial plane. In one stereoisomer, the phenyl was attached to the phosphorus at an equatorial position and was *trans* to the phenyl attached to the phospholene ring. In the other stereoisomer, the two phenyls were in a *cis* relationship. In both isomers the alkoxy groups occupied an equatorial and an apical position. In the dimethyl phenylphosphonite derivative, rapid positional exchange among the methoxy groups occurred above 5°. Positional exchange involving the phenyl at phosphorus occurred above 52°. Rupture of the P–O bond of the phospholene ring was noted above $+70°$. At $+125°$, the structure was that of an open dipolar ion. The cyclic oxyphosphoranes derived from the reaction of phosphinite esters, $(RO)P(C_6H_5)_2$, with 3-benzylidene-2,4-pentanedione were obtained in only one form at $+25°$. It is suggested that the alkoxy group is in the apical position and the two phenyl rings are at equatorial positions in the trigonal bipyramid of the pentavalent phosphorus. Opening of the phospholene ring to a dipolar structure occurred at higher temperature.

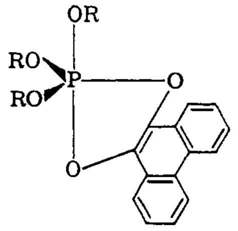
The first authentic derivative of the 2,2-dihydro-1,2-oxaphospholene-4 ring system,[2] II, was obtained from the reaction of 3-benzylidene-2,4-pentanedione, I (BPD), with trimethyl phosphite.[3,4] The pentacovalency of the phosphorus in adduct II was deduced from the positive value of the P^{31} nmr shift[3] relative to that of H_3PO_4.



I

II, $\delta P^{31} = +27.9$ ppm

No evidence for the molecular geometry of the oxyphosphorane II was available. However, the X-ray analyses[5] of related derivatives of the 2,2-dihydro-1,3,2-dioxaphospholene ring system, III and IV, showed that, in the crystalline state, the phosphorus was at the center of a nearly regular trigonal bipyramid with the phospholene ring in an apical–equatorial plane.[6] The P^{31} nmr shift in this type of oxyphosphorane was also positive.[7]



III, R = CH_3; $\delta P^{31} = +44.7$ ppm
IV, R = i-C_3H_7; $\delta P^{31} = +48.6$ ppm

The H^1 nmr spectrum of the 5-cyclic pentaoxyphosphoranes of types III and IV showed that the three alkoxy groups were magnetically equivalent at $+25°$; no significant change was noted[8] in the spectra at $-60°$. The three methoxy groups of the 5-cyclic tetraoxyalkylphosphorane II were also magnetically equivalent[3] at $+25°$. However, it was recently found[9] that the three methoxy groups of II became magnetically nonequivalent at $-65°$, as would be expected of a rigid trigonal bipyramid analogous to III.

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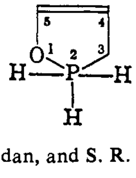
[2] The name 2,2-dihydro-1,2-oxaphospholene-4 for this ring system implies the pentacovalency of the phosphorus and is in accord with the nomenclature of *Chemical Abstracts*. In our previous paper, compound II was named 2,2,2-trimethoxy-3-phenyl-4-acetyl-5-methyl-Δ^4-oxaphospholene.



[3] F. Ramirez, O. P. Madan, and S. R. Heller, *J. Amer. Chem. Soc.*, **87**, 731 (1965).

[4] B. A. Arbuzov, T. D. Sorokina, N. P. Bogonosteva, and V. S. Vinogradov [*Dokl. Akad. Nauk SSSR*, 171, 605 (1966)] have recently and erroneously stated that: "the formation of intermediate cyclic unsaturated phosphoranes [from the reaction of α,β-unsaturated carbonyl compounds with trialkyl phosphites] has been postulated. They have not been isolated." In spite of this statement, the Russian authors included in their paper ref 3, where the crystalline phosphorane II was isolated and fully characterized.

[5] (a) W. C. Hamilton, S. J. LaPlaca, and F. Ramirez, *J. Amer. Chem. Soc.*, **87**, 127 (1965); (b) W. C. Hamilton, S. J. LaPlaca, F. Ramirez, and C. P. Smith, *ibid.*, **89**, 2268 (1967); (c) R. D. Sprately, W. C. Hamilton, and J. Ladell, *ibid.*, **89**, 2272 (1967).

[6] This geometry had been suggested by P. C. Haake and F. H. Westheimer [*ibid.*, **83**, 1102 (1961)] for the *transition states* of the acid-catalyzed hydrolysis of ethylene hydrogen phosphate and of the exchange of oxygen between the latter and the water solvent.

[7] For a review of this subject, see F. Ramirez, *Pure Appl. Chem.*, **9**, 337 (1964), and R. Ramirez, *Bull. Soc. Chim. Fr.*, 2443 (1966).

[8] (a) F. Ramirez and N. B. Desai, *J. Amer. Chem. Soc.*, **85**, 3252 (1963); (b) F. Ramirez, M. Nagabhushanam, and C. P. Smith, *Tetrahedron*, in press.

[9] (a) D. G. Gorenstein and F. H. Westheimer, *J. Amer. Chem. Soc.*, **89**, 2762 (1967); (b) F. Ramirez. *Trans. N. Y. Acad. Sci.*, in press.

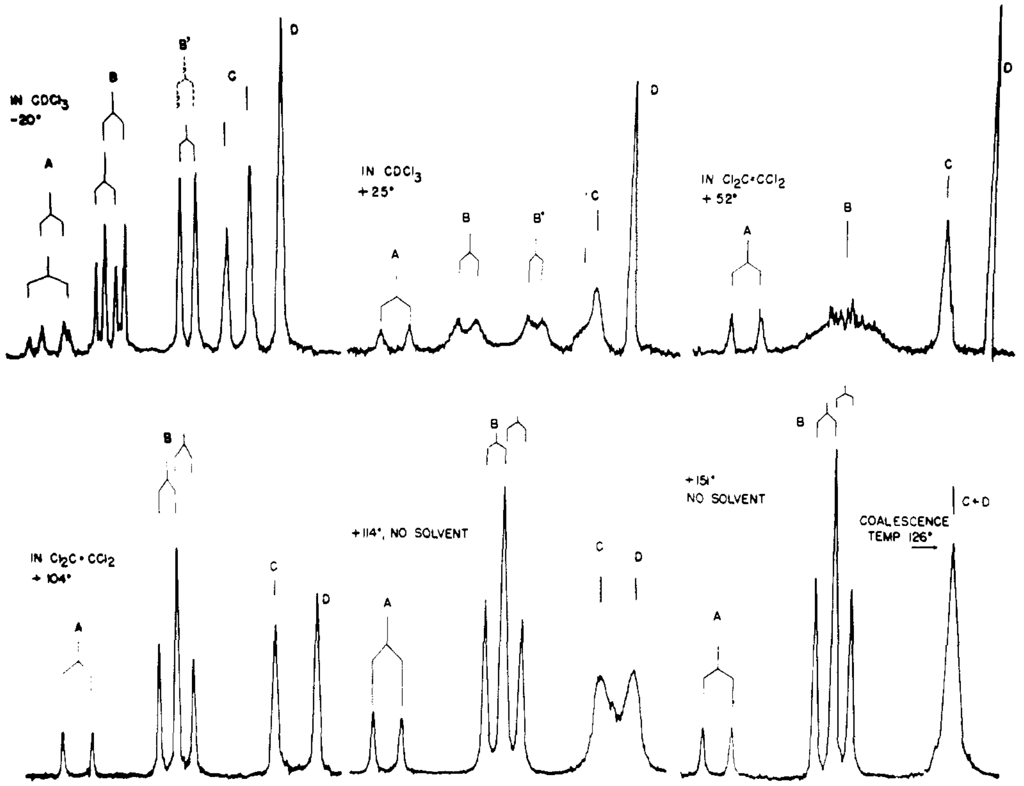
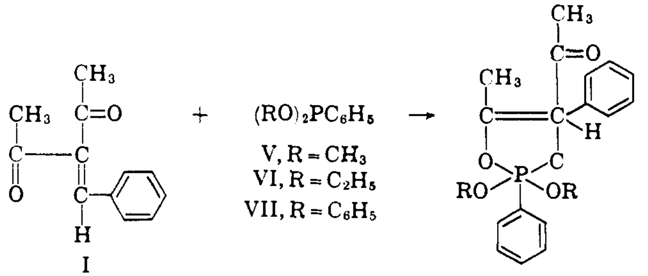


Figure 1. H^1 nmr spectrum of the adduct made from $(CH_3O)_2PC_6H_5$ and 3-benzylidene-2,4-pentanedione. In $CDCl_3$ at −20 and +25°. In $Cl_2C{=}CCl_2$ at +52 and +104°. In the melt without solvent at +114 and +151°.

Continuing our previous work,[3] we describe now the behavior of 3-benzylidene-2,4-pentanedione toward a series of phosphonite and phosphinite esters, $(RO)_2PC_6H_5$ and $(RO)P(C_6H_5)_2$.

Results

Reaction of the Phosphonite Esters with 3-Benzylidene-2,4-pentanedione. The α,β-unsaturated ketone I reacted with dimethyl phenylphosphonite (V) in methylene chloride solution at 20° to give a crystalline adduct, VIII, whose properties are summarized in Table I. The infrared spectrum was very similar to the spectrum of the adduct II previously made from trimethyl phosphite.[3]



I

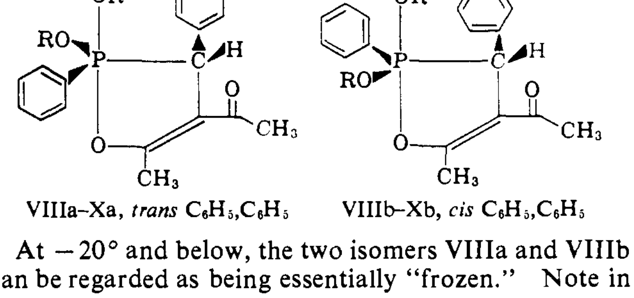
V, R = CH_3
VI, R = C_2H_5
VII, R = C_6H_5

VIII, R = CH_3
IX, R = C_2H_5
X, R = C_6H_5

The H^1 nmr spectrum at −20° is reproduced in Figure 1. The corresponding values for the chemical shifts and the coupling constants are given in Table II. The spectrum was very similar in the range of −60 to −10°. The H^1 nmr spectrum at +25° is also shown in Figure 1. This spectrum did not change significantly in the range of +25 to +10°.

The P^{31} nmr spectrum of a methylene chloride solution of the crystalline adduct VIII showed two signals at +25°. Both signals had positive shifts relative to H_3PO_4 as shown in Table III. The signal at higher magnetic field was approximately twice as intense as the signal at lower magnetic field; repeated recrystallizations did not affect the relative intensities of these signals.

These observations suggested that the oxyphosphorane VIII was capable of existing in solutions as two distinct stereoisomers at phosphorus. In both isomers, the phospholene ring occupies an apical–equatorial plane in a trigonal bipyramid, the phenyl ring attached to the phosphorus occupies an equatorial position, one methoxy group occupies an equatorial position, and the other an apical position. In one isomer, however, the phenyl at phosphorus and the phenyl on the phospholene are *trans* to each other as shown in formula VIIIa, while in the other isomer, the two phenyl rings are in a *cis* configuration as shown in formula VIIIb. For reasons indicated below, it is probable, but not certain, that the major isomer with the phosphorus shift at higher magnetic field has the *trans* C_6H_5,C_6H_5 configuration, VIIIa.



VIIIa–Xa, *trans* C_6H_5,C_6H_5 VIIIb–Xb, *cis* C_6H_5,C_6H_5

At −20° and below, the two isomers VIIIa and VIIIb can be regarded as being essentially "frozen." Note in

Table I. Analyses and Main Infrared Bands of the Adducts[a] Derived from the Reaction of 3-Benzylidene-2,4-pentanedione with Phosphonite and Phosphinite Esters, X_2YP

No.	X	Y	Mp, °C	Molecular formula	Calcd, %			Found, %			Yield, %	Ir bands,[b] μ
					C	H	P	C	H	P		
VIII	CH_3O	C_6H_5	105–107[c]	$C_{20}H_{23}O_4P$	67.0	6.4	8.7	66.9	6.6	8.5	84	*6.05*, *6.35* (sh), *6.42*, 7.32, 7.62, 8.16, 8.65, 9.00, 9.25, 9.60, 10.60
IX	C_2H_5O	C_6H_5	63–66[d]	$C_{22}H_{27}O_4P$	68.4	7.0	8.0	68.7	7.2	7.8	70	*6.05*, *6.35* (sh), *6.45*, 7.32, 7.62, 8.18, 8.65, 9.10, *9.35*, 9.60, 10.60, 10.80
X	C_6H_5O	C_6H_5	132–134[e]	$C_{30}H_{27}O_4P$	74.7	5.6	6.4	74.2	5.8		80	*6.03*, *6.28*, *6.40*, 6.70, 7.30, 7.60, 8.15, 8.30, 8.60, 9.00, 9.70, 10.55, 10.78, 11.50
XVI	C_6H_5	CH_3O	122–124[c]	$C_{25}H_{25}O_3P$[f]	74.3	6.2	7.7	74.0	6.2	7.8	90	*6.10*, *6.35* (sh), *6.45*, *6.50*, 6.60 (sh), 7.30, 7.60, 8.15, 8.40, 8.60, 9.00, *9.10* (sh), 9.60, 10.60
XVII	C_6H_5	C_2H_5O	169–173[e]	$C_{26}H_{27}O_3P$[g]	74.6	6.5	7.4	74.7	6.6	7.3	94	*6.08*, *6.35* (sh), *6.46*, 7.30, 7.60, 8.15, 8.40, 8.60, 9.00, 9.10, 9.55, 10.60, 10.88
XVIII	C_6H_5	C_6H_5O	182–187[h]	$C_{36}H_{27}O_3P$	77.3	5.8	6.7	77.3	5.9	6.5	92	*6.05*, *6.28*, *6.45*, *6.50*, 6.70, 7.30, 7.60, 8.15, 8.60, 9.00, 10.60, 11.60

[a] Derivatives of the ring system 3-phenyl-4-acetyl-5-methyl-2,2-dihydro-1,2-oxaphospholene-4, with substituents X and Y at position 2. [b] In CH_2Cl_2 solution; no significant changes in KBr pellet. [c] From benzene–hexane. [d] From hexane. [e] From CH_2Cl_2–C_6H_{14}. [f] Mol wt (thermoelectric in benzene) 383 (calcd 404). [g] Mol wt (thermoelectric in benzene) 388 (calcd 418). [h] From benzene.

Figure 1 the two doublets (protons A) due to the benzylic protons of isomers VIIIa and VIIIb; the signal at higher field is attributed to the *trans* isomer VIIIa. Note also the two doublets (protons B) attributed to the methoxy groups in equatorial positions in both isomers; again the signal at higher magnetic field is attributed to the *trans* isomer VIIIa. These configurational assignments are based on the assumption that the phenyl ring shields a neighboring proton more effectively than a hydrogen or a methoxy group. Hence, the signals due to the benzylic proton and the equatorial methoxy group in isomer VIIIa should be at higher magnetic field than the corresponding signals in isomer VIIIb, since the respective protons are adjacent to phenyl rings.

The methoxy groups in apical positions in the two isomers could not be resolved (see protons B′ in Figure 1). The two acetyl groups could be clearly distinguished in the two isomers (protons C); however, the protons of the methyl groups on the phospholene ring of the two isomers gave unresolvable signals (protons D).

In the temperature range of 0 to 5° the positional exchange[10] between the two methoxy groups on one isomer, VIIIa, become rapid relative to the time scale of the H^1 nmr phenomenon. The same was true for the two methoxy groups of isomer VIIIb. However, the phenyl ring attached to the phosphorus was not involved in this positional exchange. Note that at +25° the two doublets for the benzylic hydrogens (protons A) appeared as one doublet only; however, there were still two doublets due to magnetically nonequivalent methoxy protons (protons B and B′). Moreover, as mentioned above, there were two different P^{31} nmr signals at +25°. At this temperature, it was possible to distinguish two signals due to acetyl groups (protons C), although they were very close to each other.

The preference of the methoxy groups over the phenyl ring for an apical position as shown in formulas VIIIa and VIIIb is consistent with the views[11] that the higher the electronegativity of an atom[12] (oxygen, 3.5) the greater the tendency for it to occupy an apical position on a phosphorus trigonal bipyramid.[13] However, steric effects may also play a role here.[5]

In the neighborhood of +52°, the positional exchange of the phenyl rings and of the methoxy groups at phosphorus seems to become important. This exchange is reflected in the coalescence of the two doublets due to the methoxy groups and also in the coalescence of the singlets due to the two acetyl groups, as can be seen in Figure 1.

At approximately +70°, a new phenomenon was noted which gave rise to the type of spectrum more clearly seen at +104° (*cf.* Figure 1). It is suggested that in this temperature range there is an equilibrium between the cyclic oxyphosphorane II and an open dipolar structure XI. Note that there are now two doublets due to the methoxy groups in addition to signals due to the acetyl and methyl protons on the phos-

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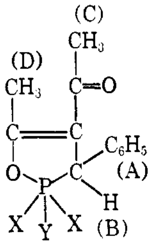
(10) The theoretical aspects of positional exchange in trigonal bipyramids have been discussed by: (a) R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960); (b) R. Schmutzler, *Angew. Chem. Intern. Ed. Engl.*, **3**, 753 (1964); (c) *ibid.*, **4**, 496 (1965); (d) E. L. Muetterties and R. A. Schumm, *Quart. Rev.* (London), **20**, 245 (1966); (e) K. W. Hansen and L. S. Bartell, *Inorg. Chem.*, **4**, 1775 (1965); (f) L. S. Bartell, *ibid.*, **5**, 1635 (1966); (g) E. A. Dennis and F. H. Westheimer, *J. Amer. Chem. Soc.*, **88**, 3432 (1966). See also L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965.

(11) (a) E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963); (b) E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *ibid.*, **3**, 1298 (1964); (c) R. R. Holmes, R. P. Carter, Jr., and G. E. Peterson, *ibid.*, **3**, 1748 (1964); (d) L. S. Bartell and K. W. Hansen, *ibid.*, **4**, 1777 (1965); (e) P. C. Van Der Voorn and R. S. Drago, *J. Amer. Chem. Soc.*, **88**, 3255 (1966).

(12) L. Pauling, "The Nature of a Chemical Bond," 2nd ed, Cornell University Press, Ithaca, N. Y., 1948, p 58.

(13) We have found definite evidence that pentavalent phosphorus compounds involving P–O bonds have greater stability than corresponding compounds with P–N bonds (N electronegativity, 3.0): *cf.* (a) F. Ramirez, A. V. Patwardhan, H. J. Kugler, and C. P. Smith, *J. Amer. Chem. Soc.*, **89**, 6276 (1967); (b) F. Ramirez, A. S. Gulati, and C. P. Smith, *ibid.*, **89**, 6283 (1967); (c) F. Ramirez, H. J. Kugler, and C. P. Smith, *Tetrahedron*, in press.

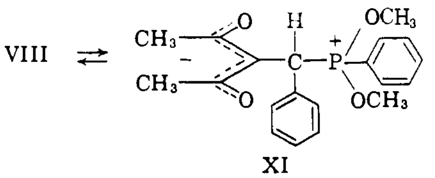
Table II. H^1 Nmr Signals of the Adducts from the Reaction of Phosphonite and Phosphinite Esters, X_2YP, with 3-Benzylidene-2,4-pentanedione in Solvents at Various Temperatures[a]



No.	X	Y	Solvent	Temp, °C	τ_H(A)	J_H(A)	τ_H(B)	J_H(B)	τ_H(B′)	J_H(B′)	τ_H(C)	τ_H(D)
VIII	CH_3O	C_6H_5	$CDCl_3$	-20^{b}	5.55	14.0	6.22	12.8	7.03^{c}	10.4	7.70	8.05^{c}
					5.50	26.0	6.10	13.6	7.03^{c}	10.4	7.43	8.05^{c}
			$CDCl_3$	$+25^{d}$	5.53^{e}	19.0	6.30	12.3	7.03	10.6	7.70^{f}	8.10
			$Cl_2C{=}CCl_2$	+52	5.60	19.0	Broad, over 60 cps at 6.6				7.80^{g}	8.30
			$Cl_2C{=}CCl_2$	+104	5.60	19.0	6.58	11.5	6.80	11.5	7.75^{g}	8.22
			None[h]	+114	5.41	19.0	6.60	12	6.80	12	7.74	8.11
			None	+151	5.42	19	6.56	11.6	6.73	11.8	7.94^{i}	
IX	C_2H_5O	C_6H_5	$CDCl_3$	−20	5.50	16.0	*j*	...	...	...	7.70	8.02^{c}
					5.48	26.0	*j*	...	...	...	7.45	8.02^{c}
			$CDCl_3$	$+25^{d}$	5.50^{e}	19	5.83	*k*	6.75	*k*	7.73^{f}	8.10^{l}
			$Cl_2C{=}CCl_2$	+70	5.58	19	Broad, over 60 cps at 6.2				7.75^{g}	8.20
			None	+110	5.41	19	6.15	*m*	6.40	*m*	Broad, 7.95	
			None	+130	5.44	19	6.15	*m*	6.40	*m*	7.97^{i}	
X	C_6H_5O	C_6H_5	$CDCl_3$	-25^{n}	5.17	13.5	None[o]	None	None	None	7.88	8.03
					4.88	28.4	None	None	None	None	8.10	8.03
			$CDCl_3$	+25	5.16^{p}	13.5	None	None	None	None	7.90	8.06^{c}
					4.92^{p}	28.4	None	None	None	None	8.12	8.06^{c}
			$CDCl_3$	+41	5.12^{q}	13	None	None	None	None	7.95^{r}	8.06^{c}
					4.96^{q}	28	None	None	None	None	8.11^{r}	8.06^{c}
			$CDCl_3$	+51	4.92	26	None	None	None	None	Broad, 8.05	
			DCB[s]	+130	4.94	25	None	None	None	None	8.03	8.08
XVI	C_6H_5	CH_3O	$CDCl_3$	+25	5.19	19.9	7.37	10.3	None[o]	None	7.73	8.06
			DCB	+100	5.10	19	7.32	10	None	None	7.00	8.05
			DCB	+120	5.10	19	7.32	10	None	None	7.90^{t}	
XVII	C_6H_5	C_2H_5O	$CDCl_3$	+25	5.19	20.0	7.30	*j*	None	None	7.78	8.05^{e}
			DCB	+100	5.05	19	7.20	*j*	None	None	7.75	8.03^{e}
			DCB	+125	5.05	19	7.20	...	None	None	7.90^{u}	
XVIII	C_6H_5	C_6H_5O	$CDCl_3$	+25	4.98	20.7	None[e]	None	None	None	7.66	8.05
			DCB	+99	4.80	21	None	None	None	None	7.65	8.05
			DCB	+137	4.80	21	None	None	None	None	7.65^{v}	8.05

[a] Measured at 60 Mcps; nmr measured in parts per million *vs.* TMS = 10 (τ values); J in cycles per second. The two values given for the phosphonite adducts at low temperatures correspond to the two stereoisomers of the trigonal-bipyramidal phosphorus. Upper values are due to isomer A; lower values are due to isomer B. [b] No changes down to −60°. [c] The signals due to the two stereoisomers could not be resolved; they were inferred from integrated relative intensities. [d] There were two stereoisomers at phosphorus at this temperature as shown by the ^{31}P nmr spectrum and by the existence of two different proton signals due to alkoxy groups (B, B′). [e] One detectable doublet only. [f] Also a poorly resolved singlet at τ 7.60. [g] Sharp singlet due to acetyl. [h] In the melt. [i] Sharp signal due to one kind of CH_3C group. [j] Complex CH_3CH_2OP region. [k] Complex signals. [l] In all derivatives of the ethyl esters there was an additional multiplet at *ca.* τ 9.00 due to CH_3CH_2OP. [m] Doublet of quartets, CH_3CH_2OP. [n] Same spectrum at −4°. In this case isomer A is the minor isomer. [o] Aromatic protons are not included. [p] Signals due to two benzylic protons (A) were observable at +25° in this case. [q] Signals were close to coalescence. [r] Signals close to coalescence and partly hidden under signal due to CH_3C (protons D). [s] *o*-Dichlorobenzene. [t] Signals due to CH_3CO and CH_3C (C, D) coalesced at about +127°; spectra similar at +130 and +150° but decomposition occurred. [u] Signals due to CH_3CO and CH_3C (C, D) coalesced at about +108°. Spectra similar at 150° but decomposition occurred. [v] Signals due to CH_3CO and CH_3C (C, D) coalesced at about 160°; there was considerable decomposition.

pholene ring.[14] The nature of this change became clearer from the spectra taken at higher temperature and shown in Figure 1. Note that as the temperature increases, the signals due to the acetyl and the methyls begin to coalesce and become a singlet. The coalescence temperature was at approximately +125°. At the highest temperatures investigated, we are observing the open dipolar structure XI exclusively. In this structure, the two methyl groups on carbon are magnetically equivalent, but the two methoxy groups on phosphorus are not.



XI

This interpretation was confirmed by the preparation of a crystalline adduct having the open dipolar structure XII from the reaction of dimethylphenylphosphine with 3-benzylidene-2,4-pentanedione.[15] In this case, the adduct existed as the dipolar form at +25° as shown by the negative value of the P^{31} nmr shift and by the H^1 nmr spectrum. The latter at +25° was strikingly similar to that of the phosphonite adduct XI at +151°.

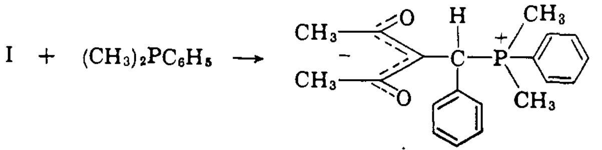
(14) The signal is not a triplet but the superposition of two doublets since the relative intensities are as 1:2:1 and not as 1:3:1.

(15) F. Ramirez, J. S. Pilot, and C. P. Smith, *Tetrahedron*, in press.

Table III. P^{31} Nmr Signals[a] of Phosphonite and Phosphinite Esters, X_2YP, and of Their Adducts[b] with 3-Benzylidene-2,4-pentanedione

No.	X	Y	δP^{31} of X_2YP	δP^{31} of adduct[c]
VIII	CH_3O	C_6H_5	−160.1	+16.7[d] +13.3
IX	C_2H_5O	C_6H_5	−153.6	+17.0[e] +15.0
X	C_6H_5O	C_6H_5	−157.9	+30.0[f] +24.8
XVI	C_6H_5	CH_3O	−115.9	+25.7
XVII	C_6H_5	C_2H_5O	−109.8	+26.3
XVIII	C_6H_5	C_6H_5O	−110.0	+40.1

[a] Measured at 40.5 Mcps; nmr in parts per million *vs.* H_3PO_4; in CH_2Cl_2 at +25°. [b] The original reaction mixtures and the corresponding isolated crystalline adducts had the same spectra. [c] The phosphonite adducts existed in two stereoisomeric forms of trigonal-bipyramidal phosphorus. [d] Signal intensities *ca.* 2:1, from high to low field. [e] Signal intensities *ca.* 1.5:1. [f] Signal intensities *ca.* 1:1.5.



XII, $\delta P^{31} = -10.9$ ppm

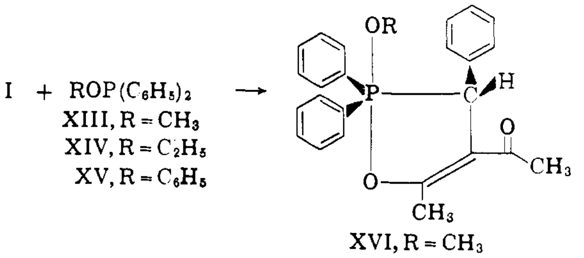
It was suggested earlier[8,16,17] that cyclic oxyphosphoranes could under certain conditions exist in equilibrium with open dipolar structures. This was recently demonstrated in the case of the cyclic triaminodioxyphosphoranes, where both forms, one with quintuply connected phosphorus and the other with quadruply connected phosphorus, were obtained in crystalline states.[18] Their equilibration in solution was demonstrated by P^{31} nmr and infrared spectrometry.

The changes in the H^1 nmr spectra illustrated in Figure 1 were found to be reversible although as expected irreversible changes began to occur at the higher temperatures.[19]

The reaction of diethyl phenylphosphonite (VI) with the unsaturated ketone I gave analogous results. The properties of the corresponding oxyphosphorane IX are listed in Table I. The H^1 and P^{31} nmr spectral data are given in Tables II and III, respectively. Note that there were two stereoisomers, IXa and IXb, at phosphorus at room temperature. The temperature at which the signals due to the protons of the acetyl and methyl groups attached to the phospholene ring coalesced into one signal was 15° lower in the ethyl derivative IX than in the methyl derivative VIII. This coalescence temperature is related to the formation of the open dipolar structure XI and of the corresponding ethyl analog and may reflect differences in the stability of the corresponding oxyphosphoranes.

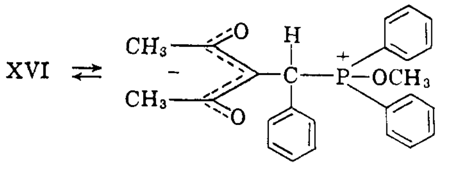
Diphenyl phenylphosphonite (VII) gave also an oxyphosphorane (X) from the reaction with 3-benzylidene-2,4-pentanedione. Data for this compound are shown in Tables I, II, and III. Note again the existence of two diastereomers at phosphorus, Xa and Xb. In this case it was possible to observe two doublets due to the benzylic protons (protons A) and two different acetyl signals in the H^1 nmr spectrum at +25°. This is the temperature at which two P^{31} nmr signals were observed, suggesting the presence of the two stereomers at phosphorus, Xa and Xb. At temperatures above +50°, only one doublet due to the benzylic protons was noted. At that temperature the signals due to the two acetyl groups (protons C) had coalesced and apparently appeared at the same position as the signal due to the methyl group on the phospholene ring (protons D).

Reaction of the Phosphinite Esters with 3-Benzylidene-2,4-pentanedione. Methyl diphenylphosphinite (XIII) reacted with the α,β-unsaturated ketone I and gave the corresponding oxyphosphorane XVI. The properties of this adduct and the spectral data are given in Tables I, II, and III. *In this case, the P^{31} nmr spectra showed the presence of only one phosphorus nucleus in the original reaction mixture and in solutions of the isolated compound.* The data suggest that this adduct existed in solution at +25° as a trigonal bipyramid with the lone methoxy group in an apical position, the two phenyl rings at equatorial positions, and the phospholene ring in an apical–equatorial plane as shown in formula XVI. Note in particular the relatively small coupling constant of the methoxy group in an apical position (J_{HP} = 10.3 cps).



XVI, R = CH_3
XVII, R = C_2H_5
XVIII, R = C_6H_5

At elevated temperatures, the phospholene ring of the phosphinite adduct XVI was broken at a P–O bond to give an open dipolar structure, XIX. In XIX there is



XIX

one type of methyl group attached to carbon. The temperature at which the signals due to the acetyl and the methyl protons (protons C and D) of the phosphorane XVI coalesced into one signal due to the methyl

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(16) (a) F. Ramirez and N. B. Desai, *J. Amer. Chem. Soc.*, **82**, 2652 (1960); (b) F. Ramirez, R. B. Mitra, and N. B. Desai, *ibid.*, **82**, 265 (1960); (c) *ibid.*, **82**, 5763 (1960); (d) F. Ramirez, S. B. Bhatia, R. B. Mitra, Z. Hamlet, and N. B. Desai, *ibid.*, **86**, 4394 (1964).

(17) V. A. Kukhtin, K. M. Kirillova, R. Shagidullin, Yu. Yu. Samilov, N. A. Lyazine, and N. F. Rakova, *J. Gen. Chem. USSR*, **32**, 2300 (1962).

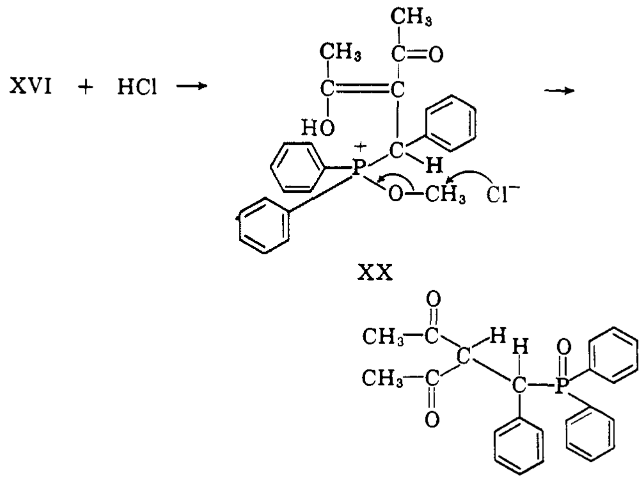
(18) F. Ramirez, A. V. Patwardhan, H. J. Kugler, and S. P. Smith, *Tetrahedron Letters*, 3053 (1966).

(19) After this investigation had been completed, and the results submitted to this journal, an article by D. G. Gorenstein and F. H. Westheimer appeared in *Proc. Nat. Acad. Sci. U. S.*, **58**, 1747 (1967). These authors described the ^1H nmr spectrum of the adduct made from 3-benzylidene-2,4-pentanedione and dimethyl phenylphosphonite at various temperatures. In general, their conclusions are similar to ours. We acknowledge having been informed by Dr. F. Westheimer of his findings, after submission of his article to the *Proceedings of the National Academy of Sciences* and before the appearance of the article in that journal.

groups of the dipolar structure XIX was approximately 127° in *o*-dichlorobenzene solution.

Ethyl diphenylphosphinite (XIV) gave the corresponding oxyphosphorane XVII. The data are given in Tables I, II, and III. The temperature at which the signals due to the acetyl and the methyl groups on the phospholene ring coalesced to one signal was approximately 20° lower in the case of the ethyl compound XVII than the methyl compound XVII.

The oxyphosphorane XVIII derived from phenyl diphenylphosphinite (XV) is described in the tables. The temperature for the coalescence of the signals due to the acetyl and the methyl protons was at *ca.* 160° in *o*-dichlorobenzene.



XX

XXI, δP^{31} = 31.0 ppm

Although the opening of the ring of derivatives of the 2,2-dihydro-1,2-oxaphospholene-4 heterocycles, II, VIII–X, XVI–XVIII, occurred at relatively high temperatures, the rupture of the ring was extremely rapid under the influence of acids. For example, anhydrous hydrogen chloride converted the phosphinite adduct XVI into the phosphine oxide XXI at low temperatures. The likely intermediate in this reaction is the oxyphosphonium chloride XX.

Experimental Section

The analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

Reactions of the Phosphonite and Phosphinite Esters with 3-Benzylidene-2,4-pentanedione. The reactions were carried out by mixing equimolar amounts of the reagents in methylene chloride solution at 20° under anhydrous conditions. The solutions were stirred at room temperature for approximately 12 hr. The solvent was removed under reduced pressure. The residue was analyzed by infrared and by ^1H and ^{31}P nmr spectrometry. The residues were treated with hexane at 0° to achieve crystallization. The analytical samples were obtained by recrystallization from the solvent indicated in Table I. The elemental analyses are given in Table I.

Reaction of the Methyl Diphenylphosphinite–3-Benzylidene-2,4-pentanedione Adduct XVI with Hydrogen Chloride. The phosphorane XVI (3.0 g) in CH_2Cl_2 (20 ml) was treated with anhydrous hydrogen chloride at 20° for 3 min. The solution was treated with ether (50 ml) and the solid (1.3 g, mp 182–184°) was recrystallized from methylene chloride–ether.

Anal. Calcd for $C_{24}H_{23}O_3P$: C, 73.9; H, 5.9; P, 7.9. Found: C, 74.0; H, 6.2; P, 7.9.

The infrared spectrum in CH_2Cl_2 had bands at (μ) 5.88 with shoulder at 5.80, 7.00, 7.40, 8.42, and 8.95. The H^1 nmr spectrum had signals at τ 7.91 and 8.20 due to the two acetyl groups which are magnetically nonequivalent.

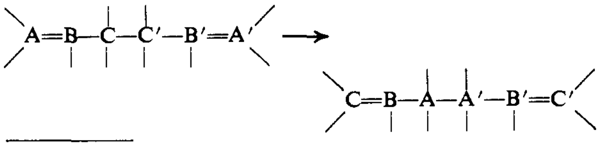
Calculated Energies and Geometries along the Reaction Path in Cope Rearrangements

Massimo Simonetta, Giorgio Favini,[1] Carla Mariani, and Paole Gramaccioni[2]

Contribution from the Institute of Physical Chemistry, University of Milan, Milan, Italy. *Received September 13, 1967*

Abstract: A modification and extension of the Westheimer approach have been used to calculate the geometry and energy of cyclopropane, cyclobutane, hexa-1,5-diene, *cis*-1,2-divinylcyclopropane, *cis*-1,2-divinylcyclobutane, *cis,cis*-cyclohepta-1,4-diene, and *cis,cis*-cycloocta-1,5-diene. The geometrical and energetic changes during the pertinent Cope rearrangements were calculated as a function of the degree of advancement of the reaction and reasonable agreement with experiment was found.

The Cope reaction, discovered a long time ago,[3] is a thermal rearrangement that obtains in diallylic systems (eq 1). Experimental results have been extensively reviewed[4] and lead to the following conclusions. The reaction is insensitive to external catalytic influence (including solvent) and follows first-order kinetics. The intramolecular course is demonstrated by the fact that during the rearrangement of a mixture of two diallylic compounds of comparable rates of reaction no exchange of allyl groups is observed. The considerably negative values of the activation entropy (of the order of −12 eu) measured for several Cope rearrange-


$$\mathrm{A{=}B{-}C{-}C'{-}B'{=}A'} \longrightarrow \mathrm{C{=}B{-}A{-}A'{-}B'{=}C'} \qquad (1)$$

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[1] Institute of Physical Chemistry, University of Catania, Catania, Italy.

[2] Department of Physics, Catholic University Medical School, Rome, Italy.

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[4] (a) E. Vogel, *Angew. Chem. Intern. Ed. Engl.*, 2, 1 (1963); (b) S. J. Rhoads in "Molecular Rearrangement," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 655; (c) W. von E. Doering and W. R. Roth, *Angew. Chem. Intern. Ed. Engl.*, 2, 115 (1963).