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COMPOUNDS WITH PENTAVALENT PHOSPHORUS AND WITH TETRAVALENT PHOSPHORUS FROM THE REACTIONS OF TRIVALENT PHOSPHORUS COMPOUNDS WITH α,β-UNSATURATED KETONES

DIPOLAR IONS FROM THE REACTIONS OF TERTIARY PHOSPHINES WITH 3-BENZYLIDENE-2,4-PENTANEDIONE

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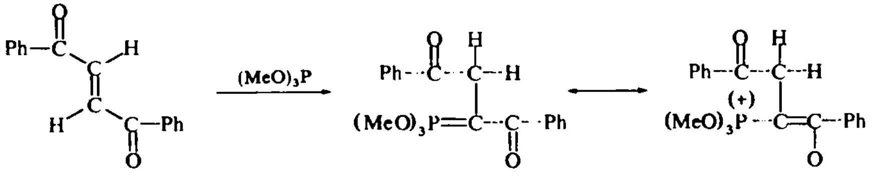
Abstract—The phosphorus of trialkyl phosphines, R_3P, and dialkylarylphosphines, R_2PhP, added to the β-carbon of the α,β-unsaturated ketone, 3-benzylidine-2,4-pentanedione. The crystalline 1:1 adducts had the structure of open dipolar ions with tetravalent phosphorus. These gave negative ^{31}P NMR shifts relative to H_3PO_4. The 1:1 adducts made from the reactions of the same unsaturated ketone with phosphite, phosphonite, and phosphinite esters, $(RO)_3P$, $(RO)_2PhP$, $(RO)Ph_2P$, had the structure of 5-membered cyclic oxyphosphoranes with pentavalent phosphorus. These gave positive ^{31}P NMR shifts. These differences are attributed mainly to the higher electronegativity of oxygen than of carbon, which tends to favor the pentacovalent state of the phosphorus. The operation of steric effects is indicated by the relative instability of the adducts made from dialkylaryl-phosphines and triaryl phosphines, which tend to dissociate into the tertiary phosphine and the unsaturated ketone.

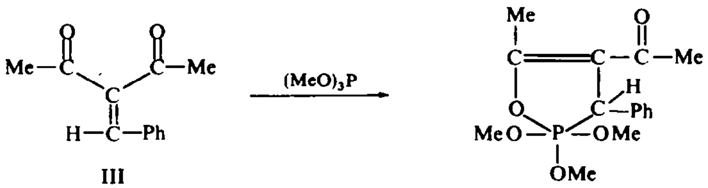
INTRODUCTION

The structure of the products from the reaction of α,β-unsaturated ketones with trivalent phosphorus compounds depend critically on the structure of the ketone. For example, the reaction of *trans*-dibenzoylethylene,[1] I, with trimethyl phosphite



I

II: $\delta P^{31} = -56\cdot2$ ppm



III

IV: $\delta P^{31} = +27\cdot9$ ppm

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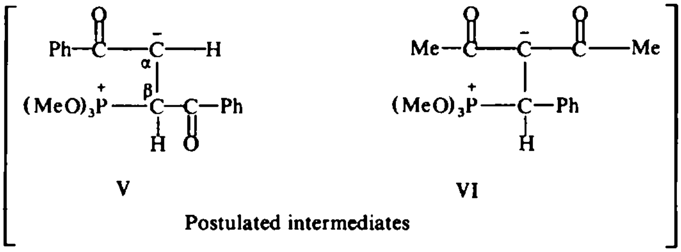
gave a phosphitemethylene or phosphorus ylide, II, while the reaction of 3-benzylidene-2,4-pentanedione,[2] III, with the same phosphite gave a cyclic oxyphosphorane, IV.

The formation of these products, II and IV, can be explained as an addition of the phosphorus to the β-carbon of the unsaturated ketone leading to dipolar ions like V and VI. In one case, a proton adjacent to a phosphonium group migrated to an α-carbon to give a new anion, II, which was more stable than the original one, V. In the other case, there was no proton migration, and the dipolar ion, VI, cyclized to the oxyphosphorane, IV.

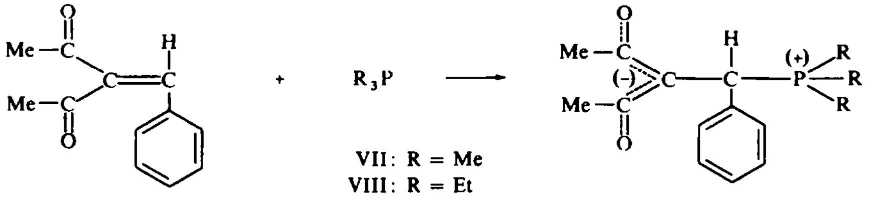

V VI

Postulated intermediates

The nature of the trivalent phosphorus compound could also affect the structure of the adducts with α,β-unsaturated ketones. For example, the electronegativity[3] of the groups X attached to P in X_3P could affect the mobility of the proton adjacent to the phosphonium group in the dipolar ions, V and VI. More importantly, the electronegativity of the atoms attached to the phosphorus may affect the tendency of a phosphorus to become pentavalent.[4] We have already shown that phosphinite esters, trialkyl phosphines, and triaminophosphines reacted with *trans*-dibenzoylethylene[1] to give phosphorus ylides analogous to those made from trialkyl phosphites. The purpose of the present investigation was to examine the behavior of the trialkyl phosphines and of the triaryl phosphines toward 3-benzylidene-2,4-pentanedione.

RESULTS

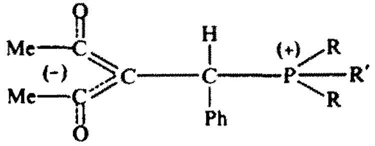
Trialkylphosphines. Trimethylphosphine, VII, reacted with 3-benzylidene-2,4-pentanedione, III, in methylene chloride at 0° and gave a crystalline 1:1 adduct which is formulated as the open dipolar ion, IX. The experimental data supporting this structure are given in Tables 1 and 2.



III

IX: R = Me
X: R = Et

TABLE 1. ANALYSES AND MAIN INFRARED BANDS OF THE ADDUCTS DERIVED FROM THE REACTION OF 3-BENZYLIDENE-2,4-PENTANEDIONE WITH ALKYL AND ARYL PHOSPHINES, $R_2R'P$



No.	R	R′	m.p.°	Mol. Formula	Calc. C	Calc. H	Calc. P	Found C	Found H	Found P	Yield %	IR bands,[a] μ
VII	Me	Me	143–146[b]	$C_{15}H_{21}O_2P$[c]	68·2	8·0	11·7	68·2	8·2	11·8	76	$\underline{6{\cdot}80}$, 7·30 10·30, 10·45
VIII	Et	Et	117–126[d]	$C_{18}H_{27}O_2P$[e]	70·6	8·8	10·1	70·9	9·0	10·0	80	$\underline{6{\cdot}80}$, 7·30, 9·60, 10·55
XII	Me	Ph	163–166[b]	$C_{20}H_{23}O_2P$	73·6	7·1	9·5	73·7	7·2	9·3	95	$\underline{6{\cdot}80}$, 7·20, 7·35, 10·55
XIII	Et	Ph	110–112[f]	$C_{22}H_{27}O_2P$	74·6	7·6	8·8	74·7	7·8		95	$\underline{6{\cdot}80}$, 7·20, 7·35, 10·55

[a] In CH_2Cl_2 solution and in KBr pellets. When the adducts underwent dissociation in solns as indicated, the expected differences in the IR spectra were noted.

[b] From benzene.

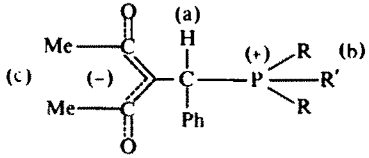
[c] Mol. wt, Calc. 264; Found, 277 (thermoelectric in CH_2Br_2).

[d] From benzene–hexane; the broad m.p. is attributed to thermal decomposition.

[e] Mol. wt, Calc. 306; Found, 304 (thermoelectric in acetonitrile).

[f] From CH_2Cl_2–hexane.

TABLE 2. NMR DATA[a] FOR THE ADDUCTS DERIVED FROM THE REACTION OF 3-BENZYLIDENE-2,4-PENTANEDIONE WITH ALKYL AND ARYL PHOSPHINES, $R_2R'P$



No.	R	R'	δP^{31} of $R_2R'P$	δP^{31} of adduct	^{1}H NMR signals[b] $\tau H^{(a)}$	$J_{H(a)P}$	$\tau H^{(b)}$	$J_{H(b)P}$	$\tau H^{(b')}$	$J_{H(b')P}$	$\tau H^{(c)}$
VII	Me	Me	+62·0	−10·9	5·45	12·4	8·47	12·4	none	none	7·73
VIII	Et	Et	+19·1	−32·5	4·93	14·3	8·0[c] 9·00[d]	... 17·1	none	none	7·71
XII	Me	Ph	+46·0	−8·1	4·90	12·2	8·08	13·0	8·23	11·5	7·78[e]
XIII	Et	Ph	+17·0	−26·3	4·58	13·5	7·8[f] 9·0	... ...	...[f]	...[f]	7·80

[a] ^{31}P NMR in ppm vs H_3PO_4; in CH_2Cl_2 at 25° and 40·5 Mc/s ^{1}H NMR in ppm vs TMS = 10 (τ values); in $CDCl_3$ at 25° and 60 Mc/s. J in c/s.

[b] When $R \neq R'$, the two R groups are magnetically non-equivalent; protons b and b' refer to these groups, respectively. The two methyls attached to carbon are equivalent. Aromatic protons are not included. The integrated intensities of the signals were as expected from the given structure.

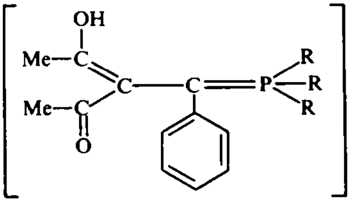
[c] Multiplet due to three CH_3CH_2P groups.

[d] Doublet J_{HP} = 17·1 c/s of triplets, J_{HH} = 7·0 c/s due to three $CH_3\underline{CH_2}P$ groups.

[e] This signal showed a long-range coupling of 0·7 c/s.

[f] The signals due to the CH_3CH_2P groups were complex.

The IR spectrum of the dipolar ion, IX, was significantly different from that of the oxyphosphorane,[2] IV, made from trimethyl phosphite. The spectrum of the ion had a strong and broad band at 6·80 μ which is attributed to the stretching frequency of the C—O bond of an enolate carbonyl function. The spectrum lacked absorption in the region 5·6 to 6·4 μ and any other feature that would correspond to the keto or enol forms of a phosphinemethylene or phosphorus ylide such as XI.



XI: Not observed

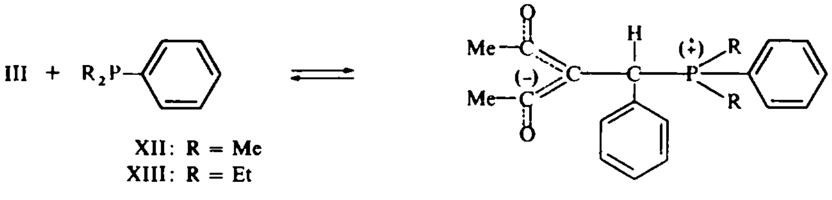
The ^{31}P NMR shift given in Table 2 also rules out the oxyphosphorane structure analogous to IV, and the phosphine–methylene structure, XI. The former should give a shift at significantly higher magnetic field,[2, 5] while the latter should give a shift at a lower magnetic field.[1d] The ^{1}H NMR spectrum summarized in Table 1 also establishes a dipolar structure IX. Note that the benzylic proton gave a relatively large coupling with the phosphorus; the signal due to this proton did not correspond to that expected of the enol or keto forms of the phosphinemethylene, XI. The two Me's attached to the carbon gave a 6 H^1 singlet in agreement with structure IX. Likewise, the three Me's attached to the phosphorus gave one doublet only; this would be expected of the three equivalent Me groups of IX which are coupled with the phosphorus.

The behavior of triethylphosphine, VIII, toward 3-benzylidene-2,4-pentanedione, III, was very similar. The properties of the crystalline dipolar ion, X, are given in Tables 1 and 2. In particular, a comparison of the IR and the ^{1}H NMR spectra with those of the Me-adduct, IX, disclosed the structural analogy. Note that the ^{31}P NMR shift of the Et-adduct, X, is now in the range of the shifts of phosphinemethylenes, and this datum alone would not have served to exclude the ylide structure,[1d] XI.

The crystalline, analytically pure, Et-adduct, X, gave a rather broad m.p., which suggested a decomposition near the melting temperature. However, there was no indication of dissociation of the dipolar ions IX and X into the phosphine and the unsaturated ketone in solutions at 20°.

Dialkylarylphosphines. Dimethylphenylphosphine, XII, gave a crystalline dipolar ion, XIV, with 3-benzylidene-2,4-pentanedione, III. The properties are given in Tables 1 and 2. Note that the ^{31}P NMR shift is clearly outside the range to be expected of a phosphorus ylide[1d] and of an oxyphosphorane.[5]

The ^{1}H NMR of the adduct XIV at room temperature showed that the two Me groups attached to the carbon were equivalent as in previous cases, but now each of the two Me groups attached to the phosphorus gave a doublet.



XII: R = Me
XIII: R = Et

XIV: R = Me
XV: R = Et

The ^1H NMR was also examined at −20° and at −40°. In both cases there were no significant changes in the signals due to the Me groups attached to the carbon or to the phosphorus. This showed that no cyclization of the dipolar ion to an oxyphosphorane analogous to IV was occurring in this temperature range. The doublet due to the benzylic protons broadened significantly at the lower temperatures.

The ^1H NMR spectrum at −60° showed again a sharp doublet due to the benzylic proton and further changes which were not interpretable at this time.

An examination of the IR and of the NMR spectra of methylene chloride solutions of the dipolar ion XIV showed significant dissociation of the adduct into the starting materials, namely, the phosphine XII and the unsaturated ketone, III, at room temperature.

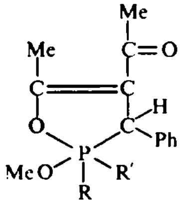
Diethylphenylphosphine, XIII, reacted with 3-benzylidene-2,4-pentanedione, III, and gave the corresponding dipolar ion, XV. The properties are listed in Tables 1 and 2. Again there was evidence for significant dissociation of the adduct into the starting materials.

No crystalline adduct could be obtained from the reaction of triphenylphosphine with the α,β-unsaturated ketone, III.

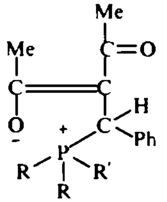
DISCUSSION

This investigation provided the first demonstration of the existence, as finite intermediates, of open dipolar ions in the additions of trivalent phosphorus compounds to α,β-unsaturated ketones. These intermediates, for example V and VI, had previously been postulated[1,2] but had not been detected experimentally.

An important result of this investigation is the finding that a quadruply-connected phosphorus has a tendency to combine with an O atom to form an oxyphosphorane provided that at least one of the four groups already attached to the phosphorus is an O atom. This conclusion is evident from the results of the addition of phosphite,



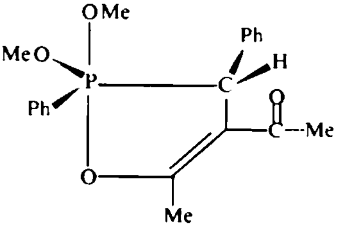
IV: R = R′ = OMe
XVI: R = OMe, R′ = Ph
XVII: R = R′ = Ph



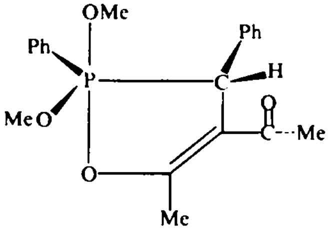
IX: R = R′ = Me
XIV: R = Me, R′ = Ph

phosphonite, and phosphinite esters and of tertiary phosphines to 3-benzylidene-2,4-pentanedione, as illustrated in formulas IV, XVI, and XVII, and IX and XIV. These differences are presumably related to the increased tendency for the formation of pentacovalent phosphorus when groups with high electronegativity[3,*] are bonded to the phosphorus.[4] This question is intimately related to the molecular geometry associated with the pentacovalent state of the phosphorus as discussed below.

The isolation of dipolar ions IX, X, XIV, and XV provided experimental verification for a suggestion recently made[6] concerning the ^{1}H NMR spectrum of the oxyphosphoranes XVI and XVII, in the temperature range of −60° to +150°. It was observed[6] that the reaction of 3-benzylidene-2,4-pentanedione, III, with dimethyl phenylphosphonite, $(MeO)_2PhP$, gave two diastereomeric phosphoranes, XVIa and XVIb, *which existed as different molecular entities in solutions at* +25°. Structures XVIa and XVIb were proposed for these diastereomers. In one of them, the phenyl groups attached to the phosphorus and to the carbon were *trans* to each other, and in the other, these groups were *cis* to each other. The two isomers gave different ^{31}P NMR shifts.

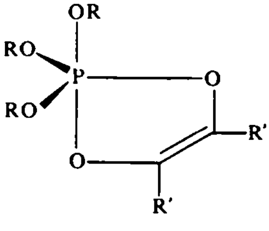


XVIa: $\delta P^{31} = +16{\cdot}7$ ppm

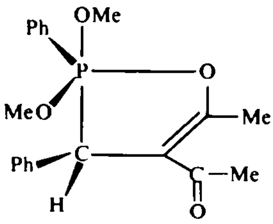


XVIb: $\delta P^{31} = +13{\cdot}3$ ppm

The oxyphosphoranes XVIa and XVIb were written[6] as trigonal bipyramids with the 1,2-oxaphospholene-4 ring system in an apical equatorial plane by analogy with the geometry of a related 1,3,2-dioxaphospholene ring system, XVIII, which had been elucidated by X-ray crystallographic analysis.[7,†] The oxygen atom of the 1,2-oxaphospholene-4 ring in XVIa and XVIb was placed in the apical position and the C atom of the ring in the equatorial position following previous suggestions to the effect that groups having greater electronegativity tend to occupy apical positions in trigonal bipyramidal phosphorus.[4]



XVIII



XVIc

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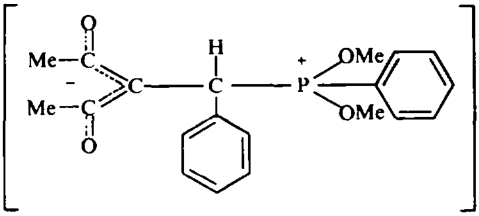
[*] In Pauling's electronegativity scale, 0 = 3,5 and C = 2·5; cf. Ref. 3.

[†] The X-ray analysis of the 1,3,2-dioxaphospholene XVIII provided the first experimental proof for the pentacovalency of the phosphorus in an oxyphosphorane which until then had been based on NMR and IR spectrometry; cf. Ref. 5.

The ^1H NMR spectrum of a solution containing both oxyphosphoranes,* XVIa and XVIb, at −60° showed that these molecules were essentially "frozen" relative to the time scale of the NMR phenomenon. In the temperature range of approximately 0° to +40°, positional exchange among the methoxy groups[5,8] in apical and equatorial positions was detected in the ^1H NMR spectrum. However, the Ph ring was not involved since there was no equilibration between isomers XVIa and XVIb in that temperature range. The positional exchange among the two methoxy groups of each isomer is presumably accomplished by the pseudo-rotation mechanism suggested by Berry[9] and subsequently discussed by several authors.[4h,4k,4n,10,11] One pseudo-rotation of the trigonal bipyramid XVIa about the P—Ph bond as "pivot" would give trigonal bipyramid XVIc in which the methoxy groups have exchanged positions.† Note that in the new bipyramid, XVIc, the Ph ring remained in an equatorial position but the C atom of the phospholene ring is in an apical position. The reluctance of the low electronegative carbon[3] to occupy an apical position[4] should make the trigonal bipyramid XVIc relatively unstable, compared with the bipyramids XVIa and XVIb. *Note Added in Proof.* The available evidence suggests that an important factor in determining the difference in energy between trigonal bipyramids like XVIa and XVIc, and the barrier to the pseudorotation, is the steric interaction among the two groups attached to the ring-carbon and the groups attached to the phosphomer. Note that in the latter two both apical positions are occupied by O atoms. This situation may explain why the rapid positional exchange among the OMe groups did not occur until the relatively high temperature of 0°.

At temperatures above +50°, the Ph ring appeared to be involved in the positional exchange. An equilibration of trigonal bipyramids XVIa and XVIb was noted. This equilibration without bond rupture can be achieved by four successive pseudo-rotations. ‡

Above 70° rupture of the P—O bond of the 1,2-oxaphospholene-4 ring system began to occur, giving rise to an equilibrium between the oxyphosphoranes XVIa



XIX: Postulated

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* Both stereomeric phosphoranes XVIa and XVIb were obtained as a mixture in the crystalline state. They could not be separated by conventional fractional crystallization procedures.

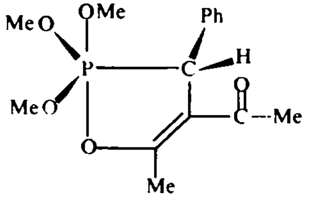
† To convert trigonal bipyramid XVIa into XVIc by pseudo-rotation, the following operations are performed: (1) select the phenyl attached to the phosphorus as the "pivot atom", which defines the bond joining the phosphorus and the phenyl as the "pivot axis"; (2) push back the two groups in the apical positions and pull forward the two groups in the equatorial positions (other than the pivot atom); (3) the resulting trigonal bipyramid is rotated around the pivot axis 90° counterclockwise; (4) the trigonal bipyramid is turned up-side-down to give the new trigonal bipyramid, XVIc.

‡ Note that the first pseudo-rotation of XVIa about the P—Ph bond as pivot axis gave XVIc. A second pseudo-rotation of XVIc about the P—OMe (equatorial) as pivot axis would give a new trigonal bipyramid with the phospholene-carbon in an equatorial position, a Ph ring in an apical position, and the two OMe groups in equatorial positions. Two more rotations lead to trigonal bipyramid XVIb.

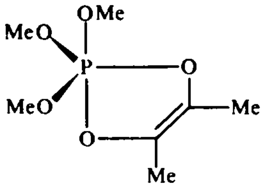
and XVIb on the one hand, and the open dipolar ion, XIX, on the other hand. At 150°, apparently the adduct existed exclusively as the open dipolar ion, XIX.

This description of the changes in molecular geometry of the oxyphosphorane XVI deduced from the ^{31}P NMR spectrum at 25° and from the ^{1}H NMR spectrum[6] in the region of $-60°$ to $+150°$ was strikingly confirmed in the present investigation. *It was found that the* ^{1}H *NMR spectrum of the phosphine adducts,* IX, X, XIV, *and* XV, *at* 25° *and of the phosphonite adduct,* XVI, *at* $+150°$, i.e. *of the dipolar ion* XIX, *were entirely analogous.* In both cases there was only a singlet at very similar magnetic field due to the six protons of the two equivalent Me groups attached to the carbon. In both cases, there were two doublets due to the non-equivalent groups attached to phosphorus, i.e. methoxy groups in XIX and Me groups in XIV.

The three OMe groups of the trimethyl phosphite-3-benzylidene-2,4-pentanedione adduct, IV, were magnetically equivalent at 25° since under these conditions they gave only one doublet in the ^{1}H NMR spectrum.[2] However, it was recently shown[12] that at $-65°$, the three OMe's of this same compound IV became magnetically equivalent and gave rise to three doublets as expected from the trigonal bipyramidal structure, IV. These authors[12] explained their observations in terms of the same pseudo-rotation mechanism discussed above.[4h, 4k, 4n, 9, 10, 11] It should be noted that the three OMe groups of the trimethyl phosphite–biacetyl adduct, XX, were magnetically equivalent[5, 8, 13] in solution *not only at* 30° *but also at* $-60°$. In this case, the pseudo-rotation was much easier than in the case of the benzylidene adduct, IV, presumably because the pseudo-rotation* places only O atoms in apical positions in the case of XX.†



IV



XX

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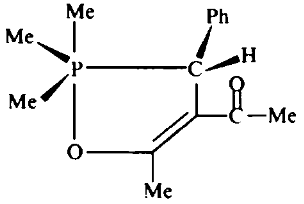
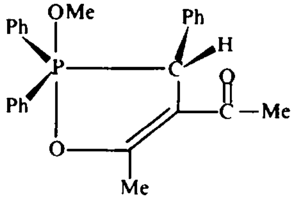
* It is possible to effect positional exchange by pseudo-rotation in the tetraoxyphosphorane without placing a carbon in an apical position. This involves pseudo-rotation about the P—C bond in the phospholene ring. However, the process requires the expansion of the C—P—O ring angle from 90° to 100° and probably also represents a hinderance to the pseudo-rotation.

† After our investigation on the addition of trivalent phosphorus compounds to 3-benzylidene-2,4-pentanedione had been completed, and the results submitted for publication, an article by Gorenstein and Westheimer appeared in the October issue of Proceedings of the National Academy of Sciences; cf. Reference 14. In this preliminary Communication, the authors described the ^{1}H NMR spectrum of the adduct made from the addition of dimethyl phenylphosphonite to 3-benzylidene-2,4-pentanedione, at various temperatures. In general, their conclusions in this particular system are similar to ours. We acknowledge having been informed by Dr. F. Westheimer of Harvard University 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. Our observation of two diastereoisomeric oxyphosphoranes, XVIa and XVIb, of the 3-benzylidene-2,4-pentanedione-dimethyl phenylphosphonite adduct was first made on January 21, 1966, when the ^{31}P NMR spectrum of that adduct was recorded. (Spectrum No. 1258, NMR Laboratory, Department of Chemistry, State University of New York, Stony Brook).

It becomes clear now why the adducts derived from the reaction of tertiary phosphines with 3-benzylidene-2,4-pentanedione do not cyclize to oxyphosphoranes but remain as open dipolar ions, IX, X, XIV, and XV. *Note that this cyclization would require the placement of the low electronegative carbon in an apical position as shown in formula* XXI. Apparently, this type of structure is unstable relative to the open form with tetravalent phosphorus. In contrast, the product of the reaction of methyl diphenylphosphinite with the same unsaturated ketone was a stable phosphorane, XXII, in which the OMe group was in the apical position and the two phenyls and the phospholene carbon were in equatorial positions. *This structure was "frozen" in this configuration in solution at* 25° *in the time scale of the* ^{1}H *NMR*.[6]



XXI: Not observed



XXII: Observed. "Frozen" in solution at 25°

EXPERIMENTAL

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

Reaction of trialkylphosphines and of dialkylarylphosphines with 3-*benzylidene*-2,4-*pentanedione*

The reactions were carried out by mixing equimolar amounts of the reagents in CH_2Cl_2 solns at 0° under anhydrous conditions. The solns were stirred at 20° for approximately 3–5 hr. The solvent was removed under reduced press, and the solid adduct was recrystallized from the solvents indicated in Table 1. The elemental analyses and the spectral properties are given in Tables 1 and 2.

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