Tetrahedron, 1966, Vol. 22, pp. 567 to 582. Pergamon Press Ltd. Printed in Northern Ireland

REACTION OF TRIVALENT PHOSPHORUS COMPOUNDS WITH α,β-UNSATURATED KETONES

REACTION OF AMINO, ALKYL AND ARYL PHOSPHINES WITH *trans*-DIBENZOYLETHYLENE ^{31}P NUCLEAR MAGNETIC RESONANCE[1]

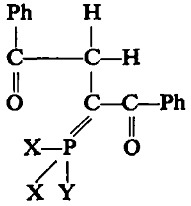
F. Ramirez,[2] O. P. Madan and C. P. Smith
Department of Chemistry of the State University of New York at
Stony Brook, L.I., N.Y.

(*Received* 9 *July* 1965)

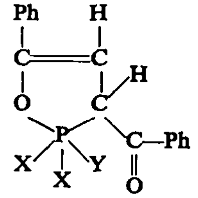
Abstract—Crystalline *β-ketoylides*, $X_2YP{=}C(CO{\cdot}C_6H_5)(CH_2{\cdot}CO{\cdot}C_6H_5)$, were prepared from the reaction of *trans*-dibenzoylethylene with amino, alkyl, and aryl phosphines. The ylides gave *enol-ether salts* with benzyl bromide, and *diketophosphonium salts* with hydrogen chloride. ^{31}P NMR shifts for ylides, oxides and sulfides, $X_2YP{=}Z$, and for phosphines and phosphonium salts, were measured at 40·5 Mc/s. ^1H-^{31}P spin-spin couplings of the β′-methylene protons were identical in β-ketoylides and in their enol-ether salts.

INTRODUCTION

The reaction of trimethyl phosphite, $(CH_3O)_3P$, with *trans*-dibenzoylethylene (DBE) yielded a *trialkoxyalkylidenephosphorane* (I)[1b,3] and not a 1,2-*oxaphospholene* derivative with pentacovalent phosphorus, (III) as had been assumed.[4–7] Ethyl diphenylphosphinite, $(C_2H_5O)P(C_6H_5)_2$, likewise, reacted with DBE to give an ylide (II)[8] instead of an oxaphospholene (IV) as claimed.[7]



I; X = Y = OMe
II; X = Ph; Y = OEt



III; X = Y = OR
IV; X = Ph; Y = OEt
NOT FORMED

[1a] Stable Phosphorus Ylides, Part XI; preliminary report: F. Ramirez, O. P. Madan and C. P. Smith, *Tetrahedron Letters* No. 3, 201 (1965); [b] Part X: F. Ramirez, O. P. Madan and C. P. Smith, *J. Org. Chem.* **30**, 2284 (1965).

[2] This investigation was supported by the National Science Foundation (GP 3341) and by Public Health Service Grant No. CA-04769-06 from the National Cancer Institute.

[3] F. Ramirez and O. P. Madan, *Abstracts, Division of Organic Chemistry*, 148*th National Meeting of the American Chemical Society* p. 135. Chicago, Ill., Aug (1964).

[4] V. A. Kukhtin and K. M. Orekhova, *J. Gen. Chem., U.S.S.R.* **30**, 1539 (1960).

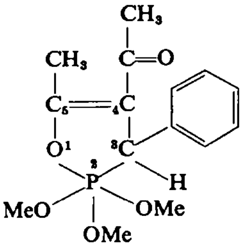
[5a] G. Kamai and V. A. Kukhtin, *J. Gen. Chem., U.S.S.R.* **27**, 2431 (1957); [b] *Ibid.* **27**, 2436 (1957); [c] *Ibid.* **31**, 1621, (1961); [d] c.f, *Chem. Abstr.* **52**, 7127d (1958) and **52**, 9948f (1958).

[6a] V. A. Ginsburg and A. Ya. Yakubovich, *Zh. Obshch. Khim.* **30**, 3979 (1960); [b] *J. Gen. Chem., U.S.S.R.* **30**, 3944 (1960).

[7a] R. G. Harvey and E. V. Jensen, *Tetrahedron Letters* No. 26, 1801 (1963); [b] E. R. De Sombre, R. G. Harvey and E. V. Jensen, *Abstracts, Division of Organic Chemistry*, 146*th National Meeting of the American Chemical Society* p. 216. Denver, Colo., Jan (1964),; [c] R. G. Harvey and E. V. Jensen, *Abstracts, Division of Organic Chemistry*, 144*th National Meeting of the American Chemical Society* p. 61M. Los Angeles, Cal. April (1963).

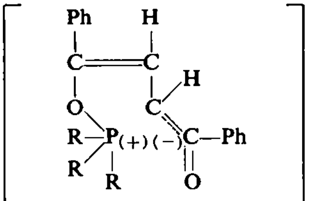
[8] F. Ramirez, O. P. Madan and C. P. Smith, *J. Amer. Chem. Soc.* **86**, 5339 (1964).

The first authentic 2,2,2-*trialkoxy*-1,2-*oxaphospholene* (V) was prepared[9] from 3-benzylidene-2,4-pentanedione. The phosphorus of the oxyphosphorane V[9] gave a NMR signal at higher field than that of the reference 85% H_3PO_4, while the signal of the ylide-phosphorus (I; II) was at much lower field.[1b,3,8]

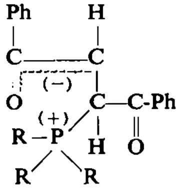


V; $\delta P^{31} = +27{\cdot}9$ ppm

This paper deals with the reaction of amino, alkyl and aryl phosphines with DBE. The phosphine-DBE *adducts* have been formulated[10,11] as O-*phosphonium dipolar ions* (VI). Speculation[7] has centered on the possible equilibration of VI with C-*phosphonium betaines* (VII) *via* 1,2-oxaphospholenes analogous to III and IV. There is no experimental evidence to support structures of type VI.



VI; R = C_2H_5: n − C_4H_9; Ph
NOT FORMED



VII

RESULTS

Triaminophosphines. The reaction of trisdimethylaminophosphine (IX) with DBE (VIII) was rapid and exothermic in methylene chloride at 5°. The resulting crystalline 1 : 1-*adduct* is formulated as *trisdimethylamino*-(*benzoylphenacyl*)*methylene-phosphorane* (XIa ↔ XIb) from the spectral and chemical data presented below. Evidently, the unsaturated ketone underwent a 1,4-addition at carbon, but the resulting C-phosphonium betaine (X) rearranged to the more stable *ylide* (XI). No metastable precursor of XI could be detected in an spectral investigation of the course of the reaction.

Analogous proton shifts have been observed in the reaction of triphenylphosphine with *p*-benzoquinone,[12,13] and with maleic anhydride.[14]

The ^{31}P NMR shift of the amino-ylide (XI) is listed in Table 1. The negative value

---

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

[10] L. Horner and K. Klupfel, *Liebigs* Ann. **591**, 69 (1955); *cf.* pp. 79 and 94.

[11] I. Kuwajima and T. Mukaiyama, *J. Org. Chem.* **29**, 1385 (1964).

[12] F. Ramirez and S. Dershowitz, *J. Amer. Chem. Soc.* **78**, 5614 (1956).

[13] See also H. Hoffman, L. Horner and G. Hassel, *Chem. Ber.* **91**, 58 (1958). For another prior formulation of the *p*-benzoquinone-phosphine adduct see Ref. 10, p. 76.

[14] R. F. Hudson and P. A. Chopard, *Helv. Chim. Acta* **46**, 2178 (1963).

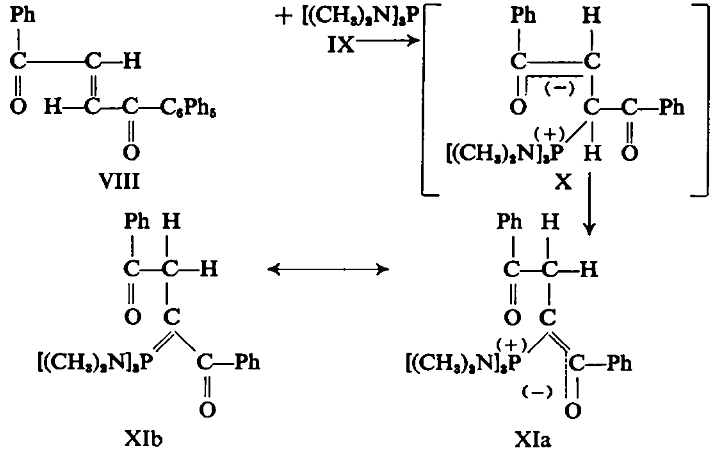


TABLE 1. REACTION OF X_2YP WITH *trans*-DIBENZOYLETHYLENE. PROPERTIES[a] OF β,γ′-DIKETOYLIDES, $X_2YP{=}C(CO{\cdot}C_6H_5)(CH_2{\cdot}CO{\cdot}C_6H_5)$ AND OF RELATED COMPOUNDS

No	X_2YP X	Y	Ylide Mp°	δp^{31} X_2YP	δp^{31} $X_2YP{=}O$	δp^{31} $X_2YP{=}C\langle$	Ylide CH₂ τ	$J^{\beta\prime}$HP	Ylide C=O,μ Phen.	Bz.	Ylide P=C,μ
1	$(CH_3)_2N$	$(CH_3)_2N$	137	−122·0	−23·2	−63·2	6·31	18·5	5·94	6·62	7·22
2	n-C_4H_9	n-C_4H_9	97	+32·6	−45·9	−21·3	6·23	17·2	5·92	6·68	7·20
3	C_2H_5	C_6H_5	121	+17·0	−42·4	−21·1	6·10	18·5	5·92	6·68	7·20
4	C_6H_5	C_2H_5O	124	−109·8	−31·1	−54·2	6·33	21·0	5·95	6·65	7·25
5	CH_3O	CH_3O	—	−140·0	−2·4	−56·2	—	—	5·95	6·62	7·20
6	C_6H_5	C_6H_5	122	+5·7	−26·5	−16·9	6·25	20·0	5·95	6·68	7·20

[a] δp^{31} at 40·5 Mc/s, in ppm *vs* 85% H_3PO_4·H^1 NMR at 60 Mc/s, in ppm *vs* tetramethyl silane = 10 (τ values). J in c/s, solvents: $CDCl_3$ or CCl_4 for ^1H NMR. $CDCl_3$ or CH_2Cl_2 for ^{31}P.

of the shift is inconsistent with an oxaphospholene structure. The shifts of the parent phosphine and of its oxide were remeasured[15] at 40·5 Mc/s and are included in Table 1. These data will be discussed below.

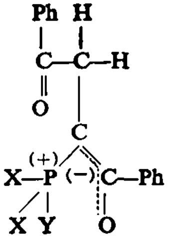
Proton NMR spectroscopy supports the ylide structure (XI) as can be seen in Table 1. The two protons which were originally present in DBE were found as *equivalent* protons in the adduct XI. This signal was a doublet, with a rather large coupling J, due to ^1H-^{31}P spin–spin splitting.

The IR spectrum of the adduct XI had the carbonyl-bands to be expected from a β,γ′-diketoylide.[16] The yellow substance absorbed strongly at 260–290 mμ, with λ_{max} = 276 mμ, ε = 4,700 and at 236 mμ, ε = 13,500.

Alkyl and aryl phosphines. Tri-n-butylphosphine reacted with DBE in methylene chloride at 0° and gave *tri-n-butyl-(benzoylphenacyl)methylenephosphorane* (XII). The spectral data in support of the ylide structure are given in Table 1.

[15a] Previous values have been compiled by R. A. Y. Jones and A. R. Katritzky, *Angew Chem.* (Int. Ed) **1**, 32 (1962); [b] W. A. Henderson, Jr. and S. Buckler, *J. Amer. Chem. Soc.* **82**, 5794 (1960); [c] K. Moedritzer, L. Maier and L. C. D. Groenweghe, *J. Chem. Eng. Data.* **7**, 307 (1962); [d] J. R. Van Wazer and L. Maier, *J. Amer. Chem. Soc.* **86**, 811 (1964); [e] H. Tolkmith, *Ibid.* **85**, 3246 (1963); [f] G. Martin and G. Mavel, *C.R. Acad. Sci., Paris* **255**, 2095 (1962).

[16] F. Ramirez and S. Dershowitz, *J. Org. Chem.* **22**, 41 (1957).



XII; X = Y = n − C_4H_9
XIII; X = C_2H_5; Y = Ph
XIV; X = Y = Ph

Diethylphenyl-(benzoylphenacyl)methylenephosphorane (XIII), was obtained from diethylphenylphosphine and DBE. These two ylides, (XII and XIII) showed no tendency to dissociate into DBE and the phosphine in methylene chloride solution at 20°. Addition of ylide to more DBE was not observed.

Diethylphenylphosphine caused the instantaneous isomerization of *cis* into *trans* dibenzoylethylene; the latter, then formed the ylide XIII. It is assumed that the C-phosphonium betaine adduct, analogous to X, was an intermediate in the *cis* → *trans* isomerization, which was followed spectrophotometrically in the IR.

Triphenyl-(benzoylphenacyl)methylenephosphorane (XIV) was isolated in 45% yield when the reaction between triphenylphosphine and DBE was carried out in dimethoxyethane in which XIV is sparingly soluble. This ylide (XIV) dissociated readily into *trans*-DBE and triphenylphosphine in methylene chloride or in xylene solutions. The reversibility of this process could be studied by IR spectrometry, when one moleequivalent of *trans*-DBE was added to a 2M solution of triphenylphosphine in methylene chloride at 20°. The ylide XIV disappeared also in a slow irreversible process.

The formation of DBE and triphenylphosphine from the reaction of triphenylbenzoylmethylenephosphorane, $(C_6H_5)_3P{=}CH\cdot CO\cdot C_6H_5$, with phenacyl bromide has been observed.[17] This is understandable since the C-alkylation of the ylide by phenacyl bromide, followed by the loss of an α-proton, would give XIV, and hence, the observed dissociation products.[17,18]

Reaction of ylides with benzyl bromide. The ylides XI, XII and XIII underwent O-alkylation with benzyl bromide at 20°. The properties of the corresponding *enolethers* (XV, XVI and XVII) are listed in Table 2. O-alkylation of β-ketoylides has been previously observed.[18,19]

When the butylphosphine-ylide (XII) or the diethylphosphine-ylide, (XIII) were heated together with benzyl bromide, a different reaction occurred. The products were tri-n-butylbenzylphosphonium bromide, or diethylphenylbenzylphosphonium bromide, respectively. This shows that, at elevated temperatures, dissociation of ylide into DBE and phosphine, is faster than ylide-alkylation. The reaction of the

---

[17] M. Siemiatycki and H. Strzelecka, *C.R. Acad. Sci., Paris*, **250**, 3489 (1960); *cf.* S. Trippett, *Quart. Revs.* **17**, 424 (1963).

[18] H. Bestmann and H. Schulz, *Angew. Chem.* **73**, 620 (1961).

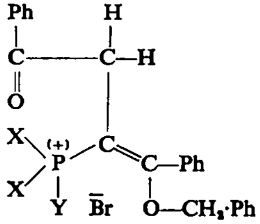
[19] C-alkylation of a β-ketoylide by phenacylbromide has been reported (*cf.* Ref. 17). We have noted that the reaction of triphenylbenzoylmethylenephosphorane with benzyl bromide, *at* 20°, gave mostly *O-alkylated product*, plus derivatives of the minor C-alkylated product. At *elevated temperature*, only C-alkylated product was obtained. The O-alkylated product was decomposed into ylide or was rearranged into the C-alkylated product at elevated temperature, depending on conditions (F. Ramirez, O. P. Madan, and C. P. Smith, In Press).

TABLE 2. PROPERTIES OF ENOL-ETHERS DERIVED FROM β,γ′-DIKETOYLIDES

$$C_6H_5{\cdot}CO{\cdot}CH_2{-}\underset{\displaystyle Z}{\underset{|}{C}}{=}C(OCH_2C_6H_5)(C_6H_5)$$

No	Z	Mp°	δP^{31}	$C_6H_5{\cdot}CO{\cdot}CH_2$ τ	$C_6H_5{\cdot}CO{\cdot}CH_2$ $JH^{\beta}P$	$OCH_2C_6H_5$ τ	C═O,μ	C═C,μ
1	$\overset{-}{Br}[(CH_3)_2N]_3\overset{+}{P}$	144	−50·4	6·08	18	5·30	5·96	6·22
2	$\overset{(-)}{Br}[n\text{-}C_4H_9]_3\overset{(+)}{P}$	—	−28·8	5·70	17	5·30	5·95	6·20
3	$\overset{-}{Br}[(C_2H_5)_2C_6H_5]\overset{+}{P}$	99	−28·0	5·35	17	5·78	5·95	6·20
4	$(C_6H_5)_2P(O)$	179	−28·6	6·10	17	6·00	5·95	6·16
5	$(CH_3O)_2P(O)$	122	−22·0	6·25	19	5·31	5·95	6·18
6	$\overset{-}{Br}[C_6H_5]_3\overset{+}{P}$	230	−20·9	5·85	19	5·85	5·95	6·20

triphenylphosphine-ylide (XIV) with benzyl bromide gave some triphenylbenzylphosphonium bromide, even at 20°, although the major product was the enol-ether (XVIII).



XV; $X = Y = (CH_3)_2N$

XVI; $X = Y = n{-}C_4H_9$

XVII: $X = C_2H_5$; $Y = Ph$

XVIII; $X = Y = Ph$

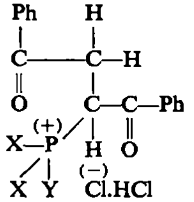
Reaction of ylides with hydrogen chloride. The ylides, XI, XII, XIII and XIV, were converted into crystalline *hydrochlorides* by anhydrous hydrogen chloride in methylene chloride solution. The elemental analysis showed that two moles of HCl had combined with one mole of ylide. The second molecule of HCl can be part of the anion,[20] $(HCl_2)^-$ or it can be hydrogen-bonded to the carbonyl groups of the diketophosphonium salts (XIX, XX, XXI, XXII). The properties are listed in Table 3.

TABLE 3. REACTION OF β,γ′-DIKETOYLIDES WITH HCl GAS IN CH_2Cl_2.
PROPERTIES OF $\overset{(-)}{Cl}X_2Y\overset{(+)}{P}{-}CH(CO{\cdot}C_6H_5)\,(CH_2{\cdot}CO{\cdot}C_6H_5)\,(HCl)$ AND OF
$X_2(O)P{-}CH(CO{\cdot}C_6H_5)\,(CH_2{\cdot}CO{\cdot}C_6H_5)$

No.	X	Y	Mp°.	δP^{31}	C═O,μ
1	$(CH_3)_2N$	$(CH_3)_2N$	130	−54·9	5·95
2	$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	116	−35·7	5·95
3	C_2H_5	C_6H_5	214	−34·1	5·92
4	C_6H_5	—	164	−27·5	5·95
5	CH_3O	—	121	−24·8	5·97
6	C_6H_5	C_6H_5	107	−25·7	5·95

---

[20] J. A. Salthouse and T. C. Waddington, *J. Chem. Soc.* 4664 (1964).



XIX; $X = Y = N(CH_3)_2$

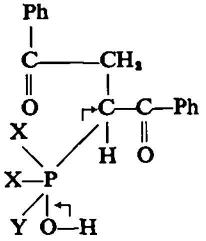
XX; $X = Y = n{-}C_4H_9$

XXI; $X = C_2H_5$; $Y = Ph$

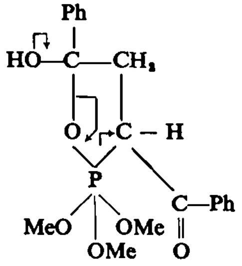
XXII; $X = Y = Ph$

The hydrochloride made from triphenylbenzoylmethylenephosphorane under comparable conditions analyzed for the ylide plus 1·5 moles of HCl. The ^{31}P shift of this hydrochloride was −20·7 ppm, while that of the corresponding ylide was −16·7 ppm.[21]

Hydrolysis of β-ketoylides. The reaction of the trimethoxyylide (I) with water in methylene chloride was nearly instantaneous at 20°; the main products were trimethyl phosphate and 1,2-dibenzoylethane. The ylides derived from alkyl and aryl phosphines underwent hydrolysis very slowly under comparable conditions; the products were the phosphine oxides and dibenzoylethane. Triphenylbenzoylmethylenephosphorane, with only one β-ketogroup was not affected by water.[22] These hydrolyses may involve intermediates like XXIII and XXIV.



XXIII



XXIV

^{31}P NMR shifts of triply- and quadruply-connected phosphorus compounds. The availability of a series of derivatives, $(X_2YP{=}Z \leftrightarrow X_2Y\overset{(+)}{P}{-}\overset{(-)}{Z})$ of quadruply-connected phosphorus, in which the "semipolar" atom, Z was 0, S and C, and in which the singly-bonded atoms, X and Y, could be varied, permitted several generalizations concerning the relationship between structure and ^{31}P NMR shifts. These are shown in Fig. 1 and in Table 4.

(1) Conversion of a phosphite ester, of a trisaminophosphine, and of a phosphinite ester to a sulfide, an ylide and an oxide, resulted in a *positive increment* of the shift; i.e. resonance occurred at higher magnetic field, indicating a more effective shielding of the ^{31}P nucleus by electrons, increasing in the order given. The magnitude of these increments are given in Table 4. Note that replacement of an "isolated" oxygen [Z in $X_2YP{=}Z$] by a sulfur and by an ylide-carbon causes a negative increment of the shift.[23]

---

[21] The values for the P^{31} shifts of this ylide and of its hydrochloride given by A. J. Speziale and K. W. Ratts, *J. Amer. Chem. Soc.* **85**, 2790 (1963), are in error.

[22] This ylide was converted into triphenylphosphine oxide and acetophenone in 30% aqueous EtOH, after 10 hr reflux; Ref. 16.

[23] L. C. D. Groenweghe, L. Maier and K. Moedritzer, *J. Phys. Chem.* **66**, 901 (1962) have given the values of −70 and −9 ppm for the changes $\Delta^{\text{sulfide}}_{\text{oxide}}$, in the systems $(RO)_3PO$ and R_3PO, respectively.

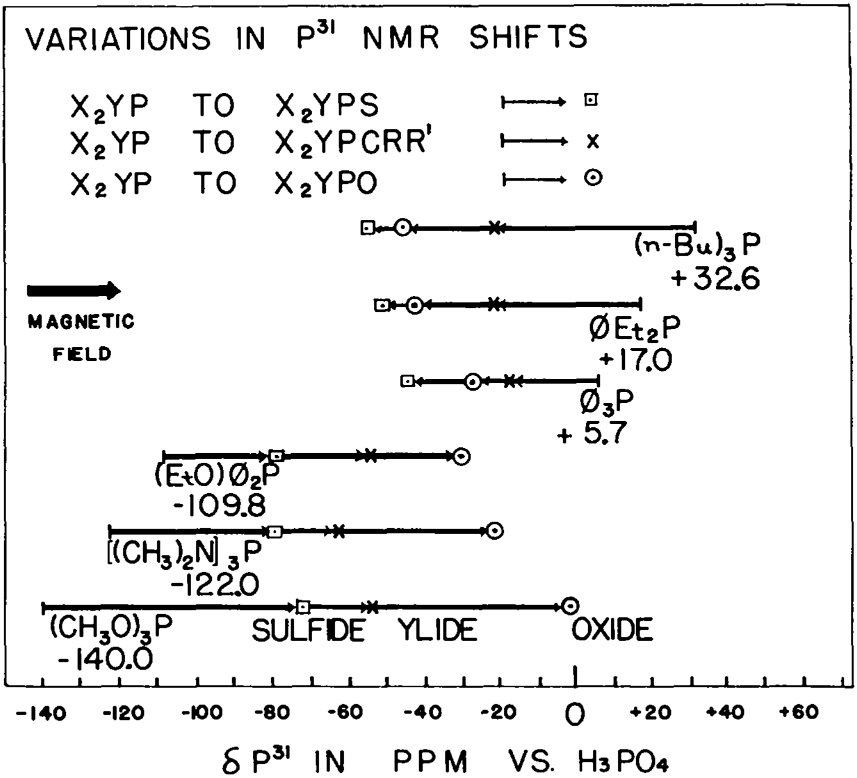


Fig. 1.

Table 4. Variations[a] in P^{31} NMR shifts, δ in ppm

X	Y	$\Delta^{\text{Sulfide}}_{\text{PYX}_2}$	$\Delta^{\text{Ylide}}_{\text{PYX}_2}$	$\Delta^{\text{Oxide}}_{\text{PYX}_2}$	$\Delta^{\text{Sulfide}}_{\text{Oxide}}$	$\Delta^{\text{Ylide}}_{\text{Oxide}}$
n-C_4H_9	n-C_4H_9	−86	−54	−78	−8	+24
C_2H_5	C_6H_5	−69	−38	−59	−9	+21
C_6H_5	C_6H_5	−49	−23	−32	−17	+9
C_6H_5	C_2H_5O	+30	+55	+78	−49	−23
$(CH_3)_2N$	$(CH_3)_2N$	+40	+59	+100	−59	−41
CH_3O	CH_3O	+67	+84	+138	−71	−54

[a] $\Delta^{\text{Sulfide}}_{\text{PYX}_2} = [\delta(X_2YPS)] - [\delta(X_2YP)]$, and corresponding notations.

(2) Conversion of alkyl and aryl phosphines to sulfides, oxides and ylides resulted in a *negative increment* of the shift, indicating a less effective shielding of the ^{31}P nucleus by electrons, in the order shown. Note that now the replacement of the "isolated" oxygen, Z, by a sulfur causes a small negative increment,[23] while the replacement of the oxygen by an ylide-carbon results in a *positive increment.*

(3) The resonance of the sulfides occurred always at the *lowest magnetic field*, regardless of the nature of the groups X, Y, attached to the phosphorus, i.e. the derivative with the least shielded P-nucleus was always the sulfide. However, resonance at the *highest magnetic field* did not always occur in the same derivative. The derivative with the most shielded P-nucleus was the oxide, if one or more of the atoms X, Y

attached to the phosphorus had an unshared electron-pair. The derivative with the most shielded P-nucleus was the ylide, when X and Y, both, lacked unshared electron-pairs.

A correlation between the ^{31}P NMR shifts of trivalent phosphorus compounds and the differences in electronegativities between the phosphorus and the atoms X in X_3P, has been suggested.[24b] The shifts became less positive as the electronegativity of X increased from small values toward some intermediate value (2·8). The shifts became more positive as the electronegativity of X increased above this intermediate value. Some useful trends have been pointed out in the ^{31}P NMR of quadruply-connected compounds.[25] There seems to be an increase in the positive value of the shift with an increase in electronegativity of the atoms[26] which is being replaced in $(RX)_3PZ$, both as a "bridging atom", X, or as an "isolated atom" Z. This was attributed[25] mainly to changes in the distribution of π-bonds among the four σ-bonds.

An examination of Fig. 1 and of Table 4 shows that the trivalent phosphorus compounds must be discussed in two groups.

(1) Consider the compounds in which oxygen or nitrogen is attached to phosphorus as one of the bridging atoms, X, Y. Note the effect of placing sulfur, carbon and oxygen as the isolated atom, Z. Sulfur and carbon have about the same electronegativity (2·5), while that of oxygen is higher (3·5). Higher electronegativity, in the absence of other factors, would result in lower-field resonance (i.e. less shielding). Therefore, the data is consistent with significant p–d π-bonding in this series of compounds, in particular, with more π-bonding among the oxides than among the ylides, and least among the sulfides; (p–d π-bonding should be reflected in a higher-field resonance). Furthermore, the extent of π-bonding, and the redistribution of π-bonding among the four σ-bonds in oxides, ylides and sulfides seems to be more accentuated in the phosphite than in the aminophosphine series, and least in the phosphinite series.

(2) Consider the compounds in which carbon is attached to phosphorus as the X,Y groups. Again, note the effect of placing S, C and O as the isolated atom Z. Now the ylides are at higher field than the oxides, which is consistent with the lower electronegativity of carbon *vs* oxygen, if little p–d π-bonding were involved. That some π-bonding effects may be involved in the *β-ketoylides* (rather than in the oxides) of this type is suggested by the much less negative shifts of the ylides *vs* the sulfides, although the S, C electronegativities are similar.

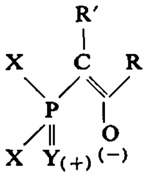
^{31}P NMR shifts in β-ketoylides, their enol-ethers and their hydrochloride salts. Tables 1, 2 and 3 show that the P-NMR of an ylide can occur at *higher or at lower* magnetic field than the resonance of the corresponding enol-ether phosphonium salt and hydrochloride. The former was observed when four carbon atoms were bonded to the phosphorus. The latter was the case when amino groups were attached to the phosphorus.

[24a] H. S. Gutowsky and D. W. McCall, *J. Chem. Phys.* **22**, 162 (1954); [b] A. Saika and C. P. Slichter *Ibid.* **22**, 26 (1954); [c] J. R. Van Wazer, C. F. Callis, J. N. S. Shoolery and R. C. Jones, *J. Amer. Chem. Soc.* **78**, 5715 (1956); [d] N. Muller, P. C. Lauterbur and J. Goldenson, *Ibid.* **78**, 3557 (1956), [e] J. R. Parks, *Ibid.* **79**, 757 (1957).

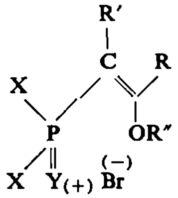
[25] J. R. Van Wazer, *Phosphorus and its Compounds* p. 43. Interscience, New York, N.Y. (1958).

[26] Note however the very high value for Br_3PO, $\delta p^{31} = +102$ ppm. Although the Br electronegativity is only 2·8.

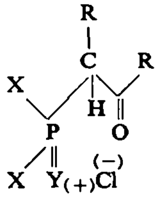
A P-signal at higher field in an ylide than in its enol-ether or hydrochloride is what would be expected from some p–d π-bonding involving the *ylide-carbon* and the phosphorus ("phosphorane" contribution). The "abnormal" lower-field resonance in the amino-ylide, XI, relative to its enol-ether and hydrochloride may reflect differences in p–d π-bonding contributions involving the groups X and Y, as shown in the formulas XXV, XXVI and XXVII. Probably, when the resonance of an oxide is below that of an ylide, the corresponding phosphonium salts will also give resonance below the ylide and *vice-versa.*[27]



XXV

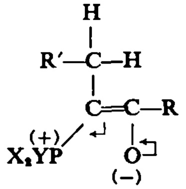


XXVI

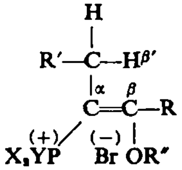


XXVII

^{1}H-^{31}P spin-spin coupling in β-ketoylides and in their enol-ethers. The coupling constant, JHCCP, should be related to the stereoelectronic properties of the molecule, in particular to the dihedral angle formed by the planes H—C—C and P—C—C.[28] Tables 1 and 2 show that the proton in the β′-positions of the ylides (XXVIII) and the enol-ethers (XXIX) are coupled with the phosphorus to the same extent. This suggests that the *β-ketoylides* have more "phosphonium-betaine" character than "alkylidenephosphorane" character.



XXVIII



XXIX

DISCUSSION

The following observations on the behaviour of *carbonyl compounds having α,β-unsaturation* toward trivalent phosphorus compounds, have been made in this and in preceding investigations. (1) The phosphorus of trimethyl phosphite attacked the *oxygen atom* of *p*-benzoquinone, of 2,5-dichloro-*p*-benzoquinone, and of *p*-chloranil;[29]

---

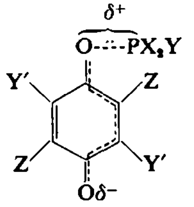
[27] This generalization is restricted to β-ketoylides with no α-hydrogens. Among derivatives of triphenylbenzoylmethylenephosphorane, ylide-resonance was above that of the hydrochloride but below that of the enol-ether phosphonium bromides (F. Ramirez, O. P. Madan and C. P. Smith, In Press).

[28a] C. E. Griffin and M. Gordon, *J. Organometal. Chem.* 3, 414 (1965); [b] J. B. Hendrickson, N. L. Maddox, J. J. Sims, and H. D. Kaesz, *Tetrahedron* 20, 449 (1964), [c] F. Ramirez, A. V. Patwardhan, N. B. Desai, and S. R. Heller, *J. Amer. Chem. Soc.* 87, 549 (1965); [d] J. G. Verkade, T. H. Huttemann, M. K. Fung, and R. W. King, *Inorg. Chem.* 4, 83 (1965), [e] J. G. Verkade and R. W. King, *Ibid.* 1, 948 (1962), [f] G. O. Dudek, *J. Chem. Phys.* 33, 624 (1960); [g] R. C. Axtmann, W. E. Shuler, and J. H. Eberly, *Ibid.* 31, 85*j* (1959).

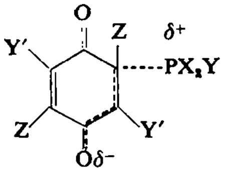
[29a] F. Ramirez and S. Dershowitz, *J. Org. Chem.* 22, 856 (1957); [b] *Ibid.* 23, 778 (1958); [c] *J. Amer. Chem. Soc.* 81, 587 (1959); [d] F. Ramirez, E. H. Chen and S. Dershowitz, *Ibid.* 81, 4338 (1959).

(2) Triphenylphosphine attacked the *oxygen* of *p*-chloranil only; in the other two *p*-quinones, attack was on carbon;[12] (3) Diethylphenylphosphine did not attack the *oxygen* atom of *p*-chloranil at all, but went instead to carbon;[30] (4) Trimethyl phosphite[1b,3] triphenylphosphine, and diethylphenylphosphine, as well as other trivalent phosphorus compounds,[8,9] exhibited no tendency to attack the *oxygen atom* of an α,β-unsaturated ketone, *trans*-dibenzoylethylene, (DBE). In all these cases, the phosphorus added to the carbon in a 1,4- addition pattern; (5) The reactivity of trivalent phosphorus compounds toward DBE was in the order: triamino ~ tri-n-butyl ~ diethylphenyl > ethoxydiphenyl > trimethoxy ≫ triphenyl.

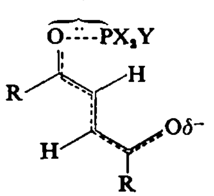
Most of the observations can be rationalized in terms of the transition states for oxygen attack (XXX, XXXII, "oxophilic") and for carbon-attack (XXXI, XXXIII, "carbophilic").



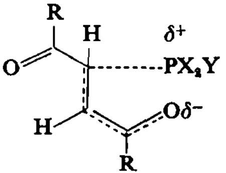
XXX



XXXI



XXXII



XXXIII

Other things being equal, a *p*-quinone will exhibit some tendency toward *oxygen-attack* by a trivalent phosphorus compound, while an α,β- unsaturated ketone will not exhibit such a tendency, because in the former, but not in the latter, the transition state for oxygen attack, XXX, benefits from an incipient aromatization.

Charge-separation in the transition state is relatively larger for O-attacks than for C-attacks in both, *p*-quinones and unsaturated ketones. Indeed, charge-separation can be quite small in C-attacks on the latter, as shown in formula XXXIII.

Trialkyl phosphites tend to give oxygen-attack on *p*-quinones possibly because of a most favorable situation for p–d π-bonding involving the unshared electrons of both the oxygen being attacked and the oxygens already present in the phosphite molecule. Apparently, this assistance is not sufficient to direct the phosphorus of trimethyl phosphite to the oxygen of *trans*-dibenzoylethylene or of 3-benzylidene-2,4-pentanedione.[9]

Oxygen-attack by phosphines on *p*-quinones is probably due mainly to steric factors, in both the quinone and the phosphine. However, the oxidation-potential of the quinone and the related ability to form complexes with phosphines may also be a factor.[31] Note the difference between tetrachloro- and 2,5-dichloro-*p*-quinone toward triphenylphosphine,[12] and the carbon-attack by diethylphenylphosphine[30] on the former.

The slow reaction of DBE with triphenylphosphine is probably a steric effect, since the ylide, once formed, also tended to dissociate in solution. The rapid reaction of DBE with the other alkyl and alkylarylphosphines is consistent with higher nucleophilicity[32] and smaller size. The lower reactivity at carbon of the less nucleophilic trimethyl phosphite, and the intermediate reactivity of the phosphinite, are also reasonable. The very high reactivity of the triaminophosphine will not be discussed further at this time. The aminophosphine could, indeed, be highly nucleophilic;[33] however, the incomplete evidence now available on this type of phosphorus compound indicates a marked tendency for attack by phosphorus on the oxygen in certain carbonyl compounds.* More data is required for sound generalization in this system.

Aminoalkylidenephosphoranes have been reported in solutions and as intermediates in olefination reactions,[34] but they have not been isolated in pure crystalline state. A liquid with several of the physical properties to be expected from monomeric trisdimethylaminodifluoromethylene-phosphorane was isolated recently.[35] However, the value of +65·5 ppm to *high field* of 85% H_3PO_4 found for the P^{31} shift of this material is difficult to reconcile with the value of −63·2 ppm to *low field* of 85% H_3PO_4 found for an aminoylide in this work. Such an effect by the two α-fluorines on the P^{31} shift of a monomeric aminoylide is unlikely.

EXPERIMENTAL

The H′ NMR spectra were examined in a Varian A-60 instrument against internal tetramethylsilane; the shifts in ppm were subtracted from 10 to obtain the τ values. The P^{31} NMR spectra were taken at 40·5 Mc/s. in a Varian HR-100 instrument. External trimethyl phosphite was used for calibration and the shifts are expressed in ppm *vs* 85% H_3PO_4. Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

Reaction of trisdimethylaminophosphine with trans-*dibenzoylethylene*

A mixture of *trans*-dibenzoylethylene (14·8 g) and dry CH_2Cl_2 (50 ml) was cooled to 5° and treated with trisdimethylaminophosphine (10·2 g; 1 mole equiv.; solution is 1·2 M), under N_2. There was an exothermic reaction; the solution became brown and the color faded to yellow within 5 min (stirring). About one-half of the solvent was removed in vacuum. Ether (150 ml) was added and the solution was kept 1 hr at 20°. The solid which separated was collected, washed with ether (50 ml) and dried in vacuum. The yield of crude triaminoylide XI, m.p. 131–135°, was 21·3 (87%). Recrystallization from CH_2Cl_2–ether (1:5) gave *trisdimethylamino-(benzoylphenacyl) methylene-phosphorane* (XI) as yellow needles, m.p. 137–138°. (Found: C, 66·1; H, 7·8; N, 10·7; P, 7·4. $C_{22}H_{30}O_2N_3P$ requires: C, 66·2; H, 7·5; N, 10·5; P, 7·7%.) The spectral characteristics were:

---

* *Note Added in Proof.* The phosphorus of trisdimethylaminophosphine adds to the *oxygen* atom of phenanthrenequinone, of diphenylpropanetrione and of diethyloxomalonate. The central carbonyl-oxygen is attacked in the last two compounds. The *1:1 adducts* thus formed have *open dipolar structures* with large negative ^{31}p NMR shifts. F. Ramirez, A. V. Patwardhan and C. P. Smith, *J. Am. Chem. Soc.* **87**, 4973 (1965).

[30] F. Ramirez, D. Rhum and C. P. Smith, *Tetrahedron* **21**, 1941 (1965).

[31] E. A. C. Lucken, F. Ramirez, V. P. Catto, D. Rhum and S. Dershowitz, *Tetrahedron* **22**, 637 (1966).

[32a] R. F. Hudson, *Pure and Appl. Chem.* **9**, 371 (1964); [b] R. F. Hudson, *Chimia* **16**, 173 (1962).

[33] V. Mark, *J. Amer. Chem. Soc.* **85**, 1884 (1963).

[34a] G. Wittig, H. D. Weigmann and M. Scholsser, *Chem. Ber.* **94**, 676 (1961); [b] H. Oediger and K. Eter, *Liebigs Ann.* **682**, 58 (1965); [c] W. Ried and H. Appel, *Ibid.* **679**, 51 (1964); [d] W. A. Hart and H. H. Sisler, *Inorg. Chem.* **3**, 617 (1964).

[35] V. Mark, *Tetrahedron Letters* No. 42, 3139 (1964).

bands at 5·94 (C=O), 6·62 (C=O), 7·22 (P=C), 7·73, 8·27, 8·47, 8·97, 9·40 and 10·2 (V.S.) μ (in CH_2Cl_2). A 10H′ multiplet at τ 2·2 and 2·7 (aromatics), a 18H′ doublet, J_{HP} = 9·3 c/s, at τ 7·30 (CH_3N) (in $CDCl_3$). λ_{max} 236 mμ (ε 13,500), broad absorption at 260–290 mμ with λ_{max} 276 mμ (ε 4,760) (in CH_2Cl_2); see also Table 1.

The solid ylide showed little decomposition after 60 days in a desiccator. Solutions of the ylide in methylene chloride turned brown within 2 days.

Reaction of the triaminoylide, (XI), *with benzyl bromide at* 20°

A solution of the triaminoylide, XI, (3·34 g) in CH_2Cl_2 (25 ml) was treated with 1·71 g purified benzyl bromide (1·2 mole equiv.), at 20°. IR analysis revealed little ylide after 1 hr. The mixture was kept 15 hr at 20° and then was evaporated to ca. one-half of its volume (at 18 mm) and was diluted with ether (150 ml). The crystalline solid (4·3 g; 93% m.p. 143–144°) gave, after one recrystallization from CH_2Cl_2–ether (1:3), colorless *trisdimethylamino-(1-phenacyl-2-phenyl-2-benzyloxy)vinylphosphonium bromide* (XV), m.p. 143–144°. (Found; C, 61·5; H, 6·8; N, 7·3; P, 5·1; Br, 14·2. $C_{29}H_{37}N_3O_2PBr$ requires: C, 61·1; H, 6·5; N, 7·4; P, 5·4; Br, 14·0%.) Spectral characteristics were: bands at 5·95 (C=O), 6·22 (C=C, nearly as strong as the C=O), 6·31 (aromatic, V.S), 7·69, 8·23, 8·46, 8·77 and 10·1 (V.S) μ (in CH_2Cl_2). A 15H′ multiplet at τ 2·1 and 2·6 (aromatics), and a 8H′ doublet, J_{HP} = 9·8 c/s, at τ 7·25 (CH_3N) (in $CDCl_3$); see also Table 3.

Reaction of amino-ylide (XI), *with hydrogen chloride*

A solution of XI, (3·57 g) in CH_2Cl_2 (30 ml) was cooled to 0° and treated with anhydrous HCl gas, to saturation. The yellow solution became colorless; the solvent was removed at 18 mm, after 5 min. The solid (4·0 g; m.p. 121–124°) was dissolved in CH_2Cl_2 (20 ml); the clear solution was filtered and the filtrate was diluted with ether (25 ml). The solid which separated at 20° (3·6 g; m.p. 126–128°) was again recrystallized from CH_2Cl_2–ether (25:25 ml), giving colorless *trisdimethylamino-*(1,2-*dibenzoyl*)*ethylphosphonium chloride-hydrogen chloride* adduct (XIX; 3·3 g) m.p. 129–130°. The IR spectra of the three solid phases described above were very similar. (Found: C, 55·8; H, 7·4; N, 9·2; P, 6·7; Cl, 14·6. $C_{22}H_{31}O_2N_3PCl{\cdot}HCl$ requires: C, 55·9; H, 7·8; N, 8·9; P, 6·6; Cl, 15·0 ($C_{22}H_{31}O_2N_3PCl$ requires: C, 60·6; H, 7·1; N, 9·6; P, 7·1; Cl, 8·1%).) Spectral characteristics were: bands at 5·95 with shoulder at 5·93 (C=O), 6·28 and 6·32, 7·75, 8·12, 8·5, 9·40 and 10·1 (v.s.) μ (in CH_2Cl_2). (The strong ylide bands at 6·62 and 7·22 μ had disappeared.) A 1H′ singlet at τ-1·91 (HCl of complex), a 10H′ multiplet at τ 1·9 and 2·4 (aromatics), a 2H′ multiplet at τ 5·9 (phenacyl) and a 18H′ doublet, J_{HP} = 10 c/s, at τ 7·20 (CH_3N) (in $CDCl_3$). The lone methine proton signal, split by the phosphorus and by the two phenacyl protons was not located.

Reaction of tri-n-butylphosphine with trans-*dibenzoylethylene*

trans-Dibenzoylethylene (11·11 g) was added to a stirred solution of tri-n-butylphosphine (9·51 g; 1 mole equiv.) in dry CH_2Cl_2 (20 ml), kept at 0° in an ice-bath. (The solution is 2·3M.) There was an immediate reaction; the deep-brown solution was kept 15 min at 0° and 10 min at 20°. The solvent was removed at ca. 40° (18 mm; last traces at 1 mm) and the non-crystalline residue was dissolved in dry ether (50 ml). Crystals formed after several hr at 20° and then at −15°, for 2 days. The yield of crude XII, m.p. 95–97°, was 15·7 g. (76%). Recrystallization from benzene–hexane (1:1) gave 13 g *tri-n-butyl-*(*benzoylphenacyl*)*methylenephosphorane* (XII) as yellow needles, m.p. 96–97°. (Found: C, 76·4; H, 8·8; P, 6·1. $C_{28}H_{39}O_2P$ requires: C, 76·7; H, 8·9; P, 7·0%). The spectral characteristics were: bands at 5·92 (C=O), 6·68 (C=O), 7·22 (P=C), 8·28, 9·00 and 10·15 μ (in CH_2Cl_2). A 10H′ multiplet at τ 2·3 and 2·7 (aromatics), and 3 multiplets at τ 7·8, 8·5 and 9·1, integrating as 27H′ (n-butyl groups) (in $CDCl_3$); see also Table 1.

Relative reactivities of trisdimethylaminophosphine and of tri-n-butylphosphine with trans-*dibenzoylethylene*

A 0·1M solution of *trans*-dibenzoylethylene (20 ml) in CH_2Cl_2 was treated with a 0·1M solution of the trisaminophosphine (20 ml), and of the tri-n-phosphine (20 ml), at 20°, in separate experiments. The color changes (to red and brown, respectively) were nearly instantaneous. The IR spectra were examined within 2 min and disclosed that most of the dibenzoylethylene had disappeared and that the 3 characteristic bands of the ylides had reached about equal intensities in both solutions. Probably, the reaction of the trisaminophosphine is somewhat faster than that of the butylphosphine.

Reaction of the tri-n-butylylide, (XII), *with benzyl bromide at* 20°

A mixture of XII, and excess of benzyl bromide was kept 24 hr at 20°. Ether was added and the resulting non-crystalline precipitate was collected, washed with ether and dried. This material could not be obtained crystalline or analytically pure; however, the spectral characteristics were in agreement with the structure XVI. It had bands at 5·95, 6·20 and 6·30 μ; the 15 aromatic H′ were at τ 2·1 and 2·8; the 27H′ of the butyl groups were in 3 multiplets at τ 7·5, 8·5 and 9·1 ($CDCL_3$); see also Table 3.

Reaction of the tri-n-butylylide, (XII), *with boiling benzyl bromide*

A mixture of XII, (1·11 g) and benzyl bromide (10 ml) was kept 5 min at reflux temp. The cooled mixture was diluted with ether (60 ml). The resulting solid (0·91 g; 72%; m.p. 144–148°) was identified as tri-n-butylbenzylphosphonium bromide, having a m.p. of 153–154° (CH_2Cl_2–ether.) (Found: C, 61·1; H, 9·5; P, 8·6; Br, 19·3. Calc. for $C_{19}H_{34}PBr$: C, 61·1; H, 9·1; P, 8·3; Br, 21·4%). The 2H′ of the benzyl group gave a doublet, J_{HP} = 15·7 c/s. at τ 5·67 (in $CDCl_3$). $\delta P^{31} = -31{\cdot}5$ ppm ($CDCl_3$).

Reaction of butyl-ylide (XII) *with hydrogen chloride*

A solution of XII, (6·47 g) in CH_2Cl_2 (30 ml) was cooled to 0° and was saturated with HCl gas. The solvent was removed at 20° (18 mm) and the residue was dissolved in dry ether. The solution deposited crystals of the hydrochloride (7·0 g; m.p. dec. 116–127°) after 2 days at 20°. This was dissolved in CH_2Cl_2 (25 ml) and the solution was diluted with ether (125 ml) and kept at −20°. The recrystallized *tri-n-butyl-*(1,2*-dibenzoyl*)*ethylphosphonium chloride-hydrogen chloride adduct* (XX) decomposed at ca. 116–127°. (Found; C, 66·0; H, 8·1; P, 6·0; Cl, 12·7; $C_{28}H_{40}O_2PCl.HCl$ requires: C, 65·7; H, 8·0; P, 6·1; Cl, 13·8%. ($C_{28}H_{40}O_2PCl$ requires: C, 70·8; H, 8·4; P, 6·5; Cl, 7·5%).) Spectral characteristics were: bands at 5·95 (C=O), 6·28, and 6·35; 6·82, 6·92, 8·15 μ (in CH_2Cl_2). A 1H′ singlet at τ −2·97 (HCl of complex), a 10H′ multiplet at τ 1·9 and 2·5 (aromatics), a 2H′ multiplet at τ 5·7 (phenacyl) and a set of multiplets at τ 7·4, 8·5 and 9·1 due to the 27H′ of the butyl groups (in $CDCl_3$). The lone methine proton signal split by the P^{31} and by the two phenacyl protons, was not located.

Hydrolysis of the tri-n-butylylide (XII). A solution of XII (3·48 g) in CH_2Cl_2 (20 ml) was treated with 0·28 ml water (2 mole equiv.) at 20°. The IR spectrum of the stirred mixture was examined after 42, 66 and 90 hr. The hydrolysis to tributylphosphine oxide and 1,2-dibenzoylethane was complete after 66 hr. The solvent was removed at 18 mm and the residue was kept under ether (25 ml) for 1 hr at 20°. The insoluble dibenzoylethane (1·62 g; 87%; m.p. 144–146°) was filtered and the filtrate was evaporated to yield tri-n-butylphosphine oxide (P=O band at 8·68 μ; $\delta P^{31} = -45{\cdot}8$ ppm).

Reaction of diethylphenylphosphine with trans*-dibenzoylethylene*

trans-Dibenzoylethylene (10·00 g) was added to a stirred solution of diethylphenylphosphine (7·04 g; 1 mole equiv.) in *dry* CH_2Cl_2 (20 ml; 1 M) at 20°. The immediate, exothermic reaction produced a brown solution which became red in 3 min. After 5 min, the solution was diluted with *dry* ether (80 ml), when yellow crystals of XIII (11·42 g; 67%; m.p. 120–121°) separated. The filtrate gave an additional 16% of ylide. One recrystallization from CH_2Cl_2 (4 ml/g)–ether (1:8) at −15° gave *diethylphenyl-*(*benzoylphenacyl*)*methylene phosphorane* (XIII) as yellow crystals m.p. 120–121°. (Found: C, 77·6; H, 6·8; P, 7·9; $C_{26}H_{27}O_2P$ requires: C, 77·6; H, 6·7; P, 7·7%.) The spectral characteristics were: bands at 5·95 (C=O), 6·70 (C=O), 6·75, 7·20 (P=C) and 9·04 μ (in CH_2Cl_2). A 15H′ multiplet at τ 2·2 and 2·5 (aromatics), a 4H′ multiplet at ca. τ 6·7 (CH_2 of ethyl) and a 6H′ doublet, J_{HP} = 18·5 c/s., of triplets, J_{HH} = 7·5 c/s., centered at τ 8·92 (CH_3, split by P^{31} and CH_2) (in $CDCl_3$); λ_{max} 240 mμ, (ε 21,600), broad absorption at 270–310 mμ, with λ_{max} 280 mμ (ε 8,000). (in CH_2Cl_2); see also Table 1.

A 0·1M solution of XIII in CH_2Cl_2 was examined in the IR from time to time to determine the possible existence of a reversible decomposition to *trans*-dibenzoylethylene and diethylphenylphosphine. There was less than 5% dissociation after 3 days at 20°. However, some decrease of the 6·6 μ ylide band was noted and some phosphine oxide appeared.

Reaction of diethylphenylphosphine with cis-*dibenzoylethylene*

A solution of *cis*-dibenzoylethylene (0·103 g) in dry CH_2Cl_2 (5 ml; 0·1M) was treated with 0·07 ml diethylphenylphosphine (slightly less than one mole equiv.). The IR spectrum of the pale yellow solution was examined as rapidly as possible. The bands due to the *cis*-isomer were replaced by those of the *trans*-isomer (6·05, 7·60 and 7·78 μ); in addition some ylide was formed (bands at 5·94, 6·70 and 7·20 μ). The spectrum after 1 hr was rather similar to the "zero-time" spectrum, with somewhat less *trans*-olefin and more ylide. A drop of diethylphenylphosphine was then added; the spectrum after 20 hr was that of XIII.

Reaction of the diethylphenylylide (XIII) *with benzyl bromide at* 20°

A solution of XIII, (2·40 g) in CH_2Cl_2 (5 ml) was treated with 1·5 g purified benzyl bromide, at 20°. The solvent was removed at 18 mm after 12 hr. The non-crystalline residue was difficult to crystallize; it was dissolved in benzene and the solution was diluted with ether (1:1) and filtered. The filtrate was kept several hr at 20° and then was slowly evaporated until crystals began to form (ca. 1/2 vol). The crude, crystalline bromide (2·33 g; 70%; m.p. 90–95°) became sparingly soluble in benzene; it was dissolved in CH_2Cl_2 (3 ml/g), and diluted with ether and benzene (1:2:3 respectively). Colorless *diethylphenyl-*(1*-phenacyl-*2*-phenyl-*2*-benzyloxy*)*vinylphosphonium Bromide* (XVII) m.p. 96–98° formed at 5°. (Found; C, 69·3; H, 6·1; P, 5·5; Br, 13·7. $C_{33}H_{34}O_2PBr$ requires: C, 69·1; H, 5·9; P, 5·4; Br, 13·9%.) Spectral characteristics were: bands at 5·95 (C═O), 6·20 (C═C, nearly as strong as the C═O), 6·30 (aromatic, v.s.), 8·22, 8·75, 8·95 and 10·0 μ (in CH_2Cl_2). A 20 H′ multiplet at τ 1·9, 2·3, 2·8 and 3·3 (aromatics), a 4H′ multiplet ca. τ 7·1 (CH_2) and a 6H′ doublet, $J_{HP} = 19$ c/s., of triplets, $J_{HH} = 7$ c/s., centered at τ 8·75 due to the CH_3 groups split by P^{31} and CH_2 in CH_3CH_2P (in $CDCl_3$); see also Table 3.

Reaction of the diethylphenylylide XII *with boiling benzyl bromide*

A mixture of XIII (0·65 g) and benzyl bromide (5 ml) was kept 5 min at reflux temp. The cooled mixture was diluted with ether. The solid which precipitated (0·53 g; 71%; m.p. 145–147°) was shown to be diethylphenylbenzylphosphonium bromide, m.p. 151–153° (CH_2Cl_2–ether). (Found: C, 61·0; H, 6·6; P, 9·3; Br, 20·5. Calc. for $C_{17}H_{22}PBr$: C, 60·5; H, 6·5; P, 9·2; Br, 23·0%.) The 2H′ due to the benzyl group gave a doublet, $J_{HP} = 15·2$ c/s., at τ 5·35. ($CDCl_3$). $\delta P^{31} = -32·7$ ppm ($CDCl_3$).

Reaction of diethylphenyl-ylide, (XIII), *with hydrogen chloride*

A solution of XIII, (2·0 g) in CH_2Cl_2 (20 ml) was cooled to 0° and was saturated with HCl. A crystalline precipitate appeared. (The previous hydrochlorides did not separate out of the CH_2Cl_2 solution at the concentrations employed.) Ether was added (15 ml) and the *diethylphenyl-*(1,2*-dibenzoyl*)*ethylphosphonium chloride—hydrogen chloride adduct* (XXI) (2·2 g; m.p. 214–216°) was filtered off. It was analyzed without further purification. (Found: C, 66·4; H, 5·6; P, 6·6; Cl, 15·3. $C_{26}H_{28}O_2PCl{\cdot}HCl$ requires: C, 65·7; H, 6·1; P, 6·5; Cl, 14·9%.) Spectral characteristics were: a split carbonyl at 5·93 and 5·98 μ (in KBr pellet). The hydrochloride was insoluble in CH_2Cl_2, $CHCl_3$, ether, and dimethyl formamide, but soluble in acetic acid, MeOH and water.

Hydrolysis of the diethylphenylylide (XIII). A solution of XIII, (2·47 g) in CH_2Cl_2 (15 ml) was stirred with 0·33 ml (3 mole equiv.) of water for 18 hr at 20°. The solvent was removed (18 mm) and the residue was stirred with ether (75 ml; 2 hr; 20°). The insoluble 1,2-dibenzoylethane (1·30 g; 89%) had m.p. 146–147°. The filtrate gave diethylphenylphosphine oxide (P═O at 8·52 μ; $\delta P^{31} = -42·4$ ppm).

Reaction of triphenylphosphine with trans-*dibenzoylethylene*

trans-Dibenzoylethylene (13·0 g) was added to a solution of triphenylphosphine (13·88 g; one mole equiv.) in dimethoxyethane (50 ml; dried first over Na, then CaH_2 and distilled). The unsaturated ketone was still in suspension after 4 hr, but after 12 hr it was replaced by yellow crystals of XIV. The latter (11·5 g; 44%; m.p. 120–122°) was filtered and washed with dry ether. Compound XIV, tends to decompose in solution, but it can be purified by solution in CH_2Cl_2 (2·2 ml/g at 20°) and *immediate* precipitation with ether (1:5). The analytical sample of *triphenyl-*(*benzoylphenacyl*)*-methylenephosphorane* (XIV) had m.p. 121–122°. (Found; C, 81·8; H, 5·6; P, 5·8. $C_{34}H_{27}O_2P$ requires: C, 81·9; H, 5·4; P, 6·2%.) The spectral characteristics were: 5·95 (C═O), 6·29, 6·36, 6·68 (C═O), 6·76, 6·97, 7·20 (P═C), 8·26, and 9·1 μ (*in a fresh CH_2Cl_2 solution*). A 25H′ multiplet at τ 2·2 and 2·7 (aromatics); see also Table 1.

Dissociation of triphenyl-(benzoylphenacyl)methylenephosphorane into triphenylphosphine and trans-*dibenzoylethylene*

(a) *In methylene chloride.* (1) The IR spectrum of a solution of *crystalline triphenylphosphine ylide* (XIV), in this solvent showed the characteristic bands of *trans*-dibenzoylethylene at 6·05 μ and at 7·57 and 7·75 μ, after 40 min at 20°, indicating dissociation of the ylide. (2) When 2·36 g of *trans*-dibenzoylethylene was added to a solution of triphenylphosphine (2·6 g; one mole equiv.) in CH_2Cl_2 (6 ml; 2M) at 20°, an equilibrium with the ylide was slowly established. After 20 hr the IR spectrum showed the bands due to phosphine, unsaturated ketone and ylide. The P^{31} NMR spectrum showed the phosphine signal at +5·7 ppm and the ylide signal at −16·7 ppm.

(b) *In xylene.* When the crystalline XIV, (7 mmoles) was added to boiling xylene (15 ml) rapid dissociation to *trans*-dibenzoylethylene occurred, as shown by the IR spectrum of an aliquot removed from the solution after 5 min (xylene removed and replaced by CH_2Cl_2 for IR examination).

Reaction of the triphenylylide (XIV) *with benzyl bromide at* 20°

A mixture of XIV (3·88 g) and benzyl bromide (10 ml) was kept 15 hr at 20°. Ether (75 ml) was added. The solid (about 5·3 g) which precipitated was extracted with CH_2Cl_2 (15 ml). The CH_2Cl_2–insoluble portion (1·0 g; 28%; m.p. 290–291°) was shown to be triphenylbenzylphosphonium bromide. The CH_2Cl_2-solution was treated with ether (15 ml) and then benzene (5 ml). After 2 days, crystals of XVIII (2·2 g; 42%; m.p. 228–235°) were obtained. Additional ether (23%; total: 65% yield) was obtained from the mother liquid. Pure XVIII, had m.p. 230–235° from CH_2Cl_2–ether. (Found; C, 73·5; H, 5·5; P, 4·7; Br, 12·0 $C_{41}H_{34}O_2PBr$, requires: C, 73·5; H, 5·1; P, 4·6; Br, 12·0%.) Spectral characteristics were: 5·95 (C═O) and 6·20 μ (C═C). (CH_2Cl_2). 25H′ at ca. τ 2·3; see also Table 3.

Reaction of the triphenylylide, (XIV), *with boiling benzyl bromide*

A mixture of the triphenylylide (10·3 g) and benzyl bromide (50 ml) was kept 3 min at reflux temp. Ether (250 ml) was added and the triphenylbenzylphosphonium bromide (17·2 g; m.p. 295–296°) was filtered. $\delta P^{31} = -22{\cdot}8$ ppm. (CH_2Cl_2). A 2H′ doublet, $J_{HP} = 14{\cdot}5$ c/s at τ 4·68, in addition to the 20H′ aromatic multiplet. The same material was made from triphenylphosphine and benzyl bromide.

The mother liquid afforded *trans*-dibenzoylethylene (ca. 50%).

Triphenylbenzylphosphonium bromide (1·0 g) in CCl_4 suspension (50 ml) reacted with Br_2 (1 equiv.) at 20° (20 hr) and gave a yellow tribromide (1·5 g), $\overset{-}{Br_3}\,(C_6H_5)_3\overset{+}{P}\text{—}CH_2{\cdot}C_6H_5$, m.p. 144–145° from CH_2Cl_2–ether. (Found: C, 50·4; H, 3·7; P, 5·2; Br, 39·0. $C_{25}H_{22}PBr_3$ requires: C, 50·6; H, 3·7; P, 5·2; Br, 40·5%.) $\delta P^{31} = -21{\cdot}7$ ppm. (CH_2Cl_2). A 2H′ doublet, $J_{HP} = 14{\cdot}5$ c/s, at τ 5·25, in addition to the 20H′ aromatic multiplet.

Reaction of triphenylylide, (XIV), *with hydrogen chloride*

A cold (0°) solution of XIV (4·72 g) in CH_2Cl_2 (25 ml) was saturated with HCl gas. The solvent was removed at 18 mm and the residue was washed with dry ether (50 ml). The ether-insoluble XXII (4·7 g) decomposed at 74–78° but did not completely melt until 120°. The IR spectrum (in CH_2Cl_2) was similar to that of the analytical sample. The P^{31} NMR spectrum (in CH_2Cl_2) showed a signal at $\delta P^{31} = -25{\cdot}7$ ppm and another at $\delta P^{31} = -21{\cdot}2$ ppm. The crude hydrochloride was dissolved in CH_2Cl_2 and the solution was diluted with ether. The solid which precipitated was washed with ether and analyzed; the sample again decomposed at 30–90°, but did not melt until 120°. (Found: C, 73·0; H, 5·5; P, 7·7; Cl, 12·8. $C_{34}H_{28}O_2PCl{\cdot}HCl$ requires: C, 71·5; H, 5·1; P, 5·4; Cl, 12·4%.) Spectral characteristics were: bands at 5·93 (C═O), 6·28, 6·95, 7·5, 8·2 and 9·05 μ (CH_2Cl_2).

Action of water on triphenyl-(benzoylphenacyl)methylenephosphorane (XIV)

A solution of the ylide (1·8 g) in CH_2Cl_2 (10 ml) was stirred with 3 mole equiv. of water (0·2 ml). The IR spectrum was examined after 4 hr, 20 hr and 8 days. At first, the solution contained mostly *trans*-dibenzoylethylene (6·05, 7·6 and 7·8 μ bands). Then, the unsaturated ketone began to disappear, while triphenylphosphine *oxide* was being formed (P═O band at 8·45μ). A strong band at 5·92 μ (C═O) was present after 8 days; this could be due to 1,2-dibenzoylethane and or to 1,2,3,4-tetrabenzoylbutane formed from the addition of dibenzoylethane to dibenzoylethylene.

When a solution of the ylide (2·6 g) in MeOH (20 ml) containing water (7 ml) was refluxed for 2 hr, a mixture of dibenzoylethane (ca. 25%), dibenzoylethylene, triphenylphosphine oxide and possibly triphenylphosphine, was formed.

Stability of triphenylbenzoylmethylenephosphorane to water

A solution of this ylide[34] (2·0 g) in CH_2Cl_2 (25 ml) containing water (0·2 ml; 2 mole equiv.) remained unchanged after 24 hr, 70 hr and 8 days at 20°, as shown by the IR spectrum. The ylide had been previously converted into acetophenone and triphenylphosphine oxide in 30% aqueous EtOH (10 hr at reflux temp).[16]

Phenyldiethylphosphine sulfide. This was prepared as described.[36] $\delta P^{31} = -51{\cdot}7$ ppm.

Ethyl diphenylphosphinothionate. This ester was prepared in 45% yield in the manner described[37] for the n-octyl analog. B.p. 150–151° (0·15 mm); it became crystalline under pentane at −20°, m.p. 40–42°. (Found: C, 64·0; H, 5·9; P, 11·3. $C_{14}H_{15}OPS$ requires: C, 64·1; H, 5·7; P, 11·8%.) Spectral characteristics: strong IR-bands at 7·02, 9·0, 9·7 and 10·6 μ (CCl4); no bands due to PO at 7·8 to 8·4 μ. A 2H′ doublet, J_{HP} 9·5 c/s, of quartets, J_{HH} 7·5 c/s, at τ 5·90, and a $3H^1$ triplet, J_{HH} 7·5 c/s, at τ 8·77 (in $CDCl_3$). $\delta P^{31} = -80{\cdot}5$ ppm (in $CDCl_3$).

SUMMARY AND CONCLUSIONS

The 1,4-addition of trivalent phosphorus compounds to the carbon atom of an α,β-unsaturated ketone was demonstrated. The initial adducts underwent a proton shift and became *alkylidenephosphoranes* (*P-ylides*), because in the particular ketone used, *trans*-dibenzoylethylene, the anion which resulted from the proton shift was more stable than the anion present in the initial adduct.

The properties of crystalline *β-ketoylides*, $X_2YP{=}C(CO{\cdot}C_6H_5)(CH_2{\cdot}CO{\cdot}C_6H_5)$ were correlated with the nature of the substituents, X and Y, on the phosphorus. The P^{31} NMR shifts of the *ylides*, the corresponding *sulfides*, X_2YPS, and oxides, X_2YPO, and the parent *trivalent P-compound*, X_2YP, were measured at 40·5 Mc/s. In compounds derived from phosphites, aminophosphines, and phosphinites, the P^{31} NMR occurred at increasingly *higher* magnetic field in the order: $X_2YP <$ sulfide < ylide < oxide. In compounds derived from tri-n-butyl-, diethylphenyl-, and triphenylphosphine series, the P^{31} NMR occurred at increasingly *lower* magnetic field in the order: $X_2YP >$ ylide > oxide > sulfide.

The *β-ketoylides* underwent O-alkylation with benzyl bromide at 20°, giving *enol-ether salts*. The H^1–P^{31} spin–spin coupling, involving the methylene protons did not vary significantly in going from the *β-ketoylides* to the corresponding *enol-ether salts*. This suggests similar dihedral angles for the planes H—C—C and C—C—P, and may reflect little P=C p–d π-bonding and significant $\overset{+}{P}$—C=C—$\overset{-}{O}$ contribution to β-ketoylides.

The P^{31} NMR occurred at *lower* magnetic field in the aminoylide than in its hydrochloride and enol-ether salts. The P^{31} NMR occurred at *higher* magnetic field in the alkyl-, and arylphosphine ylides than in the corresponding two salts.

The triphenylphosphine-ylide underwent dissociation into the phosphine and *trans*-dibenzoylethylene, disclosing the reversibility of the proton-shift and of the phosphorus addition to the unsaturated ketone. Diethylphenylphosphine isomerized *cis*-dibenzoylethylene into the *trans*-isomer, which then formed the ylide.

The presence of a second keto group in the γ′-position of β-ketoylides increased the rate of hydrolytic cleavage of the P—C bond.

---

[36] R. A. Zingaro and R. E. McGlothlin, *J. Chem. Eng. Data* **8**, 228 (1963).

[37] C. S. Stuebe, W. M. LeSuer and G. R. Norman, *J. Amer. Chem. Soc.* **77**, 3528 (1955).