Reactions of Phosphorus Ylids. Part III.[1] Reactions with Acetylenes

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The general applicability of the reactions of imino- and methylene-phosphoranes with dimethyl acetylenedicarboxylate has been studied, and the properties of the adducts have been investigated. Methylenehydrazonophosphoranes react with the acetylene as substituted iminophosphoranes, and not as 1,4-dipolar species.

THE mechanism of the addition of methylenephosphoranes to acetylenes is controlled by finely balanced electronic and steric factors. Phosphoranes containing an α-proton can undergo Michael addition [2,3] (in protic solvents) or cycloaddition [3,4] (in aprotic solvents) to dimethyl acetylenedicarboxylate (DMA). Our results on both iminophosphoranes and phosphoranes with no α-proton, published in preliminary form,[1,5] outlined the scope of the cycloaddition, which is followed by a ring-opening reaction to give a stable ylid.

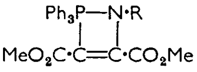
1 : 1 adducts are formed in the reactions of iminophosphoranes (I)—(VI) with dimethyl acetylenedicarboxylate. The adduct derived from the imine (II) was shown by *X*-ray analysis [5,6] to be the diester (XIV).

$Ph_3P{:}N\cdot C_6H_4\cdot R$

	R
(I)	H
(II)	*p*-Br
(III)	*p*-Ac
(IV)	*p*-CO_2Me
(V)	*p*-NO_2

$Ph_3P{:}NR$

	R
(VI)	H
(VII)	Bz
(VIII)	*p*-$Me\cdot C_6H_4\cdot SO_2$
(IX)	CO_2Et
(X)	2,4-dinitrophenyl
(XI)	pyrimidin-2-yl



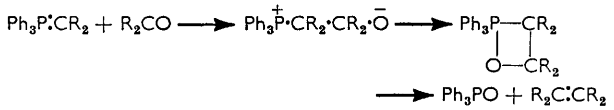
(XII)

$Ph_3P{:}C(CO_2Me)\cdot C(CO_2Me){:}N\cdot C_6H_4\cdot R$

	R
(XIII)	H
(XIV)	*p*-Br

The chemical, physical, and spectral properties of the other adducts showed them to have analogous structures. We have investigated the properties and reactions of the adduct (XIII) and its analogues in detail.

The mechanism of the adduct-forming reaction must involve an intermediate (XII), and closely resembles that of the Wittig reaction,[7] in which methylenephosphoranes convert aldehydes and ketones into olefins by nucleophilic attack on the carbonyl group.



No adducts are formed between DMA and those iminophosphoranes in which electron-withdrawing groups on nitrogen or phosphorus make such an attack impossible. Thus the imines (VII)—(XI), containing electron-attracting substituents on nitrogen, and the imines (XV)—(XVII), all do not react with DMA. In the latter series the inactivity arises from an increased donation of electrons from nitrogen to phosphorus and a correspondingly smaller contribution of a dipolar resonance structure, *e.g.*, (XVIII), to the overall structure of the ylid.

$(EtO)_3P{:}NR$

	R
(XV)	Ph
(XVI)	Bz
(XVII)	*p*-$Me\cdot C_6H_4\cdot SO_2$

$(EtO)_3\overset{+}{P}\cdot\overset{-}{N}R$

(XVIII)

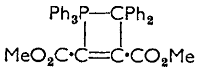
Our first report that the methylenephosphorane (XIX) reacts with DMA to give the adduct (XXIII) [5] through the assumed intermediacy of the phosphacyclobutene (XXV) was subsequently confirmed and extended to other ylids, including (XXI) and (XXII), by Bestmann and Rothe,[4] who presented chemical evidence for the assigned structures of the products. Under their unspecified conditions they found no evidence for proton migration in the intermediates (XXVI; R = Ph and CH:CHPh). The phosphorane (XX) undergoes a similar reaction, to give the new ylid (XXIV) in high yield. Structure assignments for all the compounds cited, from both imino- and methylene-phosphorane nucleophiles, follow from analytical and spectral data, and in particular from the carbonyl absorptions in the range 1610—1655 cm.$^{-1}$. This effect, arising from the dipolar resonance contribution shown, is of great diagnostic value in proving the presence of carbonyl substituents on the α-carbon atom of an ylid.[4] The chemical significance of the effect is manifest in the great stability of the

$Ph_3P{:}CRR^1$

(XIX) $R = R^1 = Ph$
(XX) $R = R^1 =$ 9-fluorenylidene
(XXI) $R = H$, $R^1 = Ph$
(XXII) $R = H$, $R^1 = CH{:}CHPh$

$Ph_3P{:}C(CO_2Me)\cdot C(CO_2Me){:}CR_2$

(XXIII) R = Ph
(XXIV) $R_2 =$ 9-fluorenylidene



(XXV)

$Ph_3\overset{+}{P}\cdot CHR\cdot C(CO_2Me){:}\overset{-}{C}\cdot CO_2Me$

(XXVI)

$$R_3P{:}CR\cdot COR \longleftrightarrow R_3\overset{+}{P}\cdot CR{:}CR\cdot\overset{-}{O}$$

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[1] Part II, G. W. Brown, R. C. Cookson, and I. D. R. Stevens, *Tetrahedron Letters*, 1964, 1263.

[2] S. Trippett, *J. Chem. Soc.*, 1962, 4733.

[3] J. B. Hendrickson, C. Hall, R. Rees, and J. F. Templeton, *J. Org. Chem.*, 1965, **30**, 3312.

[4] H. J. Bestmann and O. Rothe, *Angew. Chem. Internat. Edn.*, 1964, **3**, 512.

[5] G. W. Brown, R. C. Cookson, I. D. R. Stevens, T. C. W. Mak, and J. Trotter, *Proc. Chem. Soc.*, 1964, 87.

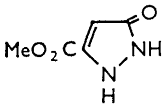
[6] T. C. W. Mak and J. Trotter, *Acta Cryst.*, 1965, **18**, 81.

[7] (*a*) S. Trippett, *Quart. Rev.*, 1963, **17**, 406; (*b*) A. W. Johnson, " Ylid Chemistry," Academic Press, New York, 1966; (*c*) H. J. Bestmann, *Angew. Chem., Internat. Edn.*, 1965, **4**, 583, 645, 830; (*d*) A. Maercker, *Org. Reactions*, 1965, **14**, 270; (*e*) R. F. Hudson, " Structure and Mechanism in Organophosphorus Chemistry," Academic Press, London, 1965.

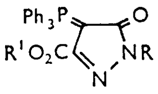
adducts, and in the modified properties of the ester substituents.

The adducts are crystalline solids which melt without decomposition and are indefinitely stable in air at room temperature. They do not react with aldehydes and ketones.

The adduct (XIII) undergoes none of the typical reactions of esters. Hydrolysis with methanolic potassium hydroxide gave only triphenylphosphine oxide; no carboxylic acid was detected. Reduction of the adduct (XIII) with lithium aluminium hydride followed by an alkaline work-up gave no alcohol, only triphenylphosphine oxide; formation of the phosphine oxide can only have resulted from phosphorus–carbon bond cleavage during the work-up. Hydrazine did not form a simple hydrazide when heated with the adduct (XIII). Three products were isolated from this reaction: the pyrazolone derivative (XXVII),[8] triphenylphosphine oxide, and the ylid (XXVIII), which was identified by spectroscopy and analysis. [Isolation of the pyrazolone was evidence against migration of the ester substituents in the adduct-forming reaction, during the structure determination of (XIII).]



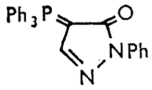
(XXVII)



(XXVIII) R = H, R' = Me

(XXIX) R = Ph, R' = Me

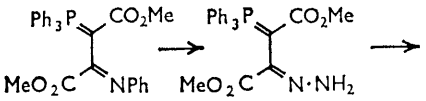
(XXX) R = Ph, R' = H



(XXXI)

The ylid (XXIX) was the only product when phenylhydrazine was heated with the adduct (XIII). It was hydrolysed to the acid (XXX), which decarboxylates cleanly at its melting-point to give the ylid (XXXI), and which was reconverted to the ester (XXIX) with diazomethane.

The mechanism of the reaction leading to the ylid (XXVIII) is probably as shown, since the interconversion of such carbonyl derivatives is unexceptional.[9]



→ (XXVIII)

Oxidation of the adduct (XIII) with hydrogen peroxide in glacial acetic acid gave only triphenylphosphine oxide. When (XIII) was pyrolysed in air at 220°, *N*-methylaniline was formed; no other product was isolated.

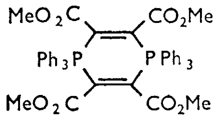
The resonance contributor (XXXII) plays a significant part in the properties of allylidenetriphenylphosphoranes,[7c] although the phosphorane (XXII) reacts with DMA by attack of the ylid α-carbon atom on the acetylene.[4] Substituted allylidenephosphoranes such as (XIII), as expected, did not react with DMA, but we anticipated that the greater electronegativity of the γ-nitrogen atom in the ylid (XXXIII)[10] would encourage reaction at that position.

$R_3\overset{+}{P}\cdot CH{:}CH\cdot\overset{-}{C}HR$
(XXXII)

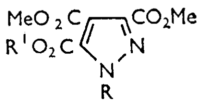
$Ph_3P{:}C(CO_2Me)\cdot N{:}NPh$
(XXXIII)

Two products isolated from the reaction of the azomethylenephosphorane (XXXIII) with an excess of DMA were identified as the ylid (XXXIV)[11] [assigned structure (XXXV) by Johnson and Tebby[12]] and the pyrazole triester (XXXVI). The mechanism remains in doubt, since attack by either the α-carbon or γ-nitrogen can give rise to the observed products, and must remain so until studies involving asymmetrically substituted acetylenes are made. Many acetylenes, such as mono- and di-phenylacetylene and methyl phenylacetylenecarboxylate are insufficiently electron-deficient to be attacked by the ylids.

$Ph_3P{:}C(CO_2Me)\cdot C(CO_2Me){:}C(CO_2Me)\cdot C(CO_2Me){:}PPh_3$
(XXXIV)

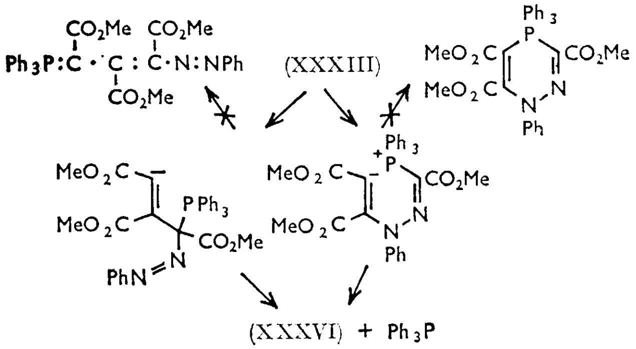


(XXXV)



(XXXVI) R = Ph, R' = Me

(XXXVII) R = H, R' = Et



The methylene hydrazonophosphorane (XXXVIII)[13] reacts with DMA to give the adduct (XL), the structure of which was assigned[1] on the basis of spectral and analytical data. Therefore there seems to be no participation by the γ-carbon atom in this reaction, in agreement with studies[14] on the reaction of methylenehydrazonophosphoranes with benzaldehyde.

$Ph_3P{:}N\cdot N{:}CRR^1$

(XXXVIII) RR^1 = 9-fluorenylidene
(XXXIX) R = H, $R^1 = CO_2Et$

$Ph_3P{:}C(CO_2Me)\cdot C(CO_2Me){:}N\cdot N{:}CRR^1$

(XL) RR^1 = 9-fluorenylidene
(XLI) R = H, $R^1 = CO_2Et$

$Ph_3P{:}N\cdot N{:}C(CO_2Et)\cdot C(CO_2Me){:}CH\cdot CO_2Me$
(XLII)

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[8] R. von Rothenberg, *Ber.*, 1893, **26**, 2053.

[9] G. E. P. Smith and F. W. Bergstrom, *J. Amer. Chem. Soc.*, 1934, **56**, 2095.

[10] G. Märkl, *Tetrahedron Letters*, 1961, 807.

[11] M. A. Shaw, J. C. Tebby, J. Ronayne, and D. H. Williams, *J. Chem. Soc.* (*C*), 1967, 944. The author is indebted to Dr. Williams for advance information.

[12] A. W. Johnson and J. C. Tebby, *J. Chem. Soc.*, 1961, 2126

[13] H. Staudinger and J. Meyer, *Helv. Chim. Acta*, 1919, **2**, 619.

[14] H. J. Bestmann and H. Fritzsche, *Chem. Ber.*, 1961, **94**, 2477.

Proof of the structure of the adduct from the methylenehydrazonophosphorane (XXXIX) and DMA in ether is more difficult to obtain, however; it is either (XLI), from attack by the α-nitrogen atom on the acetylene, or (XLII), from Michael addition by the γ-carbon atom. The n.m.r. spectrum of the adduct shows a singlet one-proton peak at τ 3·45; the parent methylenehydrazonophosphorane shows no olefinic proton outside the aromatic region. The i.r. spectrum favours the ylid (XLI); it shows a carbonyl absorption at 1660 cm.$^{-1}$, close to that found in the ylid (XL), whereas (XXXIX) shows a peak at 1680 cm.$^{-1}$. When heated in refluxing ethyl acetate the adduct decomposed to triphenylphosphine and the pyrazole triester (XXXVII).[15] The strongest evidence in favour of structure (XLI) for the adduct came from its reaction with hydrazine. The product was the ylid (XXVIII), a result easily explained by a mechanism similar to that invoked for the formation of (XXVIII) from the adduct (XIII).

$$\text{(XLI)} \xrightarrow{N_2H_4} Ph_3P{:}C(CO_2Me){\cdot}C(CO_2Me){:}N{\cdot}NH_2 + \underset{\text{(XLIII)}}{NH_2{\cdot}N{:}CH{\cdot}CO{\cdot}NH{\cdot}NH_2}$$

Under similar conditions the phosphorus–nitrogen bonds in the imines (I) and (XXXIX) were hydrolysed; the products were triphenylphosphine oxide and aniline, and triphenylphosphine oxide and the hydrazide (XLIII), respectively. The ylids (XX) and (XXXIV), which contain no such bond, were recovered after prolonged heating with hydrazine.

No degradation product containing a recognisable carbon skeleton could be obtained to support the assigned structure (XLI). Attempts to isolate a different adduct when the reaction was run in methanol[3] were thwarted by the rapid hydrolysis of the methylenehydrazonophosphorane (XXXIX) in protic solvents.

The iminohydrazonophosphorane (XLIV)[16] decomposes near 70°; below that temperature it does not react with DMA.

$$\underset{\text{(XLIV)}}{Ph_3P{:}N{\cdot}N{:}N{\cdot}SO_2{\cdot}C_6H_4{\cdot}p\text{-}Me}$$

The results presented show that the reactions of imino- and methylene-phosphoranes with DMA are only possible when the electron density on the ylid α-atom is quite large. Less electron-deficient acetylenes will not react with the ylids. Allylidene- and methylenehydrazono-phosphoranes react at the α-atom also, but there is scope for more studies on other conjugated ylids, and we hope to present results of these later.

EXPERIMENTAL

The u.v. spectra were run (95% ethanol) on a Unicam SP 700 instrument with 1 cm. silica or Supracil cells, and i.r. spectra were run on samples mulled in Nujol, with a Unicam SP 200 instrument; each i.r. spectrum was calibrated against a polystyrene reference. Iminophosphoranes were prepared by the literature method.[17]

Adduct from DMA and (p-*Nitrophenylimino*)*triphenylphosphorane*.—The phosphorane (V) (3·25 g., 8 mmoles) was heated in refluxing dry benzene with DMA (1·15 g., 8 mmoles) for 24 hr. (Other iminophosphoranes reacted much more readily). The solvent was removed and the *product* (3·58 g., 81%) crystallised from ethyl acetate, m. p. 244° (Found: C, 67·0; H, 4·4; N, 5·5; P, 5·9. $C_{30}H_{25}N_2O_6P$ requires C, 66·7; H, 4·7; N, 5·2; P, 5·7%).

Adduct from DMA and Iminotriphenylphosphorane.—The imine[18] (1·8 g., 6·5 mmoles) was dissolved in dry benzene (50 ml.) and, at 0°, was treated dropwise with the acetylene (0·92 g., 6·5 mmoles) in dry benzene (20 ml.) under nitrogen. After 12 hr. the solvent was removed at room temperature and the pale yellow *product* (2·1 g., 77%) crystallised from ethyl acetate, m. p. 170° (decomp.). The adduct was analysed as its perchlorate (Found: C, 55·6; H, 3·9; Cl, 6·8; N, 2·8; P, 6·1. $C_{24}H_{23}ClNO_8P$ requires C, 55·4; H, 4·5; Cl, 6·8; N, 2·7; P, 6·0%).

Adduct from DMA and the Iminophosphorane (III).[17]—(*p*-Acetylphenylimino)triphenylphosphorane (7·0 g., 18 mmoles) and the acetylene (2·5 g., 18 mmoles) were heated together in refluxing benzene for 10 min., and set aside overnight. Removal of the solvent *in vacuo* left a solid product which gave the *adduct* (6·57 g., 69%), m. p. 235° (from ethyl acetate) (Found: C, 71·6; H, 4·6; N, 2·8; P, 6·1. $C_{32}H_{28}NO_5P$ requires C, 71·5; H, 5·2; N, 2·6; P, 5·8%). No attempt was made in any similar reaction to find the best conditions. In general, equimolar quantities of the reagents were heated together in a refluxing solvent (usually benzene) for up to 24 hr. but usually for less than 1 hr. Yields ⩾67%.

Analyses: *ylid* (XIII) [from DMA and (I)] (Found: C, 72·5; H, 4·9; N, 3·0; P, 6·0. $C_{30}H_{26}NO_4P$ requires C, 72·7; H, 5·3; N, 2·8; P, 6·3%); *adduct* from DMA and the imine (IV) (Found: C, 69·7; H, 4·8; N, 2·7; P, 5·6. $C_{32}H_{28}NO_6P$ requires C, 69·4; H, 5·0; N, 2·5; P, 5·6%).

Adduct from DMA and Diphenylmethylenetriphenylphosphorane.—The phosphorane was prepared according to the literature,[19] but was not isolated. A solution in dry benzene was treated with a small excess of the acetylene, and the mixture was heated on a steam-bath for 5 min. The solvent was removed and the resulting oil was triturated with ether until it solidified. The *product* had m. p. 257° (from ethanol) (Found: C, 77·8; H, 5·4; P, 5·5. $C_{37}H_{31}O_4P$ requires C, 77·8; H, 5·5; P, 5·4%).

Adduct from DMA and 9-Fluorenylidenetriphenylphosphorane.—The phosphorane (5·1 g., 12 mmoles), prepared according to the literature,[20] dissolved in methylene chloride (250 ml.) was treated with the acetylene (3·4 g., 24 mmoles) in methylene chloride and was left at room temperature for 19 hr. The solvent was removed *in vacuo* and the residual oil was triturated with a small volume of ethanol to solidify. The *adduct* (6·6 g., 97%) had m. p. 210° (Found: C, 78·4; H, 4·9; P, 5·7. $C_{37}H_{29}O_4P$ requires C, 78·2; H, 5·1; P, 5·5%).

Adduct from DMA and the Azomethylenephosphorane (XXXIII).—The phosphorane[10] (2·0 g., 4·5 mmoles) and the ester (2·0 g., 13·5 mmoles) were mixed in methylene

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[15] E. Buchner, *Ber.*, 1889, **22**, 842.

[16] J. E. Franz and C. Osuch, *Tetrahedron Letters*, 1963, 841.

[17] L. Horner and H. Oediger, *Annalen*, 1959, **627**, 142.

[18] R. Appel and A. Hauss, *Chem. Ber.*, 1960, **93**, 407.

[19] D. D. Coffman and C. S. Marvel, *J. Amer. Chem. Soc.*, 1929, **51**, 3496.

[20] L. A. Pinck and G. E. Hilbert, *J. Amer. Chem. Soc.*, 1947, **69**, 723.

chloride and were set aside at room temperature for 2 days. Removal of the solvent left two products, cleanly separated when treated with boiling ethyl acetate (100 ml.). The residue, an orange solid (0·57 g., 31% based on phosphorane), was identified by m. p. and by comparison of i.r. spectra as (XXXIV). The ethyl acetate-soluble *pyrazole ester* (XXXVI) (1·0 g., 69% based on phosphorane) had m. p. 194° (from ethanol) (Found: C, 56·6; H, 4·6; N, 8·9. $C_{15}H_{14}N_2O_6$ requires C, 56·6; H, 4·4; N, 8·8%), $\lambda_{max.}$ 294 mμ (ε 16,700), ν_{CO} 1735, 1705, and 1645 cm.$^{-1}$.

Adduct from DMA and (9-*Fluorenylidenehydrazono*)-*triphenylphosphorane*.— The methylenehydrazonophosphorane [13] (1·83 g., 4 mmoles) was heated with the acetylene (3·2 g., 22 mmoles) in refluxing benzene for 27 hr. The solvent was removed and the orange *adduct* (1·64 g., 68%), washed with a little ether, had m. p. 225° (from ethanol) (Found: C, 74·5; H, 4·7; N, 5·0. $C_{37}H_{29}N_2O_4P$ requires C, 74·5; H, 4·9; N, 4·7%).

Adduct from DMA and Ethoxycarbonylmethylenehydrazonotriphenylphosphorane (XXXIX).[13]—The acetylene (5·0 g., 35 mmoles) in dry ether was added slowly to the phosphorane (11·7 g., 31 mmoles) in dry ether (200 ml.) at room temperature, and the mixture was left for 5 hr. The *product* (XLI) (13·8 g., 83%) was filtered off and purified (m. p. 140°) by precipitation from methylene chloride with light petroleum (b. p. 40—60°) at room temperature (Found: C, 65·0; H, 5·0; N, 6·0; P, 6·3. $C_{28}H_{27}N_2O_6P$ requires C, 64·8; H, 5·2; N, 5·4; P, 6·0%). No crystalline products were obtained from similar experiments run in methanol or in dioxan containing 5% deuterium oxide.

Reactions of the Adduct (XIII).—(a) *Hydrolysis*. Hydrolysis of the adduct with either saturated methanolic potassium hydroxide or concentrated hydrochloric acid gave triphenylphosphine oxide; other products were not identified.

(b) *Oxidation*. The adduct (2·0 g.) was dissolved in the minimum volume of glacial acetic acid, and hydrogen peroxide (35 ml.; 20 vol.) was added to this bright yellow solution, which was then heated on a steam-bath for 1 hr. The solvent was removed *in vacuo* and the residue was chromatographed on basic alumina (Spence H, 100—200 mesh). Some unchanged starting material (0·2 g.) was eluted with benzene, and triphenylphosphine oxide (0·3 g.) was eluted with chloroform. The oxide (27%), m. p. and mixed m. p. 154° (lit.,[21] 153°) (from cyclohexane) was the only product obtained.

(c) *Reduction with lithium aluminium hydride*. The adduct (2·0 g.) was dissolved in dry ether (150 ml.) at room temperature and, during 14 hr., was treated with lithium aluminium hydride (2·0 g.). Water (4·0 ml.) and 0·1N-sodium hydroxide solution (3 ml.) were added successively to the slurry, which was then extracted with ether. The extracts were dried ($MgSO_4$) and evaporated. The resulting oil was chromatographed on basic alumina (Spence H, 100—200 mesh) to give triphenylphosphine oxide (0·71 g., 63%) and minute traces of other, oily, products.

(d) *Pyrolysis*. The phosphorane (1·0 g.) was heated at 220° in a Woods metal bath for 6·75 hr. A liquid (0·15 g.) which appeared in the condenser above the reaction flask was identified as *N*-methylaniline (70%) (i.r. spectrum). The black tarry residue could not be separated into identifiable components by chromatography on basic alumina.

(e) *Reaction with hydrazine*. The adduct (3·0 g.) and hydrazine hydrate (0·3 ml.) were heated together in refluxing methanol (40 ml.) for 4·5 hr. The solvent was removed, and the oily product solidified. It was washed with hot benzene to leave the pyrazolone (XXVII), m. p. 225° (decomp.) (0·4 g.). The washings were evaporated and extracted with light petroleum (b. p. 40—60°); the extract yielded triphenylphosphine oxide (0·1 g.). The petroleum-insoluble fraction was the *ylid* (XXVIII) (0·06 g.). The residue was washed with ethyl acetate; the washings on evaporation gave more (XXVII) (0·05 g.) and triphenylphosphine oxide (0·6 g.), separated by their different solubilities in cyclohexane. Yields: Ph_3PO 41%, (XXVII) 59%, and (XXVIII) 2·5%. The pyrazolone was identified with an authentic sample (from hydrazine hydrate and DMA) by mixed m. p. and spectral comparisons. (XXVIII) had m. p. 284° (from ethanol) (Found: C, 68·3; H, 4·7; N, 7·2; P, 7·8. $C_{23}H_{19}N_2O_3P$ requires C, 68·6; H, 4·8; N, 7·0; P, 7·7%).

(f) *Reaction with phenylhydrazine*. The phosphorane (XIII) (24·75 g.) was heated in refluxing methanol (400 ml.) with a large excess of redistilled phenylhydrazine (25 ml.) for 30 hr. Most of the solvent was removed and the product separated out and was filtered off from the viscous red residue. This residue could not be separated into identifiable components when chromatographed down Woelm neutral alumina (activity 1). The crystalline *product* (XXIX) (11·5 g., 48%) had m. p. 290° (from ethanol) (Found: C, 73·2; H, 5·1; N, 5·9; P, 6·8. $C_{29}H_{23}N_2O_3P$ requires C, 72·8; H, 4·9; N, 5·9; P, 6·8%).

Alkaline Hydrolysis of (XXIX) *and Decarboxylation of* (XXX).—The phosphorane ester (XXIX) (4·45 g.) was hydrolysed with sodium hydroxide (4·0 g.) in refluxing methanol (150 ml.) for 2 hr. The mixture was acidified, evaporated, and extracted with chloroform from a Soxhlet thimble for 14 hr. The *acid* (4·3 g., 100%) had m. p. 202° (decarboxylates) (from ethanol).

This acid (0·875 g.) was decarboxylated during 5 min. *in vacuo* at 215°. The brown glassy *product* (0·55 g., 69%) had m. p. 241° (from acetone), ν_{CO} 1620 cm.$^{-1}$, $\lambda_{max.}$ 223 (ε 42,000), 259 (17,600), 265infl, and 273infl mμ (Found: C, 77·0; H, 5·6; N 6·6; P, 7·6. $C_{27}H_{21}N_2OP$ requires C, 77·1; H, 5·1; N, 6·6; P, 7·4%).

Reactions of the Adduct (XLI).—(a) *Pyrolysis*. The adduct (0·17 g.) was heated in refluxing ethyl acetate for 4 hr.; the originally deep yellow solution became colourless. The solvent was removed and the product mixture was fractionally crystallised from cyclohexane to give triphenylphosphine (0·07 g., 81%) and 3-ethoxycarbonyl-4,5-bismethoxycarbonylpyrazole (0·08 g., 93%), m. p. 100°, identical with a sample prepared from ethyl diazoacetate and DMA.

(b) *With hydrazine hydrate*. The adduct (1·8 g.) was set aside in hydrazine hydrate (1·0 ml.) and methanol (70 ml.) at room temperature for 24 hr. The solvent was removed, and the residue gave (XXVIII) (1·14 g., 82%), m. p. 284° (decomp.) (from ethanol).

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