OXIDATION OF TERVALENT ORGANIC COMPOUNDS OF PHOSPHORUS

By J. I. G. CADOGAN

(UNIVERSITY OF LONDON, KING'S COLLEGE)

ALTHOUGH the organic chemistry of phosphorus has been studied for over a century, widespread exploitation of the synthetical possibilities so revealed has occurred only recently. Tervalent organic compounds of phosphorus have proved to be particularly useful in this respect as a result of the high reactivity of the unshared pair of electrons and of the strength of the bonds which phosphorus forms with carbon, oxygen, sulphur, nitrogen, and the halogens, and it is doubtful whether another class of compounds exists which shows greater diversity in its chemical reactions. This Review is intended as an illustration of this, and is directed towards reactions of organic compounds of the type PXYZ, in which tervalent phosphorus is converted into quinquevalent phosphorus. Reactions of the so-called dialkyl phosphites or phosphonates, $(RO)_2P(O)H$, have not been included.

Reactions with Oxygen and Oxygen-containing Compounds.—(i) *With oxygen.* Of the reactions to be considered in this Review, those of tervalent organophosphorus compounds with air or oxygen are probably among the least satisfactorily documented. In general such compounds react more or less readily with oxygen to give the corresponding $\equiv P=O$ compounds, but in many cases, as a result of the vigour of the reaction, products have not been identified. It has been reported,[1] for example, that dialkyl alkylphosphonites, $(RO)_2PR$, are converted into the phosphonates by exposure to oxygen, but a thin film of the phosphonite on filter paper rapidly inflames in air.[2] Direct oxidation of tri-1-cyanoisopropyl[3] and tri-*p*-chlorophenyl[4] phosphites to the corresponding phosphates is moderately successful but fails with the simpler triethyl phosphite.[5] The monothiophosphites, $(RO)_2PSR$, on the other hand, react vigorously in air to give unidentified products.[6] Triphenylphosphine in benzene in contact with air and light forms triphenylphosphine oxide to the extent of 20% in five days A recent study[7] has led to the conclusion that in an oxygen-deficient atmosphere the phosphine, under photo-excitation, yields an unidentified

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[1] Razumov, Mukhacheva, and Sim-Do-Khen, *Bull. Acad. Sci. U.S.S.R.* (English Trans.), 1952, 797; see also *Chem. Abs.*, 1956, **50**, 7050.

[2] Arbusov and Rizpolozhenskii, *Doklady Akad. Nauk S.S.S.R.*, 1952, **83**, 581; *Chem. Abs.*, 1953, **47**, 3226.

[3] Kuznetsov and Valetdinov, *Trudy Kazan. Khim. Tekhnol. Inst. im S.M.Kirova,* 1956, **21**, 167; *Chem. Abs.*, 1957, **51**, 11,985.

[4] Kamai and Koshkina, *Trudy Kazan. Khim. Tekhnol. Inst. im S. M. Kirova*, 1953, **17**, 11; *Chem. Abs.*, 1956, **50**, 634.

[5] Cox and Westheimer, *J. Amer. Chem. Soc.*, 1958, **80**, 5441.

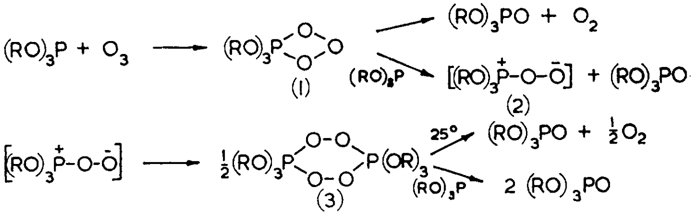
[6] Arbusov and Nikonorov, *Doklady Akad. Nauk S.S.S.R.*, 1948, **62**, 75; *Chem. Abs.*, 1949, **43**, 1004.

[7] Bartlett, Cox, and Davis, *J. Amer. Chem. Soc.*, 1961, **83**, 103.

long-lived but reactive product, possibly a peroxide, which is destroyed at the boiling point of benzene and reacts with an excess of oxygen to give the phosphine oxide but survives under limited oxygen supply. A similar peroxide has also been postulated as an intermediate in the explosive oxidation of triethylphosphine.[8] No definite evidence in favour of such intermediates is available, however.

Preparation of phosphates, phosphonates, and phosphine oxides by direct oxidation of the corresponding tervalent compounds has rarely been found to be of practical value and alternative methods are used.

(ii) *With ozone.* Triarylphosphines,[9] triaryl phosphites,[10] and trialkyl phosphites[10] in the presence of ozone afford excellent yields of the corresponding $\equiv P = O$ compounds. The mechanisms of the reaction with phosphites has been studied with the aid of nuclear magnetic resonance spectroscopy by Thompson[10] who, unexpectedly, observed that one, two, or in certain cases with triaryl phosphites, all three of the oxygen atoms in ozone could be utilised, depending on experimental factors. Although the mechanistic details have not been established, it appears that the primary product of the reaction of ozone with aryl or alkyl phosphites is a compound of type (1) which in the latter case has little stability even at low temperatures and rapidly decomposes into the phosphate and oxygen, giving an overall 1:1 ozone to phosphite stoicheiometry. In the presence of an excess of trialkyl phosphite the intermediate (1) is assumed to react, through attack by another molecule of phosphite rather than by decomposition, to give the trialkyl phosphate and a new zwitterion (2). This is also the preferred reaction with triaryl phosphites as a result of the high stability of, in this case, the intermediate (1). When the proportion of phosphite to ozone is 2:1 another mole of phosphate must be produced together with $\frac{1}{2}$ mole of oxygen. This can be accomplished by dimerisation to the cyclic peroxide (3) followed by decomposition as shown in Scheme 1.



SCHEME 1

Although many of the mechanistic details have not been satisfactorily established it is clear that the alternative zwitterion mechanism given

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[8] Engler, *Ber.*, 1897, **30**, 1670; Engler and Weissberger, *Ber.*, 1898, **31**, 3055; see also Thompson and Kelland, *J.*, 1933, 1231.

[9] Horner, Schaefer, and Ludwig, *Chem. Ber.*, 1958, **91**, 75.

[10] Thompson, *J. Amer. Chem. Soc.*, 1961, **83**, 845.

below will not accommodate all of Thompson's findings (Scheme 2).

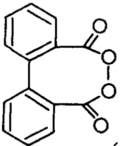
$$(RO)_3P + O_3 \rightarrow (RO)_3\overset{+}{P}\cdot O\cdot O\cdot\overset{-}{O} \rightarrow (RO)_3PO + O_2$$

$$(RO)_3\overset{+}{P}\cdot O\cdot O\cdot\overset{-}{O} + (RO)_3P \rightarrow (RO)_3\overset{+}{P}\cdot O\cdot\overset{-}{O} + (RO)_3PO$$

$$(RO)_3\overset{+}{P}O\cdot\overset{-}{O} \rightarrow (RO)_3PO + \tfrac{1}{2}O_2$$

SCHEME 2

(iii) *With peroxides, hydroperoxides, peresters, and ozonides.* The deoxygenation of dibenzoyl peroxide by triphenylphosphine to give benzoic anhydride and triphenylphosphine oxide was first observed by Challenger and Wilson,[11] and confirmed and extended by Horner and Jurgeleit[12] to include the reduction of perbenzoic acid to benzoic acid. Other diaroyl peroxides which have been successfully reduced by triphenylphosphine include phthaloyl and biphenoyl peroxides (4) which are converted into phthalic anhydride[13] and diphenic anhydride,[14] respectively.

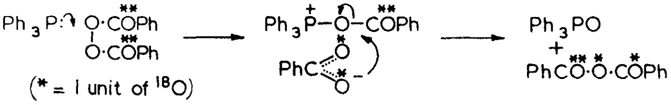


(4)

The mechanism of the reaction between triphenylphosphine and dibenzoyl peroxide has been studied by Denney and his co-workers using carbonyl-^{18}O labelled peroxide.[15] They established that the heavy isotope appeared in the resulting anhydride and not in the phosphine oxide, so that any mechanism involving transfer of carbonyl-oxygen to tervalent phosphorus can be eliminated. Examination of the isotopic distribution in the anhydride revealed that oxygen atom (α) contained an amount of ^{18}O equivalent to that in the corresponding oxygen atom in the original peroxide, while atoms (β) and (γ) each contained equal amounts of ^{18}O equivalent to half of the remaining ^{18}O. Such a distribution is compatible

$$PhC\overset{\alpha}{O}\cdot\overset{\beta}{O}\cdot C\overset{\gamma}{O}Ph$$

only with attack of the phosphine on peroxidic oxygen to give an ion pair which subsequently decomposes by nucleophilic displacement to give the observed products:



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[11] Challenger and Wilson, *J.*, 1927, 213.
[12] Horner and Jurgeleit, *Annalen*, 1955, **591**, 138.
[13] Horner and Brueggemann, *Annalen*, 1960, **635**, 27.
[14] Ramirez, Desai, and Mitra, *J. Amer. Chem. Soc.*, 1961, **83**, 492.
[15] Greenbaum, Denney, and Hoffmann, *J. Amer. Chem. Soc.*, 1956, **78**, 2563.

A free-radical path to the reaction products is discounted since no attack on the solvent occurs and it has been shown that foreign anions can participate in the reaction. In accordance with these conclusions it has been noted[12,16] that unsymmetrically substituted peroxides react with tributylphosphine to give the corresponding unsymmetrical anhydride. Denney and Greenbaum[16] have further shown by the use of oxygen-18 tracers that the phosphine displaces the more electropositive oxygen of the aroyl peroxide, ArCO·O·O·COAr′ as shown in the Table.

(1)(2)

Ar	Ar′	% Attack at O(1)
p-$NO_2 \cdot C_6H_4$	Ph	95
p-$NO_2 \cdot C_6H_4$	p-$MeO \cdot C_6H_4$	100
p-$Ph \cdot C_6H_4$	Ph	50

The 4-nitro-group has a marked effect on the position of attack which is due to the lowering of electron density at oxygen(1), and the effect is enhanced if a *p*′-methoxy-group is present. It is noteworthy that in these cases the ion-pair which is formed almost exclusively is the least stable thermodynamically, which suggests therefore that the process is kinetically controlled. That the reaction is random in the third case is in accord with negligible electronic effect in the ground state exerted by the *p*-phenyl group on the carboxyl group (Hammett's $\sigma = 0{\cdot}009$).

The reaction of dialkyl peroxides with triphenylphosphine has also been formulated by Horner and Jurgeleit[12] as a nucleophilic displacement on peroxidic oxygen giving rise to an ether thus:

$$Ph_3P + Bu^tO{\cdot}OBu^t \rightarrow [Ph_3\overset{+}{P}{\cdot}Bu^t\ Bu^t\overset{-}{O}] \rightarrow Ph_3PO + Bu^tOBu^t$$

Walling and Rabinowitz,[17] however, isolated bi-α-cumyl and triethyl phosphate from the products of the reaction of triethyl phosphite and di-α-cumyl peroxide conducted either thermally or photochemically at 25°. Since the isolation of bi-α-cumyl under these conditions is indicative of a homolytic process, Walling and Rabinowitz assumed that the reaction proceeded by way of an intermediate phosphoranyl radical thus:

$$RO{\cdot}OR \rightarrow 2RO{\cdot}$$

$$RO{\cdot} + (EtO)_3P \rightarrow (EtO)_3\dot{P}OR \rightarrow R{\cdot} + (EtO)_3PO$$

$$R{\cdot} + R{\cdot} \rightarrow R\text{–}R\ (R{\cdot} = Ph\dot{C}Me_2)$$

A similar process was also invoked in the case of the reduction of di-t-butyl peroxide (1 mole) by triethyl phosphite (4 moles) to give triethyl phosphate and products arising from the dimerisation and disproportionation of free t-butyl radicals. That products of decomposition of cumyl or

[16] Denney and Greenbaum, *J. Amer. Chem. Soc.*, 1957, **79**, 979.

[17] Walling and Rabinowitz, *J. Amer. Chem. Soc.*, 1959, **81**, 1243.

t-butyl radicals were not detected in these reactions is an indication that the reaction of triethyl phosphite with alkoxy-radicals is very rapid, and indeed Walling and Rabinowitz[17] calculate that for the overall reaction $Bu^tO\cdot + (EtO)_3P \rightarrow Bu^t\cdot + (EtO)_3PO$, $\Delta H = -30$ kcal. mole^{-1}. At lower ratios of phosphite to peroxide however, acetone, the product of decomposition of t-butoxy-radicals, was isolated. Since di-t-butyl ether was not detected in this reaction, Walling, Basedow, and Savas[18] re-investigated the reaction of triphenylphosphine with di-t-butyl peroxide, and found products consistent with the radical process previously postulated.[17] Walling's free-radical mechanism must be held to be correct since it is based on the sensitive gas–liquid chromatographic method of analysis, whereas Horner and Jurgeleit[12] reached their conclusion on the basis of a distillation temperature.

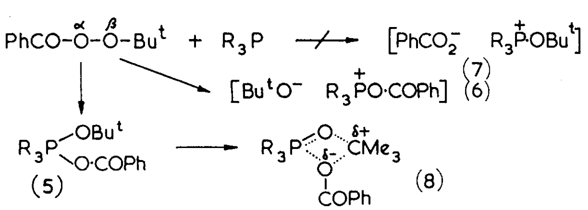
It is noteworthy that triethyl phosphite reacts with alkyl peroxides in the presence of air to give more than an equivalent of phosphate, a process attributed[17] to autoxidation involving recycling of alkyl radicals:

$$R\cdot + O_2 \rightarrow ROO\cdot$$

$$ROO\cdot + (EtO)_3P \rightarrow (EtO)_3\dot{P}O\cdot OR \rightarrow (EtO)_3PO + RO\cdot$$

$$RO\cdot + (EtO)_3P \rightarrow (EtO)_3PO + R\cdot \text{ etc.}$$

Unlike reactions involving alkyl peroxides, those between trialkyl- and triaryl-phosphines and t-butyl perbenzoate[19] resemble heterolytic reactions with diaroyl peroxides. The products of the former reaction, the corresponding phosphine oxide and t-butyl benzoate, are believed to occur by way of a transition state in which little separation of charge has taken place rather than by way of ion pairs such as (6). This conclusion follows from the observation that changes in solvating power of the solvent did not appreciably affect the rates of reaction of a series of *p*-substituted



peresters. Experiments involving perester carbonyl-labelled with oxygen-18 exclude displacement on the *β*-oxygen atom to give the ion pair (7) since the ester from its subsequent decomposition would contain equal amounts of oxygen-18 in both oxygen atoms. Formation of the ion pair (6) is also precluded because anion exchange with alcoholic solvents did not occur. The decomposition of the intermediate (5) into products is assumed to be

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[18] Walling, Basedow, and Savas, *J. Amer. Chem. Soc.*, 1960, **82**, 2181.

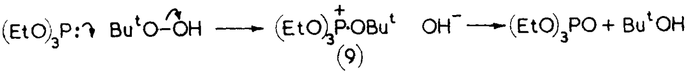
[19] Denney, Goodyear, and Goldstein, *J. Amer. Chem. Soc.*, 1961, **83**, 1727.

ionic involving ion pairs although the oxygen-18 results show that in benzene and ether completely free $Ph\cdot CO_2^-$ is not formed.

The reduction of hydroperoxides to alcohols by tertiary phosphines was first reported by Horner and Jurgeleit:[12]

$$R_3P + R'OOH \rightarrow R_3PO + R'OH$$

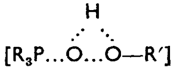
Walling and Rabinowitz[17] extended the reaction to trialkyl phosphites and formulated the extremely easy reaction as an ionic process:



Denney and his co-workers[20] in a more detailed investigation showed that the reduction of *trans*-9-decalyl hydroperoxide proceeded with retention of configuration and that reductions by triphenylphosphine carried out in ethanol–[^{18}O]water mixtures gave ^{18}O free phosphine oxide and alcohol. Provided that similar mechanisms operate for both phosphites and phosphines, intermediates such as (9) and (10) are therefore unlikely to be involved, since it would be necessary for them to decompose faster than hydroxyl ion will equilibrate with [^{18}O]water. Further, in the case of phosphites, decomposition of (9) might be expected to give two alcohols. Denny, Goodyear, and Goldstein[20] hold that the most reasonable mechanism involves either attack by the phosphine on the hydroxyl oxygen of the hydroperoxide to give an intermediate (11) which yields products by a simple proton transfer, or a simultaneous proton transfer *via* the transition state (12).

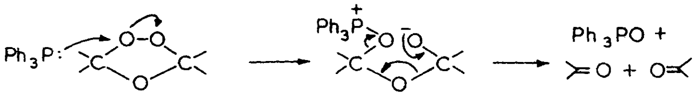
$[R_3\overset{+}{P}\cdot OR'\ HO^-]$ (10)

$[R_3\overset{+}{P}–OH\ R'O^-]$ (11)



(12)

The valuable reaction between ozonides and tertiary phosphines which gives carbonyl compounds[21] also probably proceeds by nucleophilic attack on oxygen:



(iv) *With oxides of nitrogen.* Staudinger and Hauser[22a] reported that nitrous oxide is reduced by triethylphosphine to nitrogen, while the oxidation of tertiary phosphines by dinitrogen tetroxide has also been said to be of preparative value.[12,22b] This reagent is also valuable in the

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[20] Denney, Goodyear, and Goldstein, *J. Amer. Chem. Soc.*, 1960, **82**, 1393.

[21] Staudinger and Criegee, *Annalen*, 1953, **583**, 1.

[22] (*a*) Staudinger and Hauser, *Helv. Chim. Acta*, 1921, **4**, 861; (*b*) Addison and Sheldon, *J.*, 1956, 2705.

preparation of trialkyl phosphates[5] and tetra-alkyl pyrophosphates[23] from the corresponding phosphites. The mechanism of its reaction with triethyl phosphite[5] has not been established but the major part of the reaction can be represented as

$$3(EtO)_3P + N_2O_4 \rightarrow 3(EtO)_3PO + N_2O$$

$$4(EtO)_3P + N_2O_4 \rightarrow 4(EtO)_3PO + N_2$$

Although it had been previously stated[5] that nitric oxide does not react with triethyl phosphite, this reaction has now been shown[24] to be a convenient method of oxidising phosphites to phosphates. As a result of the insensitivity of the reaction rate to the polarity and dielectric constant of the solvent, the reaction has been formulated as a radical process, although there is some doubt over the nature of the intermediate in the reaction:

$$NO\cdot + (EtO)_3P \xrightarrow{\text{slow}} (EtO)_3\dot{P}\cdot N{:}O \xrightarrow[\text{fast}]{NO\cdot} (EtO)_3PO + N_2O$$

$$\text{or}$$

$$(EtO)_3\dot{P}\cdot ON$$

Triethyl phosphite is also oxidised to a mixture of phosphate and tetraethyl pyrophosphate by nitrosyl chloride and nitryl chloride.[25] The mechanisms of these reactions are still obscure, although it is possible that formation of pyrophosphate is a side reaction:

$$(RO)_3P + Cl_2 \rightarrow RCl + (RO)_2P(O)Cl \xrightarrow{(RO)_3PO} (RO)_2P(O).O\cdot P(O)(OR)_2 + RCl$$

(v) *With amine* N-*oxides.* Phosphorus trihalides are now established[26] as excellent oxygen-acceptors for the reduction of pyridine *N*-oxides to pyridines. In general, substitution of halogen atoms in phosphorus trihalides by organic groups tends to impair the activity of the tervalent phosphorus atom as a reducing agent. Ramirez and Aguiar[27] noted without experimental details that the ease of reduction of pyridine *N*-oxide decreased in the series $PCl_3 > PhPCl_2 > Ph_2PCl \gg (PhO)_3P > (EtO)_3P \ggg Ph_3P > Bu_3P > Et_2PPh$, *i.e.*, reduction was retarded by the presence of electron-releasing groups attached to phosphorus. Contrary to the suggestion by Katritzky[28] these results indicate that the role of the tervalent phosphorus compound in the reduction is that of an electrophilic rather than a nucleophilic agent. In accord with this, 4-nitropyridine 1-oxide is reduced less readily by phosphorus trichloride than is pyridine 1-oxide.[29]

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[23] Samuel and Silver, *Chem. and Ind.*, 1961, 556.

[24] Kuhn, Doali, and Wellman, *J. Amer. Chem. Soc.*, 1960, **82**, 4792.

[25] Arbusov and Ukhvatova, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1958, 1395.

[26] See, for example, Ochai, *J. Org. Chem.*, 1953, **18**, 534.

[27] Ramirez and Aguiar, Amer. Chem. Soc., Abs. 134th Meeting, 1958, p. 42*N*; Aguiar, *Diss. Abs.*, 1960, **21**, 457.

[28] Katritzky, *Quart. Rev.*, 1956, **10**, 395.

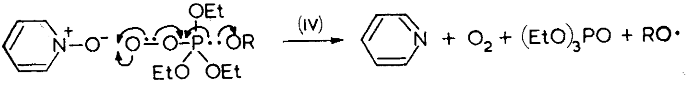
[29] Emerson, Ph.D. Thesis, University of London, 1960.

The low positions of triphenyl phosphite and phosphine in this reactivity sequence do not, however, appear to preclude their effective use as deoxygenating agents,[30,31] although, at the high temperatures (*ca.* 200°) required in the latter case, it is perhaps not surprising that an anomalous reaction occurred in the case of 4-nitropyridine 1-oxide—nitrous fumes were evolved and the fate of the remainder of the molecule could not be determined.[31]

A further demonstration of the complexities that sometimes arise in reactions of tervalent phosphorus compounds with *N*-oxides has been provided by Emerson and Rees, who observed[32] that pyridine *N*-oxide was rapidly reduced to pyridine by triethyl phosphite at room temperature in unpurified (*i.e.*, peroxidised) diethylene glycol diethyl ether in the presence of oxygen. These observations have been rationalised as follows:

$$\mathrm{RO{\cdot}OR} \xrightarrow[\mathrm{(I)}]{} \mathrm{2RO{\cdot}}$$

$$\mathrm{(EtO)_3P + RO{\cdot}} \xrightarrow[\mathrm{(II)}]{} \mathrm{(EtO)_3\dot{P}{\cdot}OR} \xrightarrow[\mathrm{(III)}]{O_2} \mathrm{(EtO)_3P(OR){\cdot}O{\cdot}O{\cdot}}$$



Stage (II) has been postulated in reactions between alkoxy-radicals and trialkyl phosphites,[17] and oxygen is regenerated in agreement with the finding that little is needed to maintain reaction. Little is known about the peroxides involved, although they are unlikely to be hydroperoxides, which react rapidly with phosphites,[17,20] and the formation of triethyl phosphate is only presumed to occur. Whatever the mechanistic details, it seems that this reaction is a further example of the high reactivity of trialkyl phosphites towards free radicals.

(vi) *With epoxides.* Both triethyl phosphite[33] and triphenylphosphine[34] smoothly reduce epoxides to the corresponding olefin. Boskin and Denney[35] noted that tributylphosphine reacted with *trans*-2,3-epoxybutane to give both *cis*- (72%) and *trans*-but-2-ene (28%) whereas the *cis*-epoxide gave *cis*- and *trans*-but-2-ene in the ratio of 19:81. These observations are only partly in accord with mechanisms proposed earlier,[33,34] which involve displacement by phosphorus on carbon, rather than oxygen, to give an intermediate (13) followed by rotation and bond

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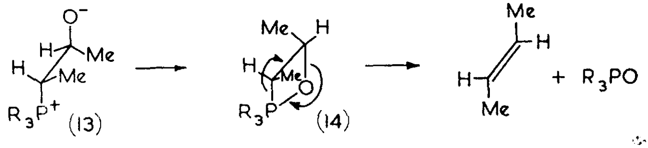
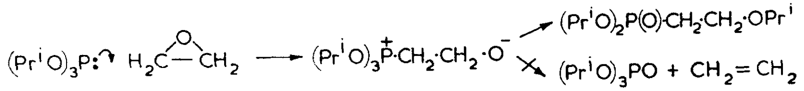
[30] Hamana, *J. Pharm. Soc. Japan*, 1955, **75**, 139; *Chem. Abs.*, 1956, **50**, 1818.
[31] Howard and Olszewski, *J. Amer. Chem. Soc.*, 1959, **81**, 1483.
[32] Emerson and Rees, *Proc. Chem. Soc.*, 1960, 418.
[33] Scott, *J. Org. Chem.*, 1957, **22**, 1118.
[34] Wittig and Haag, *Chem. Ber.*, 1955, **88**, 1654.
[35] Boskin and Denney, *Chem. and Ind.*, 1959, 330.

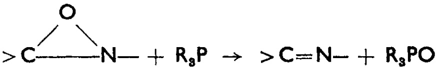
formation to give (14). Cleavage of (14) to give olefin and phosphine oxide then accounts for the bulk of the reaction but not for the minor product;



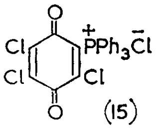
the latter requires attack of phosphorus directly on oxygen, although no other experimental evidence for this is available. The reaction of epoxides with trialkyl phosphites containing one or more secondary or tertiary alkyl groups is reported to give phosphonates rather than olefins and phosphates.[36] Clearly in this case the intermediate reacts by nucleophilic attack on an alkyl-carbon rather than by nucleophilic attack on phosphorus, thus:



A similar deoxygenation of oxazirans to imines has been reported[37] but has not been investigated in detail.


$$>C\overset{O}{—}N— + R_3P \rightarrow >C{=}N— + R_3PO$$

(vii) *With* p-*benzoquinones.* Schönberg and Ismail[38] first observed a colour on mixing triphenylphosphine and chloranil in chloroform and suggested structure (15) for the product, whereas the adduct from triethylphosphine and benzoquinone was formulated as (16).[39] This was later re-formulated as the phosphonium enolate (17).[40] Horner and his co-workers[41b] accepted the latter and advanced similar structures for the adducts of triphenylphosphine with *o*-benzoquinone and its tetrachloro-derivative.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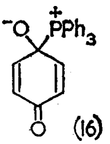
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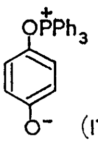
(17)

A re-examination of the reaction of triphenylphosphine and *p*-benzoquinone by Ramirez and Dershowitz[42] revealed that the adduct was in

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[36] Scott, U.S.P. 2,793,275; *Chem. Abs.*, 1951, 16,515.

[37] Horner and Jurgens, *Chem. Ber.*, 1957, **90**, 2184.

[38] Schönberg and Ismail, *J.*, 1940, 1374.

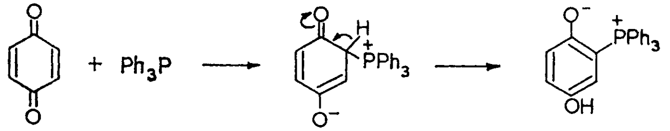
[39] Davies and Walters, *J.*, 1935, 1786.

[40] Schönberg and Michaelis, *Chem. Ber.*, 1936, **68**, 1080.

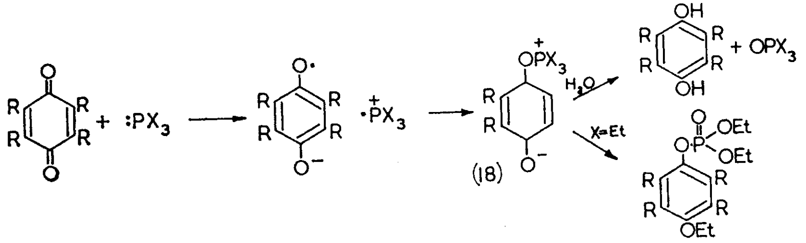
[41] (*a*) Horner and Spietschka, *Annalen*, 1955, **591**, 1; (*b*) Horner and Klupfel, *ibid.*, p. 69; (*c*) Hoffmann, Horner, and Hassel, *Chem. Ber.*, 1958, **91**, 58.

[42] Ramirez and Dershowitz, *J. Amer. Chem. Soc.*, 1956, **78**, 5614.

fact that produced by 1,4-addition to the conjugated system, and confirmation by synthesis of this structure was later provided by Horner and



his co-workers.[41c] Reactions of triphenylphosphine,[42] triphenyl phosphite,[43] and triethyl phosphite[43] with chloranil, and of triethyl phosphite with *p*-benzoquinone, 2,5-dichlorobenzoquinone, and 2,5-dimethylbenzoquinone take a different course[44] and are believed to involve initially the donation of one electron by the phosphorus compound to the quinone with the formation of a positive ion-radical exhibiting a strong electron-spin resonance signal. These reactions are exemplified by Scheme 3.

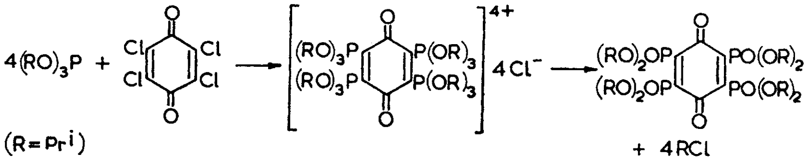


(R=H, Cl)
(X=EtO, PhO, and when R=Cl, Ph)

SCHEME 3

In all cases involving triethyl or trimethyl phosphite the zwitterion decomposes to give the corresponding monoalkylquinol phosphate. Hydrolysis of the zwitterion (18) occurs if the reactions are carried out in the presence of aqueous ethanol, excellent yields of the corresponding dihydroxybenzene and phosphate or phosphine oxide being obtained. The apparent difference in behaviour of benzoquinone and chloranil towards triphenylphosphine has been attributed[42] to the steric hindrance and higher oxidation–reduction potential of chloranil.

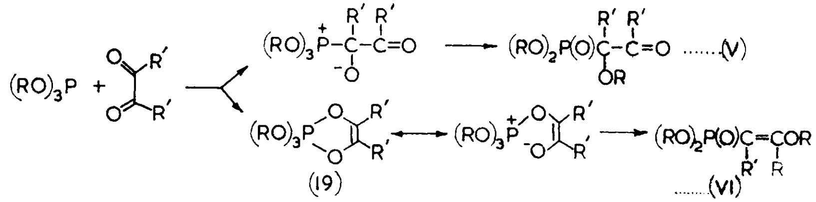
Phosphites containing secondary alkyl groups, however, react by C–P rather than O–P bond formation,[45] thus recalling their behaviour with epoxides described above:[36]



[43] Ramirez and Dershowitz, *J. Amer. Chem. Soc.*, 1959, **81**, 587.
[44] Ramirez, Chen, and Dershowitz, *J. Amer. Chem. Soc.*, 1959, **81**, 4338.
[45] Reetz, Powers, and Graham, Amer. Chem. Soc., Abs. 134th Meeting, 1958, p. 86*P*.

It is clear that slight changes in the structures of both the tervalent phosphorus compound and the quinone can bring about changes of mechanism, completely satisfactory accounts of which have yet to be given.

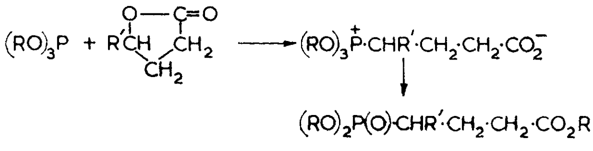
(viii) *With* o-*benzoquinone and α-diketones.* P–O rather than P–C bond formation was also originally favoured by Kukhtin[46] and by Birum and Dever[47] to account for the products of the reaction of α-diketones with trialkyl and triaryl phosphites (reaction VI).



The formulation (19) is also assumed for the adduct formed between *o*-quinones and phosphites and it is noteworthy that dealkylation to give the monoalkyl ether of the quinol phosphate apparently does not occur in this case.[41b,48] These adducts are attacked by oxygen to give the corresponding phosphate and the original diketone,[47,48] and by ozone to give peroxides such as biphenoyl peroxide (4).[14] The reactions of this peroxide have not been investigated and it seems likely that its decomposition in an inert solvent might lead to interesting products including, possibly, biphenylene.

The general agreement that reactions involving 1,2-diketones proceeded by P–O bond formation [reaction (VI)] has recently been questioned by Kukhtin and Orekhova[49] who have re-investigated the earlier results[46] and now conclude that P–C bonds are formed by reaction (V). Clearly, further investigation of these reactions is necessary.

(ix) *With lactones and anhydrides.* Lactones undergo ring scission with trialkyl phosphites:[50]



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[46] Kukhtin, *Doklady Akad. Nauk S.S.S.R.*, 1958, **121**, 426; *Chem. Abs.*, 1959, 1105.

[47] Birum and Dever, Amer. Chem. Soc., Abs. 134th Meeting, 1958, p. 101*P*.

[48] Ramirez and Desai, *J. Amer. Chem. Soc.*, 1960, **82**, 2652.

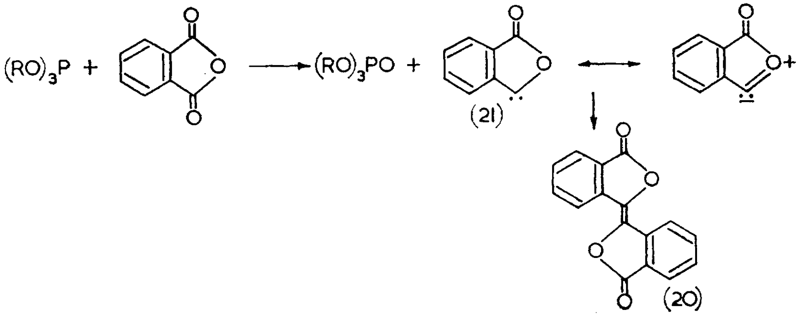
[49] Kukhtin and Orekhova, *Zhur. obshchei Khim.*, 1960, **30**, 1208; *Chem. Abs.*, 1961, 358.

[50] McConnell and Coover, *J. Amer. Chem. Soc.*, 1956, **78**, 4453; Kreutzkamp, *Naturwiss.*, 1956, **43**, 81.

while acetic anhydride similarly gives a mixture of an acylphosphonate and alkyl acetate:[51]

$$(RO)_3P + Ac_2O \rightarrow (RO)_3\overset{+}{P}{\cdot}Ac\ Ac\overset{-}{O} \rightarrow (RO)_2P(O){\cdot}Ac + AcOR$$

With phthalic anhydride and trialkyl phosphites, however, a startling difference in behaviour has been reported,[52a] the main product being 3,3′-biphthalidylidene (20) (70%). It was suggested that reaction involves attack of the phosphorus atom of the ester on a carbonyl oxygen of the anhydride to give a resonance-stabilised carbene (21) which reacts by dimerisation to give product (20), although attempts to confirm the existence of the carbene by carrying out the reaction in the presence of olefins as carbene traps were unsuccessful.



Pertinent to these conclusions, however, is the recent observation that triphenylphosphine itself reacts with carbenes to give methylenephosphoranes (see below),[52b] thus:

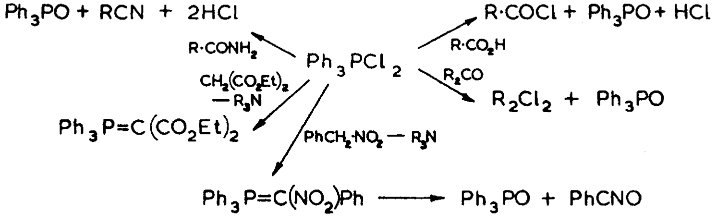
$$CH_2Cl_2 + BuLi \rightarrow :CHCl \xrightarrow{Ph_3P} Ph_3P{:}CHCl + LiCl + BuH$$

If the key to the differences in behaviour of simple anhydrides and phthalic anhydride lies in the possibility of formation of resonance-stabilised carbenes, then the reaction has interesting possibilities as a source of such intermediates.

(x) *With simple oxidising agents.* Such reactions are of interest only as preparative methods for the formation of phosphates, phosphine oxides, etc. Among the reagents which have been used with varying success are manganese dioxide and mercuric oxide,[53] lead tetra-acetate,[54] hydrogen peroxide,[55] and aqueous chloramine-T.[56]

[51] Kamai and Kukhtin, *Akad. Nauk S.S.S.R., Trudy I-Oi Konferents* 91; *Chem. Abs.*, 1958, **52**, 241.
[52] (*a*) Ramirez, Yamanaka, and Basedow, *J. Amer. Chem. Soc.*, 1961, **83**, 173; (*b*) Seyferth, Grim, and Read, *ibid.*, 1960, **82**, 1510.
[53] Ayres and Rydon, *J.*, 1957, 1109.
[54] Dimroth and Lerch, *Angew. Chem.*, 1960, **72**, 751.
[55] Stetter and Steinacker, *Chem. Ber.*, 1952, **85**, 451; but see ref. 5.
[56] Cadogan and Moulden, *J.*, 1961, 3079.

Reactions with Halogens and Halogen-containing Compounds.—(i) While trialkyl phosphites react with chlorine and bromine to give the corresponding phosphorohalidates,[57] tertiary phosphines[58] and triaryl phosphites[59] give the corresponding 1:1 adducts. Triphenylphosphine dihalides react with carboxylic acids to give acyl halides, with aldehydes and ketones to give the corresponding *gem*-dihalides, and with amides to give nitriles,[58b] while reaction with compounds containing an active methylene group result in the formation of the corresponding methylenephosphoranes (see below):[58c]



Triphenyl phosphite dihalides and the related triphenyl phosphite alkylhalides $[(PhO)_3\overset{+}{P}R\ \overset{-}{Hal}]$ have been shown to be useful in the preparation of alkyl halides, thus:[59]

$$(PhO)_3PHal_2 + ROH \rightarrow (PhO)_2P(O)Hal + RHal + PhOH$$

(ii) *With alkyl halides: the Arbusov–Michaelis and Wittig reactions.* The reaction of trialkyl phosphites and related compounds with simple alkyl halides was discovered by Michaelis and Kaehne[60] and explored later by Arbusov.[61] It is one of the most widely used methods of forming C–P bonds. Its simplest form is the reaction of an alkyl halide with a trialkyl phosphite to give a dialkyl alkylphosphonate:

$$(RO)_3P + R'X \rightarrow \underset{(22)}{[(RO)_3\overset{+}{P}R'\ \overset{-}{X}]} \rightarrow (RO)_2P(O)R' + RX$$

The mechanism receives support from (*a*) the isolation[60] of the intermediate (22) on reaction of triphenyl phosphite and methyl iodide, (*b*) physicochemical evidence,[62] and (*c*) the observations that triphenyl phosphite methiodide on treatment with optically active octan-2-ol gave inverted 2-iodo-octane,[63] and that the analogous reaction of active

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[57] McCombie, Saunders, and Stacey, *J.*, 1945, 380; cf. ref. 64.

[58] (*a*) Michaelis, *Annalen*, 1901, **315**, 43; (*b*) Horner, Oediger, and Hoffmann, *ibid.*, 1959, **626**, 26; (*c*) Horner and Oediger, *Chem. Ber.*, 1958, **91**, 437.

[59] Rydon, *Chem. Soc. Special Publ.*, No. 8, 1957, p. 61.

[60] Michaelis and Kaehne, *Ber.*, 1898, **31**, 1048.

[61] Arbusov, *J. Russ. Phys. Chem. Soc.*, 1906, **38**, 687.

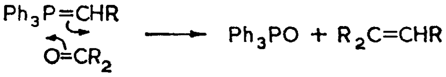
[62] Arbusov and Fuzhenkova, *Doklady Akad. Nauk S.S.S.R.*, 1957, **113**, 1269; **114**, 89.

[63] Landauer and Rydon, *J.*, 1953, 2224.

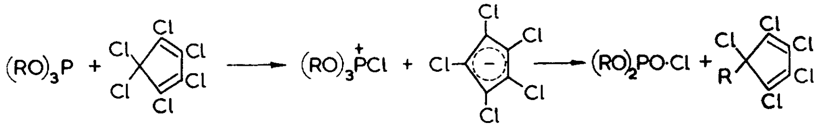
trioctyl phosphite with bromine to give bromo-octane also proceeded with inversion.[64] The reaction of alkyl halides with tertiary phosphines results in the formation of stable phosphonium halides such as (23) which on treatment with a strong base give methylenephosphoranes. Further reaction

$$\underset{(23)}{Ph_3\overset{+}{P}\cdot CHR_2\,\overset{-}{X}} \xrightarrow{PhLi} Ph_3P{=}CHR \longleftrightarrow Ph_3\overset{+}{P}\cdot\overset{-}{C}HR + LiX$$

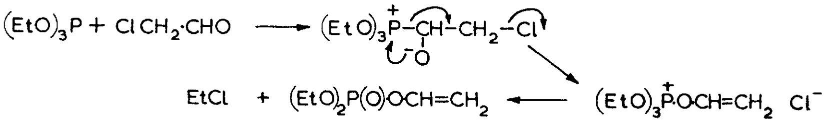
of the latter with carbonyl compounds provides a valuable route to olefins and is known as the Wittig reaction,[65] which has been reviewed.[66]



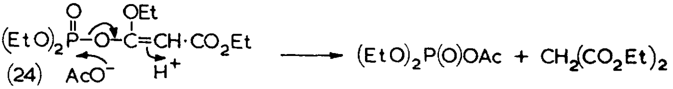
It is noteworthy that the reaction between trialkyl phosphites and hexachlorocyclopentadiene proceeds by nucleophilic displacement on allylic halogen followed by dealkylation by the cyclopentadienide ion:[67]



α-Halogeno-aldehydes do not react with trialkyl phosphites in the expected fashion to give phosphonates.[68,69] The reaction appears to involve nucleophilic attack of the phosphite on the carbonyl group, elimination of chloride ion, and subsequent dealkylation, *e.g.*:



Bromomalonic ester and triethyl phosphite similarly react to give the ester (24) which has been shown to be a very reactive phosphorylating agent for carboxylic, sulphonic, and phosphoric acids,[70] and also for adenylic acid:[71]


(24)

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[64] Gerrard and Jeacocke, *J.*, 1954, 3647.

[65] Wittig and Schollkopf, *Chem. Ber.*, 1954, **87**, 1318.

[66] Levisalles, *Bull. Soc. chim. France*, 1958, 1021; Schollkopf, *Angew. Chem.*, 1959, **71**, 260.

[67] Mark, *Tetrahedron Letters*, 1961, **9**, 295.

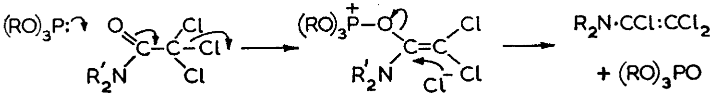
[68] Allen and Johnson, *J. Amer. Chem. Soc.*, 1955, **77**, 2871.

[69] Perkow, Krokow, and Knoevenagel, *Chem. Ber.*, 1955, **88**, 662; Perkow, *Chem. Ber.*, 1954, **87**, 755.

[70] Cramer and Gartner, *Chem. Ber.*, 1958, **91**, 704.

[71] Cramer, *Angew. Chem.*, 1960, **72**, 236.

In a related reaction between trialkyl phosphites or phosphines and *NN*-disubstituted trichloroacetamides,[72] it is probable that attack on the carbonyl oxygen occurs first, followed by formation of the corresponding phosphate and a trichlorovinylamine, thus:



Extensions of the reaction of α-halogeno-aldehydes with phosphites, the Perkow reaction, as well as those of the Arbusov reaction, have been reviewed.[71,73]

(iii) *With polyhalogenomethanes.* Methylene and ethylene dibromide react normally with trialkyl phosphites in the Arbusov reaction, one or both halogens being replaced according to the ratio of reactants,[74] but more recently side reactions have been discovered with the aid of gas–liquid chromatography.[75] Carbon tetrachloride reacts with phosphites, at temperatures lower than those required for Arbusov reactions of alkyl halides, to give high yields of diethyl trichloromethylphosphonate.[76] The reaction was first formulated as a radical-chain process by Kamai and Kharrasova,[77] and this was confirmed by Griffin.[78] Further confirmation of the homolytic nature of the reaction has recently been provided by Burn and Cadogan[79] who noted that in a reaction between triethyl phosphite and carbon tetrachloride in the presence of oct-1-ene, initiated by ultraviolet light or peroxides, characteristic free-radical addition of the halide to olefin also occurred. On this basis alternative reaction schemes can be

$$\text{A}\quad\left\{\begin{array}{l}\cdot CCl_3 + (RO)_3P \rightarrow (RO)_3\dot{P}\cdot CCl_3\\ (RO)_3\dot{P}\cdot CCl_3 + CCl_4 \rightarrow [(RO)_3P\cdot CCl_3]^+Cl^- + \cdot CCl_3\\ [(RO)_3P\cdot CCl_3]^+Cl^- \rightarrow (RO)_2P(O)\cdot CCl_3 + RCl\end{array}\right.$$

$$\text{B}\quad\left\{\begin{array}{l}\cdot CCl_3 + (RO)_3P \rightarrow (RO)_3\dot{P}\cdot CCl_3 \rightarrow (RO)_2P(O)\cdot CCl_3 + R\cdot\\ R\cdot + CCl_4 \rightarrow RCl + \cdot CCl_3\end{array}\right.$$

SCHEME 4

formulated. Under Scheme 4B diethyl ββ-dimethylphenethyl and benzyl diethyl phosphite would be expected to produce free ββ-dimethylphenethyl ($Ph\cdot CMe_2\cdot CH_2$) and benzyl radicals. The former would be expected to

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[72] Speziale and Freeman, *J. Amer. Chem. Soc.*, 1960, **82**, 903.
[73] Crofts, *Quart. Rev.*, 1958, **12**, 341; Lichtenhaler, *Chem. Rev.*, 1961, **61**, 607.
[74] Ford-Moore and Williams, *J.*, 1947, 1465.
[75] Garner, Chapin, and Scanlon, *J. Org. Chem.*, 1959, **24**, 532.
[76] Kamai and Egorava, *Zhur. obshchei Khim.*, 1946, **16**, 1521.
[77] Kamai and Kharrasova, *Zhur. obshchei Khim.*, 1957, **27**, 953.
[78] Griffin, *Chem. and Ind.*, 1958, 415.
[79] Burn and Cadogan, unpublished observation.

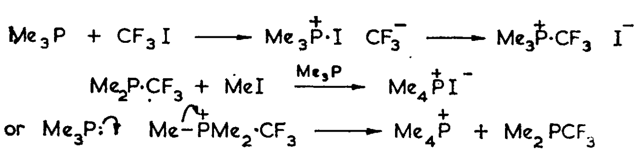
rearrange in part to the more stable αα-dimethylphenethyl radical ($\mathrm{PhCH_2{\cdot}CMe_2{\cdot}}$) and both radicals would be detectable by the products of their dimerisation and disproportionation,[80] whereas the latter would be expected to dimerise to give bibenzyl. Cadogan and Foster[81] showed that such products were not obtained from radical-induced reactions of carbon tetrachloride with benzyl and ββ-dimethylphenethyl phosphites, hence strong evidence was produced in favour of Scheme 4A. These workers pointed out, however, that with a suitable choice of substituents it is possible that the trichloromethylphosphoranyl radical might *decompose* as in Scheme 4B, since conditions are known under which the related thiophosphoranyl radical [$\mathrm{(RO)_3P{\cdot}SR'}$] can react according to both schemes, as discussed below. Bromotrichloromethane and carbon tetrabromide react extremely vigorously with trialkyl phosphites[82] also by a radical process.[83] Chloroform does not react with triethyl phosphite even under drastic conditions,[84] unless benzoyl peroxide is present, when the product, according to an unsubstantiated report without experimental detail,[83] is diethyl dichloromethylphosphonate:

$$\mathrm{CHCl_3 + (EtO)_3P \rightarrow (EtO)_2P(O)CHCl_2 + EtCl}$$

This reaction is assumed to be homolytic but in view of the heterolytic nature of the reaction between dibenzoyl peroxide and triphenylphosphine this conclusion requires further experimental substantiation. Bromoform and triphenylphosphine similarly react by a radical-chain process to give dibromoethyltriphenylphosphonium bromide:[85]

$$\mathrm{Ph_3P + {\cdot}CHBr_2 \rightarrow Ph_3\dot{P}{\cdot}CHBr_2 \xrightarrow{CHBr_3} [Ph_3\overset{+}{P}{\cdot}CHBr_2\ \overset{-}{Br}] + {\cdot}CHBr_2}$$

By analogy with these reactions, trifluoroiodomethane, which readily undergoes free-radical reactions, would be expected to react by a radical-chain process with tervalent phosphorus. Its reaction with trimethyl phosphine is described as a nucleophilic process, however[86] (Scheme 5).



SCHEME 5

Reactions with Sulphur and Sulphur-containing Compounds.—(i) Tervalent phosphorus has a high affinity for free and bound sulphur,

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[80] Urry and Kharasch, *J. Amer. Chem. Soc.*, 1944, **66**, 1438; Winstein and Seubold, *ibid.*, 1947, **69**, 2916; Smith and Anderson, *ibid.*, 1960, **82**, 656.

[81] Cadogan and Foster, *J.*, 1961, 3071.

[82] Kamai, *Doklady Akad. Nauk S.S.S.R.*, 1951, **79**, 795; *Chem. Abs.*, 1952, **46**, 6081.

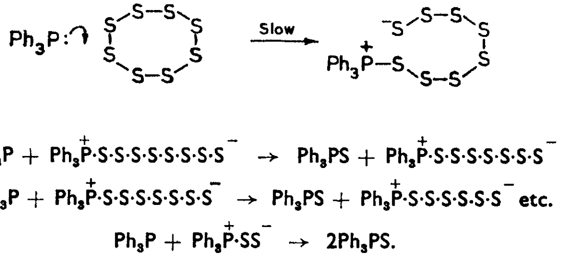
[83] Griffin, Amer. Chem. Soc., Abs. of 135th Meeting, 1959, p. 69*O*.

[84] Crofts and Kosolapoff, *J. Amer. Chem. Soc.*, 1953, **75**, 5738.

[85] Ramirez and McKelvie, *J. Amer. Chem. Soc.*, 1957, **79**, 5829.

[86] Haszeldine and West, *J.*, 1956, 3631.

presumably because its size and high polarisability enable it to utilise the empty orbital of sulphur more effectively than is the case for oxygen or nitrogen. Indeed sulphur adds readily to phosphines and phosphites in air to give the corresponding sulphide rather than the oxide,[87] $PX_3 + S \rightarrow SPX_3$. The uncatalysed reaction between freshly prepared triphenylphosphine and common monoclinic sulphur (S_8) under nitrogen has a second-order rate constant which is increased by ionising solvents and by the presence of electron-releasing groups in the phosphine,[88] and has many characteristics in common with quaternary ammonium salt formation in the Menschutkin reaction. Bartlett and Meguerian[88] have therefore concluded that the reaction proceeds by successive nucleophilic displacement reactions of sulphur on sulphur (Scheme 6).



$$Ph_3P + Ph_3\overset{+}{P}{\cdot}S{\cdot}S{\cdot}S{\cdot}S{\cdot}S{\cdot}S{\cdot}S{\cdot}\overset{-}{S} \rightarrow Ph_3PS + Ph_3\overset{+}{P}{\cdot}S{\cdot}S{\cdot}S{\cdot}S{\cdot}S{\cdot}S{\cdot}\overset{-}{S}$$

$$Ph_3P + Ph_3\overset{+}{P}{\cdot}S{\cdot}S{\cdot}S{\cdot}S{\cdot}S{\cdot}S{\cdot}\overset{-}{S} \rightarrow Ph_3PS + Ph_3\overset{+}{P}{\cdot}S{\cdot}S{\cdot}S{\cdot}S{\cdot}S{\cdot}\overset{-}{S} \text{ etc.}$$

$$Ph_3P + Ph_3\overset{+}{P}{\cdot}S\overset{-}{S} \rightarrow 2Ph_3PS.$$

SCHEME 6

In contrast to the above clear picture a number of puzzling catalytic phenomena occur if a solution in benzene of triphenylphosphine which has been kept in light in a limited supply of oxygen is used.[89] Under these conditions a product is formed which causes strong autocatalysis in subsequent reaction with sulphur and is destroyed at the boiling point of benzene in the presence of an excess of oxygen. The formation of this product is attended by the development of paramagnetic resonance absorption, consistent with the presence of the triphenylphosphonium cation radical, $Ph_3P^{\cdot+}$, which has also been postulated as an intermediate in reactions of triphenylphosphine with quinones (see above). The reaction with sulphur is also complicated by the presence of cocatalysts in the sulphur. It is noteworthy in this respect that both hexasulphur and light-produced polysulphur react very much more rapidly than does octasulphur with triphenylphosphine, and Bartlett, Cox, and Davis[89] have shown that hexa- and octa-sulphur differ by a factor of 25,000 in their reactivity toward triphenylphosphine at 7·35°. Rates of reaction of sulphur with other tervalent phosphorus compounds have not been reported.

[87] See, for example, Hoffmann and Moore, *J. Amer. Chem. Soc.*, 1958, **80**, 1150; Strecker and Spitaler, *Ber.*, 1926, **59**, 1772.

[88] Bartlett and Meguerian, *J. Amer. Chem. Soc.*, 1956, **78**, 3710.

[89] Bartlett, Cox, and Davis, *J. Amer. Chem. Soc.*, 1961, **83**, 103.

(ii) *With thiols.* An unusual light-catalysed reaction in which thiols are reduced to the corresponding hydrocarbons by trialkyl phosphites was first observed by Hoffmann and his co-workers in 1956:[90]

$$(EtO)_3P + RSH \rightarrow (EtO)_3PS + RH$$

That the reaction was homolytic was later established by Walling and Rabinowitz who concluded that direct reaction of thiyl radicals with tervalent phosphorus occurred to give an intermediate quadricovalent phosphoranyl radical, of a type similar to that formed in similar reactions with alkoxyl[17] and trichloromethyl radicals[77,78] in which phosphorus has undergone an expansion of its outer shell to accommodate nine electrons:

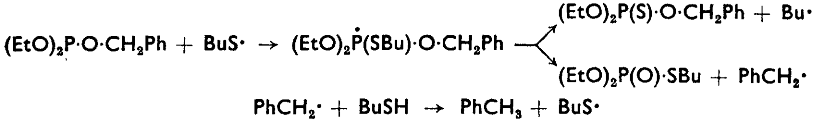
$$R'S\cdot + (RO)_3P \rightarrow (RO)_3\dot{P}{\cdot}SR' \rightarrow (RO)_3PS + R'\cdot$$
$$R'\cdot + R'SH \rightarrow R'H + R'S\cdot$$

Since the reaction occurs very rapidly with strongly electron-accepting thiyl and alkoxyl radicals, but not with alkyl radicals,[17] it is plausible, as Walling and Rabinowitz point out, that the reaction derives considerable driving force from the contribution of polar structures to the transition state:

$$RS\cdot\ P(OEt)_3 \longleftrightarrow R\bar{S}\ \cdot\overset{+}{P}(OEt)_3$$

Subsequent breakdown of the phosphoranyl radicals in turn must derive its driving force from the very strong[91] P=O or P=S bonds in the product.

Walling, Basedow, and Savas[18] investigated the possibility that R–OP fission might occur in favourable cases. The product obtained from benzyl diethyl phosphite, which could in theory give the resonance-stabilised benzyl radical and butane-1-thiol, did in fact contain toluene (3%) as well as benzyl diethyl phosphorothionate, indicating that the reactions shown in Scheme 7 had probably occurred, although the detection of the equivalent amount of *S*-butyl diethyl phosphorothioate was not



$$(EtO)_2P{\cdot}O{\cdot}CH_2Ph + BuS\cdot \rightarrow (EtO)_2\dot{P}(SBu){\cdot}O{\cdot}CH_2Ph \begin{cases} \nearrow (EtO)_2P(S){\cdot}O{\cdot}CH_2Ph + Bu\cdot \\ \searrow (EtO)_2P(O){\cdot}SBu + PhCH_2\cdot \end{cases}$$
$$PhCH_2\cdot + BuSH \rightarrow PhCH_3 + BuS\cdot$$

SCHEME 7

reported. The small amount of PO–R fission even in this favourable case is in keeping with the higher strength of the bonds involved. Decomposition of the phosphoranyl radical formed from triethyl phosphite and thiophenol [$(EtO)_3\dot{P}{\cdot}SPh$] is strongly retarded, probably as a result of the small resonance energy of the resultant phenyl radical and the possibility of additional strengthening of the Ph–S bond due to overlap between the

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[90] Hoffmann, Ess, Simmons, and Hanzel, *J. Amer. Chem. Soc.*, 1956, **78**, 6414.
[91] Chernick, Pedley, and Skinner, *J.*, 1957, 1851.

π-electron system and the unshared electrons of the sulphur. In this case largely ionic alkylation takes place and only 15% of the products are formed by the free-radical route.

$$\begin{array}{lll} \mathrm{PhSH + (EtO)_3P} & \rightarrow & \mathrm{PhSEt + (EtO)_2POH\ (Ionic{:}\ 85\%)} \\ & \searrow & \mathrm{PhH + (EtO)PS\ (Radical{:}\ 15\%)} \end{array}$$

The free-radical reduction of thiols to hydrocarbons can also be effected by trialkylphosphines.[18]

The features of the radical-chain reactions of thiols and carbon tetrachloride with trialkyl phosphites have recently been combined by Cadogan and his co-workers[81,92] to provide a new route to phosphorothiolates. Thus, triethyl phosphite on reaction with an equimolar mixture of carbon tetrachloride and butane-1-thiol gives diethyl trichloromethylphosphonate (22%), triethyl phosphorothionate (18%), and *S*-butyl diethyl phosphorothioate (60%). The major product is believed to arise as shown in Scheme 8, whereas the thionate arises by competing decomposition of the *S*-butyl phosphoranyl radical (reaction IX), and the trichloromethylphosphonate by the previously described reaction of the trichloromethyl radical with triethyl phosphite (Scheme 9). Substitution of bromotrichloromethane, which is a better chain-transfer agent, for carbon tetrachloride,[93] should favour the chain-transfer step (VII) at the expense of the decomposition (IX). In accord with this the use of this reagent in the presence of an excess of butane-1-thiol, which reacts with the trichloromethyl radicals produced in (VII), thus depressing the formation of trichloromethylphosphonate by reaction (X), results in an almost quantitative conversion of triethyl phosphite into *S*-butyl diethyl phosphorothioate. These experiments are significant since they indicate that the thiophosphoranyl radical can react by *abstraction* of a halogen atom from polyhalogenomethanes as well as by decomposition (reaction IX).

$$\mathrm{(EtO)_3P + Bu^nS\cdot \rightarrow (EtO)_3\dot{P}\cdot SBu^n}$$

$$\mathrm{(EtO)_3\dot{P}\cdot SBu^n + CCl_4 \rightarrow [(EtO)_3P\cdot SBu^n]^+Cl^- + \cdot CCl_3} \quad \ldots\ldots \quad \mathrm{(VII)}$$

$$\mathrm{[(EtO)_3P\cdot SBu^n]^+Cl^- \rightarrow (EtO)_2P(O)\cdot SBu^n + EtCl} \quad \ldots\ldots\ldots \quad \mathrm{(VIII)}$$

SCHEME 8

$$\mathrm{(EtO)_3\dot{P}\cdot SBu^n \rightarrow (EtO)_3PS + Bu^n\cdot} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad \mathrm{(IX)}$$

$$\mathrm{(EtO)_3P + \cdot CCl_3 \rightarrow (EtO)_3\dot{P}\cdot CCl_3 \xrightarrow[CCl_4]{} (EtO)_2P(O)CCl_3 + \cdot CCl_3 + EtCl} \quad \ldots \quad \mathrm{(X)}$$

SCHEME 9

[92] Bunyan and Cadogan, unpublished observations.

[93] See for example, Cadogan and Hey, *Quart. Rev.*, 1954, **8**, 308.

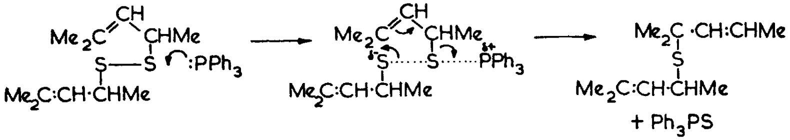
(iii) *With disulphides.* The desulphurisation of disulphides to sulphides by reaction with tertiary phosphines,[94] is generally accepted[95] to be an ionic process:

$$Ph_3P + R{\cdot}S{\cdot}S{\cdot}R \rightarrow Ph_3\overset{+}{P}SR\ R\overset{-}{S} \rightarrow Ph_3PS + RSR$$

and the reaction has recently been extended by Moore and his co-workers[96] to include the reduction of tetrasulphides to disulphides:

$$2Ph_3P + RS_4R \rightarrow 2Ph_3PS + RS{\cdot}SR$$

These workers also report that the reaction of triphenylphosphine with di-1,3-dimethylbut-2-enyl) disulphide proceeds by way of an allylic rearrangement, thus providing an example of the rather rare S_Ni' reaction.



Reduction of disulphides also occurs if trialkyl phosphites are used at high temperatures,[97,98] and in this case even diethyl disulphide, which is resistant to reduction by triphenylphosphine,[94] is reduced:

$$(EtO)_3P + EtS_2Et \rightarrow (EtO)_3\overset{+}{P}{\cdot}SEt\ Et\overset{-}{S} \rightarrow (EtO)_2P(O)SEt + EtSEt$$

The reaction is analogous to the Arbusov reaction and it is noteworthy that *O*- rather than *S*-dealkylation occurs, as is the case in related systems.[99]

An alternative reaction, similar to that between phosphite and thiols, in which triethyl phosphorothionate (106%) and the di-isobutyl monosulphide (92%) are formed has been shown to occur at lower temperatures in the presence of free-radical initiators:[17]

$$BuS{\cdot}SBu \rightarrow 2\,BuS{\cdot}$$

$$BuS{\cdot} + (EtO)_3P \rightarrow (EtO)_3\dot{P}{\cdot}SBu \rightarrow (EtO)_3PS + Bu{\cdot}$$

$$Bu{\cdot} + BuS{\cdot}SBu \rightarrow BuSBu + BuS{\cdot}$$

Small amounts of by-products included isobutane and isobutene formed by disproportionation of isobutyl radicals:

$$BuSBu \rightarrow BuS{\cdot} + Bu{\cdot}$$

The additional butanethiyl radicals so formed also react with phosphite, thus accounting for the greater-than-theoretical yield of phosphorothionate

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[94] Schönberg and Barakat, *J.*, 1949, 892; Challenger and Wilson, *J.*, 1950, 26.

[95] Parker and Kharasch, *Chem. Rev.*, 1959, **59**, 621.

[96] Evans, Higgins, Moore, Porter, Saville, Smith, Trego, and Watson, *Chem. and Ind.*, 1960, 897.

[97] Jacobsen, Harvey, and Jensen, *J. Amer. Chem. Soc.*, 1955, **77**, 6064.

[98] Poshkus and Herweh, *J. Amer. Chem. Soc.*, 1957, **79**, 4245.

[99] Burn and Cadogan, *J.*, 1961, 5532.

which is observed. The possibility that the high-temperature reaction between phosphites and disulphides involves the free-radical formation of thionate followed by isomerisation of thionate to the observed thiolate $[(EtO)_3PS \rightarrow (EtO)_2P(O)SEt]$[100] can be discounted.[17]

The homolytic reaction of disulphides with phosphites has been adapted to provide a new route to thioesters by performing the reaction under a high pressure of carbon monoxide[18] when the following series of reactions occurs:

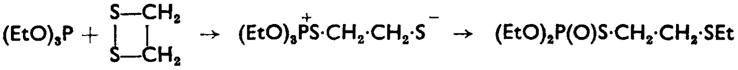
$$RS\cdot + (RO)_3P \rightarrow (RO)_3\dot{P}\cdot SR \rightarrow (RO)_3PS + R\cdot$$

$$R\cdot + CO \rightarrow R\cdot\dot{C}O$$

$$R\cdot\dot{C}O + RS\cdot SR \rightarrow R\cdot CO\cdot SR + RS\cdot, \text{ etc.}$$

The related reaction with thiols which would give aldehydes occurs only to the extent of 1—2%, however, as a result of the high rate of the reaction $R\cdot + RSH \rightarrow RH + RS\cdot$ compared with $R\cdot + RS\cdot S\cdot R \rightarrow RSR + RS\cdot$.

Cyclic disulphides have been reported[101] to react with trialkyl phosphites to give thiolates such as diethyl *S*-2-ethylthioethyl phosphorothioate, the insecticide "Systox". The concomitant formation of the thiono-isomer in these cases is extremely puzzling, however, in view of the foregoing discussion and of the known higher stability of the thiolate isomer in this case.[102]



$$(EtO)_3P + \begin{array}{l} S-CH_2 \\ |\quad\ \ | \\ S-CH_2 \end{array} \rightarrow (EtO)_3\overset{+}{P}S\cdot CH_2\cdot CH_2\cdot \overset{-}{S} \rightarrow (EtO)_2P(O)S\cdot CH_2\cdot CH_2\cdot SEt$$

The reaction has also been extended to include compounds of the type $(EtO)_2P(O)S_2Bu$ and $[(EtO)_2P(O)S]_2$.[103] In these cases the anion produced in the initial displacement is bidentate and can react to give two products (Scheme 10). The thiopyrophosphate formed in the latter reaction has the

$$(EtO)_3P + (EtO)_2P(O)S_2Bu \rightarrow (EtO)_3\overset{+}{P}\cdot SBu \quad (EtO)_2P\cdot O\overset{-}{S} \rightarrow$$
$$(EtO)_2P(O)\cdot SBu + (EtO)_2P(O)\cdot SEt + (EtO)_3PS$$
$$(EtO)_3P + [(EtO)_2P(O)S]_2 \rightarrow (EtO)_3\overset{+}{P}\cdot S\cdot P(O)(OEt)_2 \quad (EtO)_2P(O)\overset{-}{S} \rightarrow$$
$$(EtO)_2P(S)O\cdot P(O)(OEt)_2 + (EtO)_2P(O)SEt + (EtO)_3PS$$

SCHEME 10

thiono (P–S) rather than the thiolo (P–S–P) arrangement.[104]

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[100] See, for example, Burn, Cadogan, and Foster, *Chem. and Ind.*, 1961, 591.
[101] McConnell, U.S.P. 2,865,950; *Chem. Abs.*, 1959, 12,181.
[102] Fukoto and Metcalf, *J. Amer. Chem. Soc.*, 1954, **76**, 5103.
[103] Michalski and Wieczorkowski, *Bull. Acad. polon. Sci., Cl. III*, 1957, **5**, 917; *Chem. Abs.*, 1958, 6157.
[104] Jones, Katritzky, and Michalski, *Proc. Chem. Soc.*, 1959, 321.

(iv) *With thiolsulphonates and thiosulphinates.* Alkyl but not aryl esters of aliphatic and aromatic thiosulphonic acids react readily with trialkyl phosphites to give *OOS*-trialkyl phosphorothioates and the corresponding alkyl sulphinates:[105]

$$\mathrm{(EtO)_3P + R{\cdot}SO_2{\cdot}SR' \rightarrow (EtO)_3\overset{+}{P}{\cdot}SR'\ \ RSO_2^{\,-} \rightarrow (EtO)_2P(O)SR' + R{\cdot}SO_2Et}$$

The isomeric alkyl ethyl sulphone, probably arising from the bidentate nature of the sulphinic anion which is capable of forming *O*- or *S*-derivatives,[106] sometimes appears as a by-product. The corresponding reaction with aryl esters of aromatic thiosulphonic acids, *e.g.*, $\mathrm{PhS{\cdot}SO_2Ph}$, is more complicated and involves three processes, (*a*) the formation of diethyl *S*-phenylphosphorothioate and ethyl benzenesulphinate as described above, (*b*) the reduction of thiosulphonate to give diphenyl disulphide and triethyl phosphate, and (*c*) the slower reaction of diphenyl disulphide with phosphite to give the *S*-phenylphosphorothioate and ethyl phenyl sulphide,[98] as discussed in a previous section. Similar reductions of aryl thiosulphonates and of diphenyl disulphone to diaryl disulphides by tertiary phosphines have also been reported.[107]

In a related investigation, Carson and Wong[108] note that alkyl or aryl thiosulphinates react with triphenylphosphine to give high yields of disulphide and phosphine oxide, but they are undecided whether heterolytic or homolytic reaction paths are being followed. In view of the foregoing discussion of reactions of thiyl radicals with tervalent phosphorus, however, it is unlikely that Carson and Wong's homolytic formulation (below) is correct because phosphine sulphide is not formed in their reaction:

$$\mathrm{RSO{\cdot}SR \rightarrow R\dot{S}O + RS{\cdot}}$$

$$\mathrm{R\dot{S}O + Ph_3P \rightarrow RS{\cdot} + Ph_3PO}$$

$$\mathrm{RS{\cdot} + RS{\cdot} \rightarrow RS{\cdot}SR}$$

They alternatively invoke polarisation of the bivalent sulphur atom by the sulphoxide group followed by nucleophilic attack by the phosphine, while direct reaction of *electrophilic* phosphorus on the sulphoxide oxygen atom, in a manner analogous to the reaction of *N*-oxides discussed above, is not considered.

(v) *With episulphides.* That trisubstituted phosphites and phosphines could be converted into the corresponding sulphides by reaction with episulphides has been known since 1949,[109] and Davis [110] and Schuetz and

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[105] Michalski and Wieczorkowski, *Bull. Acad. polon. Sci., Cl. III*, 1956, **4**, 279, redescribed in *J.*, 1960, 1665.

[106] Gilman, "Organic Chemistry", Wiley, New York, 1947, Vol. I, 916.

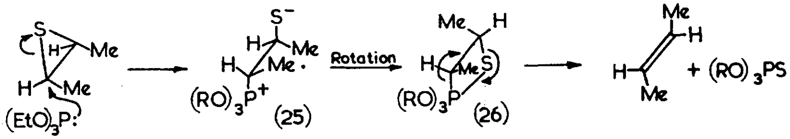
[107] (*a*) Horner and Hoffmann, *Angew. Chem.*, 1956, **68**, 473; (*b*) Horner and Nickel, *Annalen*, 1955, **597**, 20.

[108] Carson and Wong, *J. Org. Chem.*, 1961, **26**, 1467.

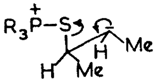
[109] Culvenor, Davies, and Heath, *J.*, 1949, 282.

[110] Davis, *J. Org. Chem.*, 1958, **23**, 1767.

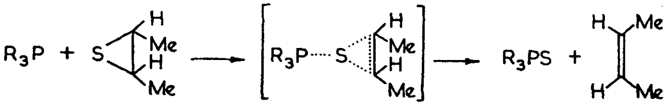
Jacobs[111] later showed that the episulphide was thereby converted into the parent olefin. Since the reaction therefore formally corresponds to that between epoxides and tervalent phosphorus compounds,[33,34] Schuetz and Jacobs[111] concluded that the reactions proceeded by similar mechanisms. That this is incorrect has been shown by Neureiter and Bordwell[112] and by Denney and Boskin.[113] The former workers demonstrated that the reactions of triethyl phosphite with *cis*-2,3-epithiobutane and the *trans*-isomer proceeded with 97% stereoselective removal of sulphur from the three-membered ring with the formation of *cis*- and *trans*-but-2-ene, respectively. This result rules out a mechanism involving nucleophilic attack by phosphorus on carbon to give intermediates such as (25) and (26), a path favoured for the comparable reaction of epoxides, since this would



lead to the opposite stereochemical result. In view of this Neureiter and Bordwell preferred to formulate the reaction as a nucleophilic attack on sulphur but were not prepared to exclude a short-lived dipolar ion $(EtO)_3\overset{+}{P}\cdot S\cdot CHMe\cdot\overset{-}{C}HMe$. Denney and Boskin,[113] on the other hand, confirmed the stereospecificity of the reaction, and considered a dipolar intermediate of this type to be unlikely because it would be required to decompose to the products faster than rotation about the central C–C bond can occur, and such rotation would have led to a mixture of olefins:



Further, a 16-fold alteration in the dielectric constant of the solvent resulted in very little change in the rate of the reaction which was bimolecular and of first order in each component. The results are therefore most consistent with the existence of a transition state which has little or no charge separation, formed by a smooth displacement reaction at the sulphur atom:



It was considered possible, however, that desulphurisation of a less sterically hindered episulphide might proceed by nucleophilic attack on

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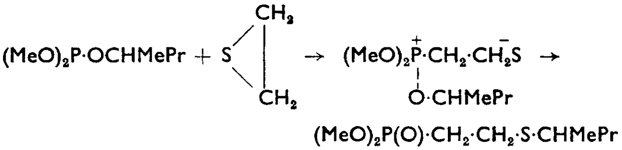
[111] Schuetz and Jacobs, *J. Org. Chem.*, 1958, **23**, 1799.
[112] Neureiter and Bordwell, *J. Amer. Chem. Soc.*, 1959, **81**, 578.
[113] Denney and Boskin, *J. Amer. Chem. Soc.*, 1960, **82**, 4736; cf. ref. 35.

carbon, but the rate constants for the reaction with 1,2-epithiobutane in solvents of different dielectric constant closely corresponded to those found for *cis*- and *trans*-2,3-epithiobutane so no change of mechanism is indicated. Attack by tervalent phosphorus on sulphur in episulphides and on carbon in epoxides may be rationalised[114] by the following: (*a*) sulphur is more electropositive and polarisable than oxygen, (*b*) the C–S dipole is small, and (*c*) bivalent sulphur in disulphides and sulphonyl halides is known to be susceptible to attack by nucleophilic reagents in displacement-type reactions.[95] A similar situation has been observed between chlorine and bromine in reactions with phenyl-lithium; whereas 1,2-dichlorocyclohexane reacts with elimination of hydrogen chloride (nucleophilic attack on hydrogen), the 1,2-dibromide reacts by elimination of bromine (nucleophilic attack on bromine).[115] The mechanism of the desulphurisation of episulphides given above does not account for the formation of dimethyl s-pentylthioethylphosphonate from the corresponding phosphite and ethylene sulphide, which apparently proceeds by nucleophilic attack on carbon:[36]



Why attack should take place at carbon rather than sulphur in this case is not clear.

(vi) *With sulphenyl chlorides, sulphonyl chlorides, and organic thiocyanates.* Trialkyl phosphites and related compounds react very rapidly with both aliphatic and aromatic sulphenyl halides at —70° to give the corresponding thiolates,[116] probably by way of an Arbusov intermediate:

$$(EtO)_3P + RSCl \rightarrow (EtO)_3\overset{+}{P}{\cdot}SR\ \overset{-}{Cl} \rightarrow (EtO)_2P(O){\cdot}SR + EtCl$$

By analogy with reactions of triphenyl phosphite with disulphides already described, the corresponding reaction with an alkanesulphenyl chloride might have been expected to yield the thionate, thus:

$$(PhO)_3P + EtSCl \rightarrow (PhO)_3\overset{+}{P}{\cdot}SR\ \overset{-}{Cl} \rightarrow (PhO)_3PS \rightarrow EtCl$$

In practice the course of this reaction is obscure since triphenyl phosphate (100%) is reported to be formed.[117] With arenesulphenyl chlorides[117,118]

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[114] Cf. Bordwell, Anderson, and Pitt, *J. Amer. Chem. Soc.*, 1954, **76**, 1082.

[115] Wittig and Henborth, *Ber.*, 1944, **17**, 306.

[116] (*a*) Gilbert and Clough, U.S.P. 2,690,450; *Chem. Abs.*, 1955, 11,682; (*b*) Morrison, *J. Amer. Chem. Soc.*, 1955, **77**, 181; (*c*) *idem*, *J. Org. Chem.*, 1956, **21**, 705; (*d*) Asinger, Thiel, and Schafer, *Annalen*, 1960, **637**, 146.

[117] Petrov, Sokolskii, and Polees, *Zhur. obshchei Khim.*, 1956, **26**, 3387; *Chem. Abs.*, 1957, 9473.

[118] Poshkus and Herweh, *J. Amer. Chem. Soc.*, 1957, **79**, 4245.

the following reaction, the mechanism of which is also not yet established, occurs:

$$(PhO)_3P + 2PhSCl \rightarrow PhS{\cdot}SPh + (PhO)_3PCl_2$$

The reaction appears to occur in two stages, probably through the intermediate $[(PhO)_3\overset{+}{P}{\cdot}SPh\ \overset{-}{Cl}]$, since passage of moist air through the reaction mixture produces triphenyl phosphate. A similar reaction has been reported with triphenylphosphine.[119]

In the presence of free-radical initiators, the reaction of tervalent phosphorus with sulphenyl halides might be expected to give the corresponding thionate and halide, although this has not yet been realised experimentally:

$$(RO)_3P + R'S{\cdot} \rightarrow (RO)_3\dot{P}{\cdot}SR' \rightarrow (RO)_3PS + R'{\cdot}$$

$$R' + R'SCl \rightarrow R'Cl + R'S{\cdot}$$

Similarly, the corresponding nitrile and phosphorothiolate are obtained in good yields from reactions of trialkyl phosphites with aryl and alkyl thiocyanates.[120] The former also react in a predictable fashion with tertiary phosphines:[121]

$$(RO)_3P + R'SCN \rightarrow (RO)_3\overset{+}{P}{\cdot}SR'\ \overset{-}{CN} \rightarrow (RO)_2P(O){\cdot}SR' + RCN$$

$$Et_3P + EtSCN \rightarrow Et_3\overset{+}{P}SEt\ \overset{-}{CN} \xrightarrow{Et_3P} Et_3PS + Et_4\overset{+}{P}\ \overset{-}{CN}$$

Although the products of the reactions of sulphonyl chlorides with phosphites are known, their modes of formation have not yet been established. Trialkyl esters[116a,122] react according to the following equation:

$$3(EtO)_3P + R{\cdot}SO_2{\cdot}Cl \rightarrow (EtO)_2P(O){\cdot}SR + 2(EtO)_3PO + EtCl$$

The formation of phosphorothiolate suggests that reduction of the sulphonyl chloride to sulphenyl chloride first occurs, followed by reaction with more phosphite, although reduction of the as yet unknown sulphonate $(EtO)_2P(O){\cdot}SO_2R$ which could be a transient intermediate cannot be entirely ruled out. Poshkus and Herweh's isolation[118] of diphenyl disulphide as well as the phosphate after reaction of triphenyl phosphite and benzenesulphonyl chloride points to the intermediate formation of benzenesulphenyl chloride but the genesis of other products is still uncertain. Uncertainty is also associated with the corresponding reaction with triphenylphosphine:[107b]

$$6(PhO)_3P + 2Ph{\cdot}SO_2Cl \rightarrow 5(PhO)_3PO + PhCl + PhS_2Ph \rightarrow (PhO)_2PCl$$

$$3Ph_3P + Ph{\cdot}SO_2Cl \rightarrow \text{An adduct} \xrightarrow{^{-}OH} PhS_2Ph + Ph_3PO + PhSH$$

$$2Ph_3P + Ph{\cdot}SO_2Cl \rightarrow \text{An adduct} \xrightarrow{^{-}OH} Ph{\cdot}SO_2H + Ph_3PO + PhS_2Ph$$

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[119] Morrison, Amer. Chem. Soc., Abs. 134th Meeting, 1958, p. 87*P*.

[120] Michalski and Wieczorkowski, *Bull. Acad. polon. Sci., Cl. III*, 1956, **4**, 4729; *Roczniki Chem.*, 1959, **33**, 105; Sheppard, *J. Org. Chem.*, 1961, **26**, 1460.

[121] Hofmann, *Annalen*, 1861, *Suppl.*, 53.

[122] Hoffmann, Moore, and Kagan, *J. Amer. Chem. Soc.*, 1956, **78**, 6413.

(vii) *With chlorides and oxychlorides of sulphur.* Sulphur monochloride and dichloride react with phosphites according to Scheme 11. Poshkus

$$S_2Cl_2 + 3(RO)_3P \rightarrow 2(RO)_3PS + RCl + (RO)_2P(O)Cl \qquad (R = \text{alkyl}^{116b})$$
$$\text{or } 2(RO)_3PS + (RO)_3PCl_2 \qquad (R = \text{aryl}^{124})$$
$$SCl_2 + 2(RO)_3P \rightarrow (RO)_3PS + RCl + (RO)_2P(O)Cl \qquad (R = \text{alkyl}^{123})$$
$$\text{or } (RO)_3PS + (RO)_3PCl_2 \qquad (R = \text{aryl}^{124})$$

SCHEME 11

and his co-workers[124] favour radical reaction paths (Scheme 12) for the reactions with triphenyl phosphite, mainly because the reactions occur readily in petrol at low temperatures. It is fair to state, however, that no

$$(ArO)_3P + SCl_2 \rightarrow (ArO)_3\dot{P}Cl + ClS\cdot$$
$$ClS\cdot + (ArO)_3P \rightarrow (ArO)_3\dot{P}SCl \xrightarrow{(ArO)_3P} (ArO)_3PS + (ArO)_3\dot{P}Cl$$
$$(ArO)_3\dot{P}Cl + SCl_2 \rightarrow (ArO)_3PCl_2 + ClS\cdot$$
$$(ArO)_3\dot{P}Cl + S_2Cl_2 \rightarrow (ArO)_3PCl_2 + ClS_2\cdot \xrightarrow{(ArO)_3P} (ArO)_3\dot{P}\cdot S_2Cl$$
$$(ArO)_3\dot{P}S_2Cl \rightarrow (ArO)_3PS + \cdot SCl$$
$$\cdot SCl + S_2Cl \rightleftharpoons SCl_2 + ClS_2\cdot$$

SCHEME 12

experimental evidence in favour of these otherwise plausible mechanisms has so far been advanced.

Similar radical intermediates are invoked to account for the reactions of triphenyl phosphite with thionyl and sulphuryl chlorides:[124]

$$(PhO)_3P + SO_2Cl_2 \text{ (or } SOCl_2) \rightarrow (PhO)_3P + SOCl_2 \text{ (or } SCl_2)$$

Elucidation of the mechanisms of these and related reactions of phosphites[125] which give sulphur dioxide, alkyl chloride, and the dialkyl phosphorochloridate, has not yet been achieved.

Reactions with Compounds having Reactive Nitrogen-containing Groups.—(i) *With azides.* Both tertiary phosphines[126] and triesters[127] react with azides by displacement of nitrogen to give imines, $R_3P + R'N_3 \rightarrow [R_3P{\cdot}N{:}N{\cdot}NR'] \rightarrow R_3P{:}NR' + N_2$, and in some cases isolation of the intermediate has been achieved.[128] The phosphinimines are particularly

[123] Poshkus and Herweh, *Chem. and Ind.*, 1961, 1316.

[124] Poshkus, Herweh, and Haas, *J. Amer. Chem. Soc.*, 1958, **80**, 5022.

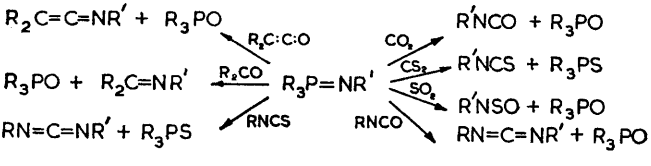
[125] Poshkus and Herweh, Amer. Chem. Soc., Abs. 136th Meeting, 1959. p. 30*N*; *J. Amer. Chem. Soc.*, 1957, **79**, 6127.

[126] Staudinger and Hauser, *Helv. Chim. Acta*, 1921, **4**, 861.

[127] Kabachnik and Gilyarov, *Izvest. Akad. Nauk S.S.S.R.*, *Otdel. khim. Nauk*, 1956, 790; *Chem. Abs.*, 1957, 1823.

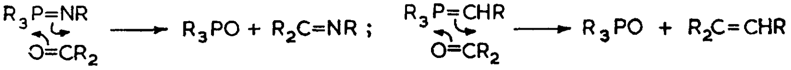
[128] Horner and Gross, *Annalen*, 1955, **591**, 117.

useful synthetical intermediates since they readily react with a variety of unsaturated compounds (Scheme 13). The Wittig reaction of carbonyl



SCHEME 13

compounds with methylenephosphoranes[65] can be considered to be an extension of these reactions which all probably proceed by way of four-membered transition states:



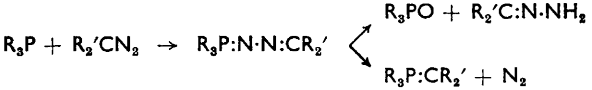
$$\begin{matrix}R_3P{=}NR\\ O{=}CR_2\end{matrix} \longrightarrow R_3PO + R_2C{=}NR\ ; \quad \begin{matrix}R_3P{=}CHR\\ O{=}CR_2\end{matrix} \longrightarrow R_3PO + R_2C{=}CHR$$

Phosphinimines derived from acyl azides afford the corresponding nitrile on thermal decomposition,[126] while those derived from α-azido-carboxylic acids can be converted into α-amino-acids:[128]

$$Ph{\cdot}CO{\cdot}N_3 \rightarrow Ph{\cdot}CO{\cdot}N{:}PR_3 \rightarrow PhCN + R_3PO$$

$$R{\cdot}CH(N_3){\cdot}CO_2H \rightarrow R{\cdot}CH(CO_2H){\cdot}N{:}PR_3 \xrightarrow{H_2O,\ HBr} R{\cdot}CH(NH_2){\cdot}CO_2H + R_3PO$$

(ii) *With diazo-compounds.* Diazomethane reacts with tertiary phosphines[129] and triesters[130] to give the so-called phosphazines which on thermal decomposition provide an alternative route to methylenephosphoranes,[131] and on hydrolysis give hydrazones:[129]



$$R_3P + R_2'CN_2 \rightarrow R_3P{:}N{\cdot}N{:}CR_2' \begin{cases} \nearrow R_3PO + R_2'C{:}N{\cdot}NH_2 \\ \searrow R_3P{:}CR_2' + N_2 \end{cases}$$

The products of the reactions of diazonium salts with triphenylphosphine vary with the proportions of reactants.[132,133,107a] A 1:1 ratio results in reduction of the diazonium compound to the aromatic hydrocarbon (50%),

$$ArN_2Cl + Ph_3P \rightarrow [Ph_3\overset{+}{P}{\cdot}N{:}NAr]\overset{-}{Cl} \xrightarrow{H_2O} ArH + Ph_3PO + HCl$$

[129] Staudinger and Meyer, *Helv. Chim. Acta*, 1919, **2**, 619.
[130] Kabachnik and Gilyarov, *Doklady Akad. Nauk S.S.S.R.*, 1956, **106**, 473.
[131] Staudinger and Meyer, *Helv. Chim. Acta*, 1919, **2**, 635; Horner and Lignau, *Annalen*, 1955, **591**, 135.
[132] Horner and Stohr, *Chem. Ber.*, 1953, **86**, 1073.
[133] Horner and Hoffmann, *Chem. Ber.*, 1958, **91**, 45.

whereas a 1 mole excess of phosphine leads ultimately to the formation of the aryl hydrazine:

$$[Ph_3\overset{+}{P}{\cdot}N{:}NAr]\overset{-}{Cl} + Ph_3P + H_2O \rightarrow [Ph_3\overset{+}{P}{\cdot}NH{\cdot}NHAr]\overset{-}{Cl} + Ph_3PO$$

$$[Ph_3\overset{+}{P}{\cdot}NH{\cdot}NHAr]\overset{-}{Cl} \xrightarrow[HCl]{H_2O} Ph_3PO + Ar{\cdot}NH{\cdot}NH_2$$

Reaction of acetate-buffered diazonium salt with triphenylphosphine, on the other hand, gives rise to aryltriphenylphosphonium salts which are also formed from the corresponding reaction with *N*-nitrosoacylarylamines. Horner and Hoffmann[133] are of the opinion that free aryl radicals are present in this reaction since the same products are obtained from the reaction of triphenylphosphine with bromobenzene in the presence of cobaltous chloride and phenylmagnesium bromide:[134]

$$Ar{\cdot}N_2Cl + Ph_3P \xrightarrow{\text{Acetate buffer}} Ph_3PAr^+\ Cl^- + N_2$$

(iii) *With nitrosobenzene.* Recent work by Bunyan and Cadogan[92] has shown that triethyl phosphite and triphenylphosphine react rapidly with nitrosobenzene to give azoxybenzene and the corresponding oxide:

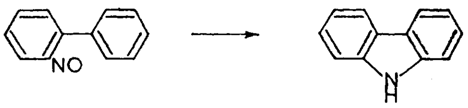
$$(RO)_3P + 2PhNO \rightarrow (RO)_3PO + PhN(O){\cdot}NPh)$$

Although the mechanism of this reaction has not been established it is possible that an electron-deficient nitrogen intermediate, an azene, is involved:

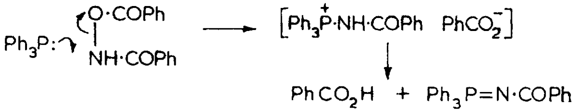
$$PhNO + (RO)_3P \rightarrow Ph\ddot{N}{:} + (RO)_3PO$$

$$Ph\ddot{N}{:} + PhNO \rightarrow PhNO{:}NPh$$

This interpretation also accounts for the ready formation of carbazole in the reaction of 2-nitrosobiphenyl with triethyl phosphite.



(iv) *With* ON-*dibenzoylhydroxylamine.* Triphenylphosphine reacts with *ON*-dibenzoylhydroxylamine by way of attack by tervalent phosphorus on nitrogen with displacement of benzoate ion followed by, or concurrent with, proton removal to give benzoic acid and triphenylphosphine benzoylimine:[135]



$$Ph_3P{:} + \begin{matrix} O{\cdot}COPh \\ | \\ NH{\cdot}COPh \end{matrix} \longrightarrow \left[Ph_3\overset{+}{P}{\cdot}NH{\cdot}COPh\ \ PhCO_2^-\right] \downarrow PhCO_2H + Ph_3P{=}N{\cdot}COPh$$

---

[134] Horner and Hoffmann, *Chem. Ber.*, 1958, **91**, 50.
[135] Wasserman and Koch, *Chem. and Ind.*, 1956, 1014.

The reaction is similar to that involving the related dibenzoyl peroxide discussed earlier. The reaction is also similar to the cleavage of N–halogen bonds by phosphines and phosphates observed in other systems, *e.g.*, in reactions of anhydrous chloramine-T:[56,136]

$$\mathrm{Ph_3P\ [or\ (RO)_3P] + Ar{\cdot}SO_2{\cdot}NNaCl \rightarrow Ph_3P{:}N{\cdot}SO_2Ar + NaCl}$$

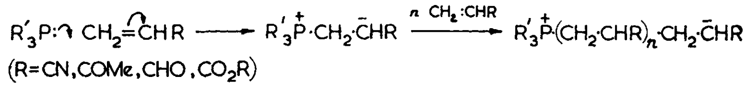
Reactions with Unsaturated Compounds.—Tertiary phosphines form stable zwitterionic phosphonium salts with compounds containing activated double bonds,[41b] *e.g.*:

$$\mathrm{ArCH{:}C(CN)_2 + R_3P \rightarrow R_3\overset{+}{P}{\cdot}CHAr{\cdot}\overset{-}{C}(CN)_2}$$

Maleic anhydride[38] reacts similarly, while the reactions of maleic and cinnamic acid with triethyl phosphite appear to involve similar resonance-stabilised intermediates[138] which are able to rearrange by dealkylation, thus:

$$\mathrm{(EtO)_3P + HO_2C{\cdot}CH{:}CH{\cdot}CO_2H \rightarrow (EtO)_3\overset{+}{P}CH(CO_2H){\cdot}\overset{-}{C}H{\cdot}CO_2H \rightarrow}$$
$$\mathrm{(EtO)_2P(O){\cdot}CH{\cdot}(CO_2H){\cdot}CH_2{\cdot}CO_2Et}$$

Such reactions are a function of the nucleophilicity of tervalent phosphorus and occur most readily when the double bond is activated by electron-withdrawing substituents. In cases where stabilisation of the initial 1:1 adduct is not pronounced, reaction with successive molecules of olefin can occur to give long-chain telomers:[139]



Similar reactions with triethyl phosphite have been reported,[140] as in Scheme 14.

$$\mathrm{(EtO)_3P + \mathit{n}\ CH_2{:}CMe{\cdot}CO_2H \rightarrow (EtO)_3\overset{+}{P}{\cdot}[CH_2{\cdot}CHMe{\cdot}CO_2H]_{\mathit{n}-1}\ CH_2{\cdot}\overset{-}{C}Me{\cdot}CO_2 \rightarrow}$$
$$\mathrm{(EtO)_2P(O){\cdot}[CH_2{\cdot}CHMe{\cdot}CO_2H]_{\mathit{n}-1}{\cdot}CH_2{\cdot}CHMe{\cdot}CO_2Et}$$

SCHEME 14

Diphenylketen[137] reacts with triethylphosphine analogously to give a 1:1 adduct, while the following conversion of *NN′*-diphenylcarbodi-imide into phenyl isocyanide and aniline by reaction with tertiary phosphine

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[136] Mann and Chaplin, *J.*, 1937, 527.

[137] Staudinger and Meyer, *Helv. Chim. Acta*, 1919, **2**, 612.

[138] Kamai and Kukhtin, *Trudy Kazan. Khim. Tekhnol. Inst. im S.M. Kirova*, 1957, **23**, 133; *Chem. Abs.*, 1958, **52**, 9948.

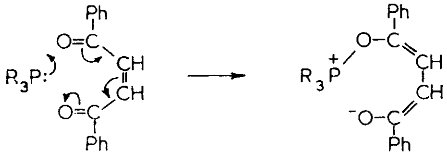
[139] Horner, Jurgeleit, and Klupfel, *Annalen*, 1955, **591**, 108.

[140] Kukhtin, Kamai, and Sinchenko, *Doklady Akad. Nauk S.S.S.R.*, 1958, **118**, 505.

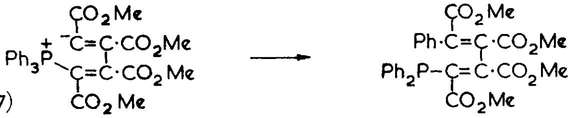
followed by hydrolysis,[41b] probably involves a similar intermediate, thus:

$$\mathrm{PhN{:}C{:}NPh + R_3P \rightarrow [R_3\overset{+}{P}{\cdot}C(NPh){:}\overset{-}{N}Ph] \xrightarrow{H_2O} R_3PO + PhNC + PhNH_2}$$

Nucleophilic attack on oxygen occurs in the reaction of tertiary phosphines with *cis*- or *trans*-dibenzoylethylene however,[41b] thus recalling similar reactions which occur with some 1,4-quinones described above.

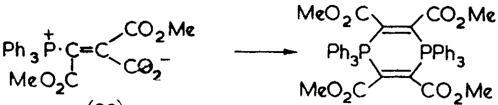


Several products have been isolated from the reaction of triphenylphosphine with dimethyl acetylenedicarboxylate under various conditions.[141] The unstable 2:1 adduct formed at −50° under nitrogen is formulated as (27) and readily isomerises to give the more stable isomer (28), which is assumed to arise by way of an unusual 1,5-migration of the phenyl group.



(27) (28)

When the reaction is in carbon dioxide, on the other hand, it is believed that the first-formed zwitterion obtained by reaction of equimolar quantities of reactants is stabilised by combination with carbon dioxide to give the product (29), which on reaction with methyl iodide, base, or dimethyl acetylenedicarboxylate gives a further product formulated as (30), and on hydrolysis gives dimethyl fumarate and triphenylphosphine oxide:



(29) (30)

It has been suggested[142] that the ready reaction of triethyl phosphite and diethyl azodicarboxylate proceeds as indicated, but confirmation of the formulation must await adequate identification of the product.

$$\mathrm{(EtO)_3P + EtO_2C{\cdot}N{:}N{\cdot}CO_2Et \rightarrow (EtO)_3\overset{+}{P}{\cdot}N(CO_2Et){\cdot}\overset{-}{N}{\cdot}CO_2Et \rightarrow}$$
$$\mathrm{(EtO)_2P(O){\cdot}N(CO_2Et){\cdot}NEt{\cdot}CO_2Et}$$

---

[141] Johnson and Tebby, *J.*, 1961, 2126.
[142] Morrison, *J. Org. Chem.*, 1958, **23**, 1072.

Wittig and Benz[143a] have shown that, in company with other nucleophilic reagents,[144] triphenylphosphine reacts with benzyne, in this case to give phenylbiphenylenephosphine. Benzyne has also been reported to convert triethyl phosphite into diethyl phenylphosphonate.[143b]

Reactions with Carboxylic Acids.—Trialkyl phosphites react with carboxylic acids to give the corresponding alkyl esters.[145] Tetra-alkylpyrophosphites, on the other hand, behave as anhydrides of diethyl hydrogen phosphite in their reactions with carboxylic acids, and as such are useful in peptide synthesis[146] (Scheme 15). The so-called "amide modification" of this process has been utilised in du Vigneaud's synthesis of oxytocin[147] (Scheme 16). Peptides as well as simple amides are also formed by reaction of phosphazo-compounds with carboxylic acids[148] (Scheme 17), and the related triamide $P(NMePh)_3$ appears to offer some

$$\mathrm{(EtO)_2P{\cdot}O{\cdot}P(OEt)_2 + R{\cdot}CO{\cdot}NH{\cdot}CHR'{\cdot}CO_2H \rightarrow R{\cdot}CO{\cdot}NH{\cdot}CHR'{\cdot}CO_2{\cdot}P(OEt)_2 + (EtO)_2P{\cdot}OH}$$

$$\mathrm{R{\cdot}CO{\cdot}NH{\cdot}CHR'{\cdot}CO_2{\cdot}P(OEt)_2 + H_2N{\cdot}CHR''{\cdot}CO_2R''' \rightarrow R{\cdot}CO{\cdot}NH{\cdot}CHR'{\cdot}CO{\cdot}NH{\cdot}CHR''{\cdot}CO_2R'' + (EtO)_2P(O)H}$$

SCHEME 15

$$\mathrm{(EtO)_2P{\cdot}O{\cdot}P(OEt)_2 + H_2N{\cdot}CHR{\cdot}CO_2R' \rightarrow (EtO)_2P{\cdot}NH{\cdot}CHR{\cdot}CO_2R' + (EtO)_2P{\cdot}OH}$$

$$\mathrm{(EtO)_2P{\cdot}NH{\cdot}CHR{\cdot}CO_2R' + R''CO{\cdot}NH{\cdot}CHR''{\cdot}CO_2H \rightarrow R''{\cdot}CO{\cdot}NH{\cdot}CHR''{\cdot}CO{\cdot}NH{\cdot}CHR{\cdot}CO_2R' + (EtO)_2P{\cdot}OH}$$

SCHEME 16

$$\mathrm{PCl_3 + 2EtO_2C{\cdot}CH_2{\cdot}NH_2 \rightarrow EtO_2C{\cdot}CH_2N{:}P{\cdot}NH{\cdot}CH_2{\cdot}CO_2Et}$$

$$\mathrm{EtO_2C{\cdot}CH_2{\cdot}N{:}P{\cdot}NH{\cdot}CH_2{\cdot}CO_2Et + 2\,HO_2C{\cdot}CH_2{\cdot}NH{\cdot}CO_2{\cdot}CH_2Ph \rightarrow 2\,EtO_2C{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}NH{\cdot}CO_2{\cdot}CH_2Ph}$$

SCHEME 17

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[143] (*a*) Wittig and Benz, *Chem. Ber.*, 1959, **92**, 1999; (*b*) Griffin and Castellucci, *J. Org. Chem.*, 1961, **26**, 629.

[144] Huisgen and Sauer, *Angew. Chem.*, 1960, **72**, 91.

[145] Kamai, Kukhtin, and Strogova, *Trudy Kazan. Khim. Tekhnol. Inst. im S.M. Kirova*, 1956, **21**, 155.

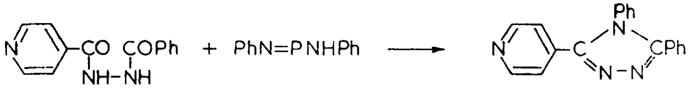
[146] Anderson, Blodinger, Young, and Welcher, *J. Amer. Chem. Soc.*, 1952, **74**, 5304; Anderson, Blodinger, and Welcher, *ibid.*, p. 5309.

[147] du Vigneaud, Ressler, Swan, Roberts, and Katsoyannis, *J. Amer. Chem. Soc.*, 1954, **76**, 3115.

[148] Goldschmidt and Lautenschlager, *Annalen*, 1953, **580**, 68; Wunsch, Fries, and Zwick, *Chem. Ber.*, 1958, **91**, 542.

advantages in the preparation of *N*-methylanilides.[149]

Phosphazo-compounds also react with diacylhydrazines to give 1,2,4-triazoles; thus *N*-benzoyl-*N'*-isonicotinoylhydrazine has been converted into 3,4-diphenyl-5-4'-pyridyl-1,2,4-triazole in 95% yield:[150]



In this reaction, as in many others involving phosphazo-compounds, the nature of the phosphorus-containing products has not been determined.

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[149] Abramovitch, Hey, and Long, *J.*, 1957, 1787; Habib and Rees, *J.*, 1960, 3371.

[150] Klingsberg, *J. Org. Chem.*, 1958, **23**, 1086.