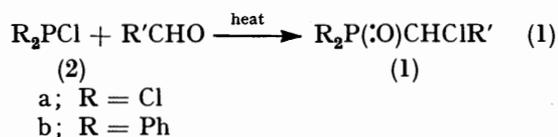


Reactions of Carbonyl Compounds with Tervalent Phosphorus Reagents. Part 12.¹ Aromatic Aldehydes with Bromophosphines and Phosphorus Tri-iodide

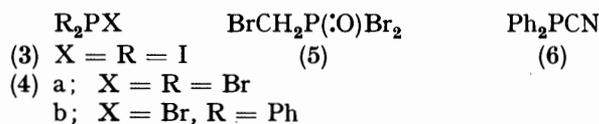
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The reactions of aromatic aldehydes with phosphorus tribromide (4a), with phosphorus tri-iodide (3), and with bromodiphenylphosphine (4b) have been investigated in detail. Both the trihalides react as electrophiles to produce high yields of the appropriate benzylidene dihalide. Thereafter, these reactions differ from each other and from that of phosphorus trichloride. Bromodiphenylphosphine (4b) reacts in biphilic fashion to produce (α -bromobenzyl)diphenylphosphine oxide (15). This oxide is readily dehalogenated under the reaction conditions and in model studies. Cyanodiphenylphosphine is unreactive towards benzaldehyde. These halogenophosphine reactions confirm the generality of the trends first observed with chlorophosphines and that the nature of the other two ligands on phosphorus determines the mode of reaction with aldehydes.

CHLOROPHOSPHINES and aldehydes are known² to react under thermal conditions to give (α -chloroalkyl)phosphoryl compounds (1), as shown in equation (1). The reaction is a general one, but its course is largely dependent upon the nature of the phosphine. Thus, when the chlorophosphine is phosphorus trichloride (2a), the phosphorus role is that of an electrophilic centre,³ but with chlorodiphenylphosphine (2b) and its alkyl analogues, the phosphorus atom is believed to act initially as an electron-pair donor.⁴



This picture would lead one to speculate that these reactions might well apply to bromo- and iodo-phosphines. However, literature on such systems is rather sparse and, to say the least, confusing. Thus phosphorus tri-iodide (3) and formaldehyde were shown by Butlerov,⁵ in 1859, to produce di-iodomethane. However, Conant *et al.*⁶ in 1923 stated that the tri-iodide (3) did not undergo reaction with benzaldehyde. On the other hand, phosphorus tribromide (4a) was shown, as part of a general study of aldehyde-phosphorus(III) halide reactions,⁷ to produce a very low (7.5%) yield of bromomethylphosphonic dibromide (5) when heated with paraformaldehyde. A subsequent report⁸ that this reaction does not give compound (5) only adds to the confusion. At first sight, this suggests that benzaldehyde might be the source of these inconsistencies, but this seemed unlikely in view of our previous experience of its facile reactivity and good yields of products of type (1). This situation encouraged us to look at the reactivity, if any, of the phosphorus trihalides (3) and (4a) with benzaldehyde. Furthermore, in view of the lack of any literature on substituted phosphine derivatives, we decided to extend this study to bromodiphenylphosphine (4b) and cyanodiphenylphosphine (6).



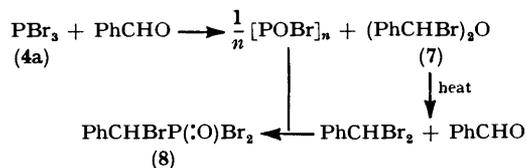
Phosphorus Tribromide.—Phosphorus tribromide (4a) and benzaldehyde (1 mol equiv.) reacted steadily at 20 °C under nitrogen until, after 24 h, all the aldehyde had been consumed. Since the ¹H n.m.r. spectrum of the mixture at this state showed only aromatic absorptions, the reaction was repeated using pentadeuteriobenzaldehyde. This revealed that the aldehyde had been converted into a compound resonating at δ_{H} 7.25 and that this accounted for more than 95% of the aldehyde.

The product of this reaction is sensitive to moisture, benzaldehyde being regenerated by hydrolysis. Gentle heating of the main reaction resulted in the formation of benzylidene dibromide in nearly quantitative yield. We therefore deduce that the initial reaction product is bis-(α -bromobenzyl) ether (7), although it was too reactive to be isolated from this reaction.

If the reaction mixture is then heated at 150 °C for several hours, the initially clean reaction becomes complex, several new, but weak, signals appearing in the ¹H n.m.r. spectrum, although benzylidene dibromide remains the predominant component in the mixture. The most important of the new absorptions was a broadened singlet (δ_{H} 5.45), but it never accounted for more than one-third of the mixture, despite considerable efforts to increase this fraction. Moreover, a hydrolytic work-up of the mixture led only to complete loss of this compound.

It therefore appears that phosphorus tribromide (4a) and benzaldehyde react initially in exactly the same way as found³ with phosphorus trichloride (2a), *i.e.* via a bis-(α -halogeno)benzyl ether (7) and a gem-dihalide, as shown in Scheme 1. A minor difference between compounds (2a) and (4a) is that the latter is somewhat more reactive. Once the gem-dihalide is formed, the systems are not comparable, since benzylidene dibromide is much more resistant to further reaction. If one makes the

reasonable assumption that benzylidene dibromide formation is accompanied by that of a polymeric species, $[\text{POBr}]_n$, as demanded by stoichiometry, then the relative unreactivity of benzylidene dibromide seems likely to be due to the difficulty of the Arbusov-type reaction, already established for $[\text{POCl}]_n$.³ It seems likely that the unassigned signal at δ_{H} 5.45 is due to (α -bromobenzyl)phosphonic dibromide (8), by analogy with the corresponding dichloride, $\text{Ph}_2\text{P}(\text{:O})\cdot\text{CHClPh}$ (9), which has δ_{H} 5.40. The lack of significant J_{PH} coupling is surprising, but less so in view of the data we later found for the bromodiphenylphosphine system (see Scheme 1).

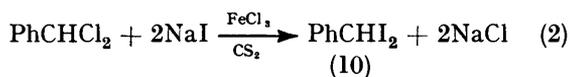


SCHEME 1

In view of the noticeably increased reactivity towards phosphorus trichloride displayed by *p*-methoxybenzaldehyde relative to benzaldehyde, it seemed sensible to see how the former would react with phosphorus tribromide. Once again *p*-methoxybenzaldehyde is very reactive and was completely consumed within 1 h at 20 °C. There is no sign of a bis-ether in this system and *p*-methoxybenzylidene dibromide is the major product. The other product is obviously the analogue of compound (8), but once again the conversion of the gem-dibromide was sluggish, being >40%. When the temperature was raised above 100 °C, evidence of demethylation of the ether function was apparent.

Phosphorus Tri-iodide.—The results with phosphorus tribromide (4a) implied that phosphorus tri-iodide (3) might be even more reactive. This turned out to be the case, but was accompanied by an increased difficulty in controlling the course of the reaction and, more important, of obtaining reproducible results. Since it was suspected that some of these difficulties were of a photochemical origin, most of our studies were undertaken in dark, oxygen-free conditions, in carbon disulphide as solvent, and were monitored by ¹H n.m.r. spectroscopy.

In reactions where the molar ratio of aldehyde to compound (3) varied in the range 1—1.5 : 1, the aldehyde was fully consumed within 3—4 h at 20 °C. Two products were always formed, although their relative amounts varied considerably. The major product was the previously unreported benzylidene di-iodide (10), δ_{H} 6.15(s). This was independently prepared by a recently developed heterogeneous halogen-exchange procedure⁹ [see equation (2)].



The second product of the reaction of phosphorus tri-iodide (3) showed a doublet (δ_{H} 5.55, J 8.5 Hz) in its ¹H n.m.r. but was not isolated because of its sensitivity to

both moisture and light. Its formation appeared to proceed *via* benzylidene di-iodide (10), since the addition of more phosphorus tri-iodide (3) to the initial product mixture resulted in conversion of benzylidene di-iodide (10) into the unknown adduct. This conversion would seem to support the n.m.r. data, which suggests that the unknown compound has an α -iodobenzyl moiety linked to a phosphorus atom, but further speculation would seem unjustified in the absence of a pure sample.

Attempts to use other aromatic aldehydes were of little help in resolving this structural problem. Thus *p*-nitrobenzaldehyde is unreactive towards the tri-iodide (3) at room temperature. On the other hand, *p*-methoxybenzaldehyde is more reactive than benzaldehyde itself and rapidly forms an adduct which is clearly the analogue of the unknown compound discussed above. Once again we were unable to handle this type of compound. There was no evidence for the intermediacy of *p*-methoxybenzylidene di-iodide in this reaction, which therefore resembles that of compound (4a) with *p*-methoxybenzaldehyde, in that an intermediate appears either to be omitted from the sequence or to be too reactive to be detected. Although these substituted aldehyde reactions were not helpful in the above aspect, they did at least confirm the view that the phosphorus(III) halides all react initially as electron-pair acceptors in these systems.

These complexities were compounded when a number of reactions of benzaldehyde with the tri-iodide (3) gave a different doublet (δ_{H} 5.70, J 3.5 Hz), as well as the singlet for benzylidene di-iodide. The former absorption was always of relatively lower intensity and it disappeared from the spectrum after prolonged stirring of the reaction mixture. Its formation was usually associated with reactions in which the tri-iodide (3) was added gradually to the aldehyde (inverse addition) and in which the rate of loss of the latter was very much slower than in the normal mode of addition. The transient nature of this unknown compound meant that we were unable to investigate it further.

Despite our inability to characterise the final product of the reactions of the tri-iodide (3) with aromatic aldehydes, it does seem fairly clear that the phosphorus trihalides initially display the same basic chemistry in these systems. In each case, the trihalide is an electrophilic reagent and, like other inorganic, non-metal halides,¹⁰ converts the aldehyde into the corresponding gem-dihalide, the reactivity of which determines the final outcome of the reaction.

Bromodiphenylphosphine (4b).—Our initial studies of the reaction between benzaldehyde and the phosphine (4b) revealed that several products were formed and that their preponderance at any stage of the reaction was essentially dependent upon the initial reactant ratio and on the reaction temperature. Only when the phosphine (4b) was at least 60 mol % of the starting mixture and only after heating the mixture to 100 °C for 2 h was the aldehyde wholly consumed. Under these circumstances, the only observable (¹H n.m.r.) products

general one and not restricted to phosphorus chlorides. It is also clear, however, that the ease with which the expected products (1) may be prepared is dependent upon the properties of intermediate halogeno-ethers or gem-dihalides, as with compounds (2a), (3), and (4a), or upon the stability of the products (1) under the reaction conditions, as with compound (4b). The basic modes of reaction in these systems are not, in the first instance, related to the nature of the halogen in the phosphorus(III) reagent, but are controlled by the nature of the other two ligands on phosphorus. Thus the present results confirm that the trihalides all react initially *via* electrophilic phosphorus, whereas the monohalogenophosphines, like (2b) and (4b), prefer a pathway in which the phosphorus displays biphilic properties.

EXPERIMENTAL

All experiments were conducted in dry solvents and in a dry nitrogen atmosphere. Where indicated, reaction vessels were completely enclosed in heavy aluminium foil. Aldehydes were purified before use and all the halogenophosphines were redistilled as required or recrystallized. Bromodiphenylphosphine,¹⁴ cyanodiphenylphosphine,¹⁵ and phosphorus tri-iodide¹⁶ were prepared by standard methods. All ¹H n.m.r. spectra were determined for solutions in deuteriochloroform using tetramethylsilane as internal standard, unless otherwise stated, and using a Perkin-Elmer R-10 instrument.

Reaction of Phosphorus Tribromide with Benzaldehyde.—Phosphorus tribromide (2.71 g, 10 mmol) was added to benzaldehyde (1.06 g, 10 mmol) under nitrogen at 0 °C. The mixture was allowed to come to room temperature and was then stirred for 30 h. During this period, analysis by ¹H n.m.r. revealed the steady loss of the benzaldehyde (consumed after 24 h), but no new non-aromatic resonances appeared. The mixture was then heated to 60 °C and during the next 2 h the formation of a new signal at δ_{H} 6.63 (s) was observed. Careful signal augmentation and t.l.c. studies suggested that this was due to benzylidene dibromide. This signal remained the only non-aromatic one observable as the temperature was slowly increased to 140 °C. After 12 h at 140 °C, some benzylidene dibromide had been consumed, and new, weaker signals appeared at δ_{H} 5.45 (br s), 5.62 (d, J 7 Hz), and 4.43 (s). The first of these new signals was by far the strongest and it was shown by t.l.c. and by n.m.r. signal augmentation that it was not due to *meso*-stilbene dibromide, (\pm)-stilbene dibromide, or to 1,1-diphenylethene. The peak at δ 4.43 coincided with benzylidene dibromide. When the crude reaction product was dissolved in ether, washed with water, dried over magnesium sulphate, and the solvent removed, an oil was obtained. Distillation of this yielded benzylidene dibromide, b.p. 122–125 °C at 20 mmHg (lit.¹⁷ 156 °C at 23 mmHg), identified by its i.r. spectrum, which was indistinguishable from a pure sample.

When benzaldehyde (10.6 g, 0.1 mol) and phosphorus tribromide (27.1 g, 0.1 mol) were stirred at 20 °C in a further experiment, all the aldehyde was consumed after 32 h although no benzylidene dibromide had been formed. The mixture was then poured into water-ether (250 ml each) and stirred vigorously for 15 min. Upon work-up of the ether layer benzaldehyde (9.5 g) was recovered.

Reaction of Phosphorus Tribromide with Pentadeuterio-

benzaldehyde.—Phosphorus tribromide (0.55 g, 2 mmol) and pentadeuteriobenzaldehyde¹⁸ (0.22 g, 2 mmol) were dissolved in deuteriochloroform (0.3 ml) containing tetramethylsilane. The tube was sealed under nitrogen and left at room temperature for 5 d. During this time most (*ca.* 96%) of the aldehyde was slowly consumed and the only new signal was at δ_{H} 7.35 (s) in the n.m.r. spectrum of the mixture. Prolonged gentle heating resulted in the gradual loss of this new signal, which was ultimately completely replaced by that due to pentadeuteriobenzylidene dibromide, δ_{H} 6.66 (s).

Reaction of Phosphorus Tribromide with p-Methoxybenzaldehyde.—Phosphorus tribromide (2.71 g, 10 mmol) and *p*-methoxybenzaldehyde (1.36 g, 10 mmol) were mixed under nitrogen in a flask cooled externally at –10 °C. The temperature of the mixture was allowed to come to 20 °C during *ca.* 30 min and ¹H n.m.r. analysis revealed that *ca.* 20% of the aldehyde remained. The major signals were at δ_{H} 7.45 (2 H) and 6.76 (2 H) for a doublet (J 9 Hz), 6.44 (1 H, s, CHBr₂), and 3.7 (3 H, s, OMe), and were fully augmented by a sample of *p*-methoxybenzylidene dibromide added to the mixture.

When this experiment was repeated and the mixture heated to 100 °C for 2 h, *p*-methoxybenzylidene dibromide remained the major component. During this period, weak signals also appeared at δ_{H} 5.40 (s) and 5.65 (d, J 7 Hz), and subsequently at δ 2.65 (s). The last of these was due to bromomethane.

Reactions of Phosphorus Tri-iodide with Benzaldehyde.—(a) *Equimolar, in the dark.* Phosphorus tri-iodide¹⁶ (5.15 g, 12.5 mmol) was dissolved in carbon disulphide (dry, 20 ml) under nitrogen at 0 °C. Benzaldehyde (1.32 g, 12.5 mol) was added *via* a syringe and serum cap. The mixture was then allowed to come to 20 °C and stirring was continued until ¹H n.m.r. spectra of aliquots indicated that all the aldehyde had reacted (*ca.* 4 h). At this stage the spectrum showed, in addition to aromatic absorptions, peaks at δ_{H} 6.16 (s) and 5.55 (d, J 8.5 Hz). The ratio of these signals was quite variable, although the former was usually the stronger of the two. In any one experiment, the ratio of these signals did not change once all the aldehyde was consumed. Addition of successive aliquots of phosphorus tri-iodide to the mixture, after the aldehyde was wholly consumed, resulted in a slow decrease in the δ_{H} 6.16 (s) peak and a simultaneous increase in the δ_{H} 5.55 (d) peaks. The singlet signal was assigned to benzylidene di-iodide (10), on the basis of n.m.r. augmentation and t.l.c. studies. Evaporation of the solvent from any of these reaction mixtures led to light and moisture sensitive residues, which were black and tarry.

(b) *1.5 Mol equiv. of benzaldehyde with inverse addition.* A solution of phosphorus trichloride (4.12 g, 10 mmol) in carbon disulphide (15 ml) was added, in the dark, to a solution of benzaldehyde (1.59 g, 15 mmol) in carbon disulphide (5 ml). The mixture was kept at 0 °C under nitrogen during the addition and once this was completed the temperature was allowed to rise slowly to 20 °C. A ¹H n.m.r. spectrum revealed that the aldehyde was only partially consumed and that new signals were present at δ_{H} 6.19 (s, benzylidene di-iodide) and 5.7 (d, J 3.5 Hz). The latter was noticeably weaker than the former and, after stirring for a further 12 h, the doublet had disappeared, leaving the singlet for benzylidene di-iodide as the only observable signal outside the aromatic region.

(c) *With pentadeuteriobenzaldehyde.* An equimolar mix-

ture of phosphorus tri-iodide and pentadeuteriobenzaldehyde¹⁸ was made up and stirred at 20 °C in carbon disulphide, exactly as in (a). After 3.5 h it was found, by ¹H n.m.r. spectroscopy, that all the aldehyde had been consumed and that there were new signals at δ_{H} 6.20 (s) and 5.61 (d, J 8.5 Hz), in an integrated ratio of 5 : 7. No other signals were detected prior to the appearance of these and no changes were detected after the mixture had been stirred for a further 24 h.

Reactions of Phosphorus Tri-iodide with Other Benzaldehydes.—(a) *p*-Nitrobenzaldehyde. A reaction was performed at 20 °C exactly as in (a) above, except that deuteriochloroform-hexadeuteriobenzene (1 : 1) was used as solvent. There was no evidence of reaction (¹H n.m.r.) after 3 d.

(b) *p*-Methoxybenzaldehyde. *p*-Methoxybenzaldehyde (1.36 g, 10 mmol) was added, in the dark, to a solution of phosphorus tri-iodide (4.12 g, 10 mmol) in carbon disulphide (15 ml) with stirring, under nitrogen at 0 °C. After 0.5 h ¹H n.m.r. spectra of the mixture showed 50% loss of the aldehyde and after 3 h at 20 °C the aldehyde was wholly consumed. The only new signals to appear during this period were at δ_{H} 7.36 (d, J 9 Hz) and 6.85 (d, J 9 Hz) for a *p*-disubstituted benzene ring, at δ_{H} 5.62 (d, J 8.5 Hz), and at δ_{H} 3.81 (s, OMe). When the mixture was refluxed for 5 h there was no change in this spectrum.

Reactions of Bromodiphenylphosphine with Benzaldehyde.—(a) *Molar ratio* 3 : 2. Bromodiphenylphosphine¹⁴ (4b) (3.97 g, 15 mmol) and benzaldehyde (1.06 g, 10 mmol) were stirred at 20 °C in deuteriochloroform under nitrogen for 2 h and then at 100 °C for 2 h. Analysis by n.m.r. showed that all the aldehyde had been consumed and that new signals were present at δ_{H} 6.68 (s) and 3.72 (d, J 14 Hz). These were assigned to benzylidene dibromide and benzylidiphenylphosphine oxide (11), respectively, on the basis of t.l.c. and n.m.r. augmentation studies. Dilution of the reaction mixture gave a white precipitate which was recrystallized from light petroleum-chloroform to give benzylidiphenylphosphine oxide (11), m.p. 192–194 °C (lit.¹⁹ 195–196 °C). The yield was 1.09 g (46%, based on aldehyde). The mother liquor was freed from volatile solvents and then distilled to give benzylidene dibromide b.p. 110–112 °C at 15 mmHg, whose i.r. spectrum was identical to that of a pure sample. The yield was 0.93 g (42%, based on aldehyde).

Careful integration of the final ¹H n.m.r. spectrum of the crude reaction mixture gave a ratio of 1 : 1 for the two product absorptions and showed that all the original aldehydic protons were accounted for by the two products.

(b) *Molar ratio* 1 : 1. Benzaldehyde (2.12 g, 20 mmol) and bromodiphenylphosphine (2.65 g, 10 mmol) were mixed in

TABLE

15 min, 20 °C: δ_{H} 6.89 (s) and 6.19 (d, J 7.5 Hz) (equal intensity); PhCHO loss ca. 40.
1 h, 20 °C: as above, plus δ_{H} 6.72 (s, PhCHBr ₂), 5.14 (d, J 8.5 Hz, [Ph ₂ P(O)CHPh] ₂ O), and 3.76 [d, J 14 Hz, Ph ₂ O(O)CH ₂ Ph].
1 h, 20 °C and 1 h, 100 °C: δ_{H} 6.74 (s, PhCHBr ₂), 6.13 [s, PhCHBrP(O)Ph ₂], 5.18 (d, J 8.5 Hz, [Ph ₂ P(O)CHPh] ₂ O), and 3.76 [d, J 14 Hz, Ph ₂ P(O)CH ₂ Ph]; PhCHO loss 50%.
1 h, 20 °C; 10 h 100 °C and 3 h 150 °C: as above, except for loss of δ 5.18 (d). The ratio of signals at δ_{H} 6.74 (s), 6.10 (br s), and 3.74 (d) was approximately 3 : 2 : 3; PhCHO loss ca. 55%.

deuteriochloroform (1 ml) and stirred in a dry nitrogen atmosphere at 20 °C in the dark. The mixture slowly became yellowish-brown in colour. Periodic ¹H n.m.r. analyses revealed the sequence of changes in the Table as the temperature was increased to 150 °C. The assignment of signals was based on the preparative work in (a) above, and on careful t.l.c. and n.m.r. signal augmentation studies with samples of (α -bromobenzyl)diphenylphosphine oxide (15) (see below), bis-[(α -diphenylphosphinoyl)benzyl]ether (12),¹¹ and benzylidiphenylphosphine oxide (11).

Reaction of Cyanodiphenylphosphine (6) with Benzaldehyde.—A mixture of benzaldehyde (1.06 g, 10 mmol) and cyanodiphenylphosphine¹⁵ (2.11 g, 10 mmol) was stirred at 20 °C in deuteriochloroform (0.8 ml) under nitrogen; no reaction was observed (¹H n.m.r. and i.r. spectroscopy). Heating to 100 °C for 10 h did not result in any reaction.

Preparation of (α -Bromobenzyl)diphenylphosphine Oxide (15).—Benzylidiphenylphosphine oxide (11) (2.9 g, 10 mmol) in 1,2-dimethoxyethane (dry, 10 ml) was treated with a 10% excess of methyl-lithium in hexane at –30 °C for 30 min. A solution of bromine (1.6 g, 10 mmol) in 1,2-dimethoxyethane (dry, 5 ml) was added, in drops at –10 °C, to the mixture. After stirring overnight, the mixture was filtered and the crude solid recrystallized from chloroform-toluene to give (α -bromobenzyl)diphenylphosphine oxide (15), m.p. 204–205 °C (lit.¹² 204–206 °C). The yield was 3.02 g crude and 1.6 g purified (46%). When tetrahydrofuran was tried as solvent in this preparation, very low conversion was observed. The oxide (15) showed δ_{H} 2.2–2.9 (15 H, m, Ph) and 6.12 (1 H, br s, PhCHBr).

Debromination Reactions of (α -Bromobenzyl)diphenylphosphine Oxide (15).—(a) *With bromodiphenylphosphine* (4b). Bromodiphenylphosphine (1.50 g, 5.5 mmol) and the oxide (15) (1.16 g, 4 mmol) were heated at 100 °C for 3 h in deuteriochloroform (1 ml) under nitrogen. Complete conversion of the oxide (15) into benzylidiphenylphosphine oxide (11), δ_{H} 3.78 (d, J 14 Hz), was observed.

(b) *With diphenylphosphine oxide* (16). Diphenylphosphine oxide (0.91 g, 4.5 mmol) and the oxide (15) (1.16 g, 4 mmol) were heated for 15 min at 90 °C in deuteriochloroform. This resulted in 96% conversion of the oxide (15) into benzylidiphenylphosphine oxide (11), δ_{H} 3.76 (d, J 14 Hz). When methanol (dry, 0.13 g, 4 mmol) in deuteriochloroform (0.25 ml) was added and the mixture was left at 20 °C for 1 h, a second doublet, δ_{H} 3.69 (d, J 11 Hz) appeared in the spectrum. This doublet was identical to that of methyl diphenylphosphinate.

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