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The Reactions of some Methylphosphorus(v) Compounds with 25 Oleum and 100% H_2SO_4

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The reactions of some methylphosphorus(v) compounds with the strongly acidic solvents 25 oleum (containing 25% free SO_3) and 100% H_2SO_4 have been investigated by ^{31}P n.m.r. spectroscopy. Solvolysis is faster in 100% H_2SO_4 than in 25 oleum, and for P–Br than for P–Cl bonds. The 'compounds' $PMeCl_2Br_2$ and PMe_2ClBr_2 have been shown to contain mixtures of the corresponding halogenophosphonium cations $PMeCl_nBr_{3-n}^+$ (n = 0—3) and $PMe_2Cl_nBr_{2-n}^+$ (n = 0—2) in these solvents. Halogen exchange has been observed between PMe_2Cl_3 and PMe_2Br_5 in 25 oleum.

Previous work on the chemistry of organophosphorus compounds in sulphuric acid and similar highly acidic solvents[1–8] has been summarised in an earlier paper from this research group on the behaviour of monophenylphosphorus(v) compounds in such media.[9] The reactions of $PMe(O)Cl_2$ with 100% H_2SO_4, 25 oleum (oleum containing 25% free SO_3), and $HSClO_3$ have subsequently been reported,[10] and $\delta(^{31}P)$ values have been measured for the cations $PMeCl_3^+$, $PMe_2Cl_2^+$, and PMe_3Cl^+ in 25 oleum.[11] In the present study, the reactions of several methylphosphorus(v) compounds with 25 oleum or 100% H_2SO_4 have been followed by ^{31}P n.m.r. spectroscopy. Solvolysis proved to be faster in 100% H_2SO_4 than in 25 oleum, as expected from previous work,[9–15] and to be more rapid for P–Br than P–Cl bonds.

Experimental

All manipulations, including n.m.r. sample preparation, were carried out either *in vacuo* or under an inert atmosphere of dry nitrogen. Chemicals of the best available commercial grade were used, generally without further purification. The commercial sample of PMe_2Cl proved to contain a small amount of $PMeCl_2$, as shown by ^{31}P n.m.r. spectroscopy.[16] Attempts to separate the constituents by distillation proved unsuccessful, however, and the material was used as such for reaction with Br_2 to prepare PMe_2ClBr_2; in consequence monomethylphosphorus(v) species were also present in the mixture, but could be readily identified from their differing chemical shifts. PMe_2Cl_3 and PMe_2Br_5 were prepared from a different starting material, as indicated below.

Dibromomethylphosphine was prepared by equilibrating an equimolar mixture of $PMeCl_2$ and PBr_3 for 10 min, with stirring. The mixture was distilled, and the fraction boiling at 412—413 K was collected. Its ^{31}P n.m.r. spectrum showed a major peak at 184.0 p.p.m. ($PMeBr_2$), with traces of PBr_3 (227.4 p.p.m.) and PMeBrCl (190.0 p.p.m.).[16] $PMeBr_4$ (which contained a little $PMeClBr_3$ as a result), $PMeCl_2Br_2$, PMe_2Br_5,[17] PMe_2ClBr_2, and PMe_3Br_2 were prepared by bromination in an appropriate solvent of $PMeBr_2$, $PMeCl_2$, $PMe_2(S)$-$PMe_2(S)$, PMe_2Cl, and PMe_3 respectively, and PMe_2Cl_3 was similarly obtained by chlorination of $PMe_2(S)PMe_2(S)$.[18] The tetrabromoborates $[PMeBr_3]BBr_4$, $[PMe_2Br_2]BBr_4$, and $[PMe_3Br]BBr_4$ were prepared by treating the appropriate bromophosphorane with an equimolar quantity of BBr_3 in a halogenated hydrocarbon solvent; the solid products were isolated, washed with low-boiling point (303—313 K) light petroleum and dried if necessary *in vacuo*. Elemental analyses for new compounds are given in Table 1. A mixture of $PMe(O)Br_2$ and $PMe(O)ClBr$ was obtained by suspending a mixture of $PMeBr_4$ and $PMeClBr_3$ in CH_2Cl_2, and bubbling SO_2 through the suspension until a yellow solution formed. The solvent was removed *in vacuo*, leaving a pale yellow liquid. Its ^{31}P n.m.r. spectrum consisted of two resonances at 25.8w and 6.5s p.p.m. (w = weak, s = strong), assigned to $PMe(O)ClBr$ and $PMe(O)Br_2$[16] respectively. $PMe_2(O)Br$ was similarly prepared from PMe_2Br_5; its ^{31}P n.m.r. spectrum consisted of a single resonance at 72.6 p.p.m.

^{31}P N.m.r. spectra were recorded at 307.2 K as described in previous papers;[10,19] chemical shifts are quoted relative to external 85% H_3PO_4, with the downfield direction taken as positive. ^{11}B N.m.r. shifts were similarly obtained relative to external $B(OMe)_3$.

Results and Discussion

(*i*) *Monomethyl Compounds*.—The ^{31}P n.m.r. spectrum of $PMeBr_4$ (containing a little $PMeClBr_3$, as indicated in the

Table 1. Elemental analyses

	Analysis (%)									
	Found					Required				
Compound	C	H	P	Br	Cl	C	H	P	Br	Cl
$PMeBr_4$	3.2	0.85	8.4	87.4		3.3	0.85	8.5	87.4	
$[PMeBr_3]BBr_4$	2.0	0.55	5.1	89.9		1.9	0.50	5.0	90.8	
$PMeCl_2Br_2$	3.9	0.90	11.4	56.0	25.8	4.3	1.1	11.2	57.8	25.6
PMe_2Br_5	5.1	1.6	6.4	86.4		5.2	1.3	6.7	86.7	
$[PMe_2Br_2]BBr_4$	3.7	1.4	5.8	85.6		4.4	1.1	5.6	87.0	
PMe_3Br_2	15.3	3.4	12.8	67.5		15.3	3.8	13.1	67.7	
$[PMe_3Br]BBr_4$	6.0	2.1	*	79.1		7.4	1.9	6.4	82.1	

* Red colour obtained, making determination of P impossible.

Experimental section) in 25 oleum showed three resonances, at 74.2w, 53.3s, and 30.7m p.p.m. (w = weak, s = strong, m = medium). These peaks were assigned to the species $\mathrm{PMe(OH)ClBr^+}$, $\mathrm{PMe(OH)Br_2^+}$, and $\mathrm{PMeBr_3^+}$ respectively. (The extent of protonation of compounds containing P=O groups will vary with concentration and with the acid strength of the solvent,[9,10,12–15,20] but such species are represented in the protonated form for clarity.) In each case the assignments were confirmed by subsequent work. After one month, an additional signal was present at 43.6 p.p.m., probably due to $\mathrm{PMe(OH)_3^+}$, for which a value of 43.0 p.p.m. in 25 oleum has been reported,[10] although the intermediate species $\mathrm{PMe(OH)_2Br^+}$ may well have a similar shift in this solvent. It is quite possible that $\mathrm{PMe(OH)_2Br^+}$ solvolyses faster than its precursor, however, as observed in other systems.[9,10,12,13] After a further two months, the peak at 74.2 p.p.m. had disappeared, and three signals were apparent at 54.9w, 45.3s, and 31.5mw p.p.m., indicating that slow solvolysis was occurring.

The compound $\mathrm{[PMeBr_3]BBr_4}$ gave ^{31}P signals at 27.5 p.p.m. in the solid state and 30.7 p.p.m. in $\mathrm{PhNO_2}$, attributed to the $\mathrm{PMeBr_3^+}$ ion. ^{11}B Shifts of −37.7 p.p.m. in $\mathrm{PhNO_2}$ solution and −41.8 (broad) p.p.m. in the solid state were also recorded, in good agreement with literature data for the $\mathrm{BBr_4^-}$ ion.[21–24] Its solution in 25 oleum showed ^{31}P resonances at 29.1vs and 62.9w p.p.m., assigned to $\mathrm{PMeBr_3^+}$ and $\mathrm{PMeClBr_2^+}$ respectively; the latter signal arose from the presence of some $\mathrm{PMeClBr_3}$ in the starting material. (This signal was presumably present in the $\mathrm{PhNO_2}$ solution spectrum also, but fewer pulses were used when this spectrum was recorded, so it remained below the detection limit.) The sample was heated in a water-bath until all reaction ceased, as shown by the presence of one ^{31}P peak only at 45.8 p.p.m., assigned to the final solvolysis product $\mathrm{PMe(OH)_3^+}$, or condensation products thereof.[10]

To confirm some of the above assignments, a mixture of $\mathrm{PMe(O)Br_2}$ and $\mathrm{PMe(O)ClBr}$ was prepared; it gave ^{31}P signals at 25.8w and 6.5s p.p.m., assigned to $\mathrm{PMe(O)ClBr}$ and $\mathrm{PMe(O)Br_2}$[16] respectively. In 25 oleum it also gave two resonances, at 72.6w and 53.3s p.p.m., readily assigned from the relative intensities to $\mathrm{PMe(OH)ClBr^+}$ and $\mathrm{PMe(OH)Br_2^+}$, and in good agreement with peaks assigned to these species from the $\mathrm{PMeBr_4}$–$\mathrm{PMeClBr_3}$–25 oleum reaction. In 100% $\mathrm{H_2SO_4}$ four ^{31}P resonances were detected, at 61.3w, 46.0vs, 36.4mw, and 25.8s p.p.m., ascribed sequentially to $\mathrm{PMe(OH)_2Cl^+}$, $\mathrm{PMe(OH)_3^+}$, $\mathrm{PMe(OH)Br_2^+}$, and $\mathrm{PMe(OH)_2Br^+}$. The values of 61.3 and 46.0 p.p.m. agree well with data given previously for these ions in 100% $\mathrm{H_2SO_4}$,[10] and the remaining assignments seem reasonable in view of the relative peak intensities and the probable solvolytic path. Solvolysis is more rapid in 100% $\mathrm{H_2SO_4}$ than in 25 oleum, as expected from the relative acid strengths. The results also show that protonation is more extensive in 25 oleum than in 100% $\mathrm{H_2SO_4}$, as indicated by larger downfield shifts in the former solvent. No signal was observed in this instance for $\mathrm{PMe(OH)ClBr^+}$. Since P–Br bonds are weaker than P–Cl bonds they are expected to solvolyse more readily, giving rise to the solvolytic paths (1) and (2). These deductions are entirely in keeping with the above results.

$$\mathrm{PMe(OH)Br_2^+ \xrightarrow{H_2SO_4} PMe(OH)_2Br^+ \xrightarrow{H_2SO_4} PMe(OH)_3^+} \tag{1}$$

$$\mathrm{PMe(OH)ClBr^+ \xrightarrow{H_2SO_4} PMe(OH)_2Cl^+ \xrightarrow{H_2SO_4} PMe(OH)_3^+} \tag{2}$$

The 'compound' $\mathrm{PMeCl_2Br_2}$ was obtained as a white solid by reaction of $\mathrm{PMeCl_2}$ with $\mathrm{Br_2}$. It dissolved in both 25 oleum and 100% $\mathrm{H_2SO_4}$ with effervescence to yield red-orange solutions.

Table 2. $\delta(^{31}\mathrm{P})$ (p.p.m.) for reaction of $\mathrm{PMeCl_2Br_2}$ with 25 oleum

$\delta(^{31}\mathrm{P})$	Assignment
120.9w	$\mathrm{PMeCl_3^+}$
95.1s	$\mathrm{PMeCl_2Br^+}$
75.8s	$\mathrm{PMe(OH)ClBr^+}$
64.5m	$\mathrm{PMeClBr_2^+}$
54.9w	$\mathrm{PMe(OH)Br_2^+}$
30.7m	$\mathrm{PMeBr_3^+}$

Table 3. $\delta(^{31}\mathrm{P})$ (p.p.m.) for reaction of $\mathrm{PMeCl_2Br_2}$ with 100% $\mathrm{H_2SO_4}$

$\delta(^{31}\mathrm{P})$	Assignment
120.9w	$\mathrm{PMeCl_3^+}$
95.1m	$\mathrm{PMeCl_2Br^+}$
74.2m	$\mathrm{PMe(OH)Cl_2^+}$
64.5s	$\mathrm{PMeClBr_2^+}$
59.6mw	$\mathrm{PMe(OH)ClBr^+}$
43.6vw	$\mathrm{PMe(OH)Br_2^+}$
30.7s	$\mathrm{PMeBr_3^+}$

The ^{31}P spectrum in 25 oleum contained several peaks, which are assigned in Table 2. The assignments are in good agreement with published data where available, and with other results obtained independently in this work. The results show clearly that a mixture of all the possible ions $\mathrm{PMeCl}_n\mathrm{Br}_{3-n}^+$ (n = 0—3) is present, together with some solvolysis products. After 5 d the solution gave signals at 95.1, 74.2, 64.5, 45.7, and 29.1 p.p.m., all considerably reduced in intensity except for the new peak at 45.7 p.p.m., which is ascribed to $\mathrm{PMe(OH)_3^+}$ or possibly $\mathrm{PMe(OH)_2Br^+}$. Solvolysis is faster in this instance than in some 25 oleum systems because HBr can be oxidised by the solvent to $\mathrm{Br_2}$, as shown by the solution colour, with a consequent reduction in acid strength, equation (3). After 2 weeks only a single peak was observed at 45.7 p.p.m., ascribed to the final solvolysis product $\mathrm{PMe(OH)_3^+}$.

$$\mathrm{2HBr + H_2S_2O_7 \longrightarrow Br_2 + SO_2 + H_2O + H_2SO_4} \tag{3}$$

The ^{31}P signals and their assignments from the 100% $\mathrm{H_2SO_4}$ solution are given in Table 3. The shifts for the cations $\mathrm{PMeCl}_n\mathrm{Br}_{3-n}^+$ are in excellent agreement with those from 25 oleum, and the value for $\mathrm{PMe(OH)Cl_2^+}$, which is expected to be the first solvolysis product of both $\mathrm{PMeCl_3^+}$ and $\mathrm{PMeCl_2Br^+}$, agrees well with a previous result of 72 p.p.m. in 100% $\mathrm{H_2SO_4}$.[10] After 1 d the signal at 120.9 p.p.m. had almost disappeared, that at 74.2 p.p.m. had increased somewhat in intensity, and there was a weak signal at 48.4 p.p.m., probably due to $\mathrm{PMe(OH)_3^+}$. After one month the only resonance present was at 48.4 p.p.m., from $\mathrm{PMe(OH)_3^+}$.

(*ii*) *Dimethyl Compounds.*—$\mathrm{PMe_2Br_5}$ was prepared as an orange solid;[17] it gave ^{31}P solution signals at 75.8 p.p.m. in both $\mathrm{PhNO_2}$ and MeCN, attributed to the $\mathrm{PMe_2Br_2^+}$ ion. In the solid state a broad resonance at 72.6 p.p.m. was recorded. The compound thus probably has the structure $\mathrm{[PMe_2Br_2]Br_3}$, similar to that of $\mathrm{PBr_7}$.[25] The presence of the $\mathrm{Br_3^-}$ ion was confirmed by a Raman band at 169 cm^{-1}.[26] The compound dissolved in both 25 oleum and 100% $\mathrm{H_2SO_4}$ with vigorous effervescence and evolution of heat; red-orange solutions were formed, and liquid bromine was deposited at the bottom of the n.m.r. tube. In 100% $\mathrm{H_2SO_4}$, three ^{31}P peaks were observed, at 92.0, 85.5, and 74.2 p.p.m., assigned to $\mathrm{PMe_2(OH)Br^+}$, $\mathrm{PMe_2(OH)_2^+}$, and $\mathrm{PMe_2Br_2^+}$ respectively. The results are in good agreement with independent data given elsewhere in this section. After 6 d only one signal was apparent, at 85.5

p.p.m., due to the completely solvolysed species $PMe_2(OH)_2^+$. Two signals were obtained from the initial spectrum in 25 oleum, at 96.0m and 74.2s p.p.m., ascribed to $PMe_2(OH)Br^+$ and $PMe_2Br_2^+$ respectively, and showing that the rate of solvolysis is much slower in 25 oleum than in H_2SO_4. After a considerable period of time this solution, too, gave a single resonance at 85.5 p.p.m., due to $PMe_2(OH)_2^+$. The downfield shift for $PMe_2(OH)Br^+$ on going from 100% H_2SO_4 to 25 oleum is consistent with more extensive protonation by the stronger acid, but $PMe_2(O)(OH)$ appears to be a strong enough base to be completely protonated by both solvents.

To confirm the above assignments, $[PMe_2Br_2]BBr_4$ was prepared as a white solid by reaction of PMe_2Br_5 with BBr_3. It gave a broad ^{31}P resonance at 70.9 p.p.m. in the solid state, and a broad ^{11}B signal at −59.7 p.p.m., while its ^{11}B solution spectrum in $PhNO_2$ consisted of a single peak at −39.4 p.p.m. The solution value is in good agreement with literature data,[21–23] and the solid-state value is similar to that found for $[NEt_4]BBr_4$.[24] It dissolved violently in 25 oleum to form a pale brown solution, the initial ^{31}P spectrum of which contained peaks at 95.1m, 87.1w, and 74.2s p.p.m. Little change was evident after 1 week, but after 2 months only one peak was observed, at 85.5 p.p.m. Hence slow solvolysis of the $PMe_2Br_2^+$ ion occurs here also. Bromine was again liberated during the reaction.

For further confirmation, $PMe_2(O)Br$ was prepared; in the liquid state it gave a single peak at 72.6 p.p.m. In 25 oleum one peak only was observed, at 89.5 p.p.m., ascribed to $PMe_2(OH)Br^+$. Nine months later the same solution gave a single signal at 86.4 p.p.m., from the final solvolysis product $PMe_2(OH)_2^+$. In 100% H_2SO_4 it gave a single resonance at 83.8 p.p.m., assigned to $PMe_2(OH)_2^+$, and showing that solvolysis is again faster in the weaker acid medium.

A shift of 123 p.p.m. has been reported for PMe_2Cl_3 in 25 oleum, confirming the presence of the $PMe_2Cl_2^+$ ion.[11] In the present work, three signals were observed, at 124.2s, 106.4m, and 85.5w p.p.m., assigned to $PMe_2Cl_2^+$, $PMe_2(OH)Cl^+$, and $PMe_2(OH)_2^+$ respectively. No change in the positions of the resonances was apparent after two months. In 100% H_2SO_4, three signals were again detected, at 123.3s, 106.4s, and 86.4m p.p.m., assigned as above.

PMe_2ClBr_2 was prepared as a white solid by reaction of PMe_2Cl with Br_2. As indicated in the Experimental section, a little $PMeCl_2$ was present in the starting material, and could not be separated by distillation. Hence monomethyl as well as dimethyl species were present in the acid solutions. The ^{31}P spectrum in 25 oleum showed a number of peaks, assigned as in Table 4. The result for $PMe_2Cl_2^+$ is in good agreement with values previously obtained in 25 oleum,[11] while the shifts for $PMe_2(OH)Br^+$ and $PMe_2Br_2^+$ agree well with results from PMe_2Br_5 and $[PMe_2Br_2]BBr_4$. The intermediate signal at 109.6 p.p.m. may thus reasonably be ascribed to PMe_2ClBr^+, as confirmed by subsequent work, although it probably also has a contribution from $PMe_2(OH)Cl^+$. Values between 91 and 100 p.p.m. have been obtained for PMe_2ClBr^+ in the solid state,[27] but with different counter ions to those present in oleum solution. A more complicated spectrum was obtained in 100% H_2SO_4; the shifts and their assignments are given in Table 5. When the same solution was reinvestigated after 5 weeks, only two signals were present, at 86.4 and 48.4 p.p.m., attributed to the final solvolysis products $PMe_2(OH)_2^+$ and $PMe(OH)_3^+$ for di- and mono-methylphosphorus species respectively.

Table 4. $\delta(^{31}P)$ (p.p.m.) for reaction of PMe_2ClBr_2 with 25 oleum

$\delta(^{31}P)$	Assignment
124.2w	$PMe_2Cl_2^+$
109.6s	PMe_2ClBr^+ and $PMe_2(OH)Cl^+$
96.0vs	$PMe_2(OH)Br^+$
75.8m	$PMe_2Br_2^+$
55.6m	$PMe(OH)Br_2^+$

An alternative method of preparing the PMe_2ClBr^+ ion was attempted by dissolving a mixture of PMe_2Cl_3 and PMe_2Br_5 in 25 oleum. Halogen-exchange reactions of phosphorus(V) halides and oxyhalides in 25 oleum have been found to occur only if a suitable source of halide ion is present,[14] which in this case would be furnished either by dissolution of PMe_2Cl_3, or by break-up of the Br_3^- ion. The ^{31}P spectrum of the mixture contained signals at 122.6s ($PMe_2Cl_2^+$), 108.6s (PMe_2ClBr^+), 93.5m [$PMe_2Br(OH)^+$], and 72.6m p.p.m. ($PMe_2Br_2^+$), showing that exchange does take place. After 2 months the same number of resonances was observed, with the signal at 93.5 p.p.m. having increased in intensity relative to the other peaks. These results show that solvolysis is slow in 25 oleum, and the P–Br bonds are solvolysed faster than P–Cl bonds.

(*iii*) *Trimethyl Compounds*.—PMe_3Br_2 was isolated as a yellow solid; it gave a broad resonance at 67.8 ± 1 p.p.m. in the solid state and a solution signal at 66.2 p.p.m. in $PhNO_2$, attributed to the PMe_3Br^+ ion. The compound dissolved in 25 oleum with effervescence to yield a pale orange solution, which gave signals at 67.8 and 106.4 p.p.m., readily assigned to PMe_3Br^+ and $PMe_3(OH)^+$ respectively. The spectrum was unchanged after 1 d, but one signal only was present after a week, at 106.4 p.p.m., consistent with complete solvolysis of the P–Br bond. In 100% H_2SO_4 a vigorous reaction occurred to give a pale yellow-orange solution, which yielded signals at 66.2w and 88.7s p.p.m., assigned to the same species as in the oleum solution. The latter signal increased rapidly in intensity at the expense of the former, and after 1 week a single resonance at 90.4 p.p.m. was present, from $PMe_3(OH)^+$. The shifts indicate that protonation is again less extensive in the weaker acid solvent, as expected. $[PMe_3Br]BBr_4$ gave a broad solid-state resonance at 64.5 p.p.m., and a solution signal in $PhNO_2$ at 66.2 p.p.m. The ^{11}B n.m.r. of the solid consisted of a broad peak at −55.7 p.p.m., and the solution in $PhNO_2$ gave a signal at −39.4 p.p.m., similar to the results for $[PMe_2Br_2]BBr_4$ and to literature data.[21–24] A solution of the compound in 25 oleum yielded ^{31}P signals at 66.2vs, 79.1vw, and 114.6m p.p.m. The first peak was readily assigned to PMe_3Br^+, but the other signals were unexpected since only one solvolysis product, $PMe_3(OH)^+$, is possible. The low-field signal is probably due to this species, the shift differing from the data above because of concentration effects, but the weak resonance at 79.1 p.p.m. presumably arises from a minor impurity and was not assigned.

We therefore conclude that 25 oleum and 100% H_2SO_4 are useful solvents for methylphosphorus(V) compounds, particularly the former since solvolysis reactions are slower. No

Table 5. $\delta(^{31}P)$ (p.p.m.) for reaction of PMe_2ClBr_2 with 100% H_2SO_4

$\delta(^{31}P)$	Assignment
124.2w	$PMe_2Cl_2^+$
106.4vs	$PMe_2ClBr^+ + PMe_2(OH)Cl^+$
92.7w	$PMe_2(OH)Br^+$
86.4s	$PMe_2(OH)_2^+$
74.2m	$PMe_2Br_2^+$
56.5mw	$PMe(OH)ClBr^+$
39.6m	$PMe(OH)Br_2^+$
30.7w	$PMe(OH)_2Br^+$ or $PMeBr_3^+$

evidence was found for sulphonation of the OH group by 25 oleum, although Haake and Ossip[6] deduced from ^1H n.m.r. measurements that in compounds of the types $PR_2(O)OH$ and $PR_2(O)X$ (R = alkyl or alkoxy) the initial protonation was followed by sulphonation of the OH group in oleums of greater than 10% SO_3 content.[6] Shift data have been obtained for $PMeBr_3^+$, $PMe_2Br_2^+$, and PMe_3Br^+, and for the mixed cations $PMeCl_nBr_{3-n}^+$ and $PMe_2Cl_nBr_{2-n}^+$, which are present in the 'compounds' $PMeCl_2Br_2$ and PMe_2ClBr_2, as well as for several solvolysis products. The ion PMe_2ClBr^+ has also been obtained in 25 oleum solution by halogen exchange between PMe_2Cl_3 and PMe_2Br_5. P–Br bonds solvolyse faster than P–Cl bonds, as expected from the relative bond strengths, and protonation of phosphoryl compounds is more extensive in 25 oleum than in 100% H_2SO_4.

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