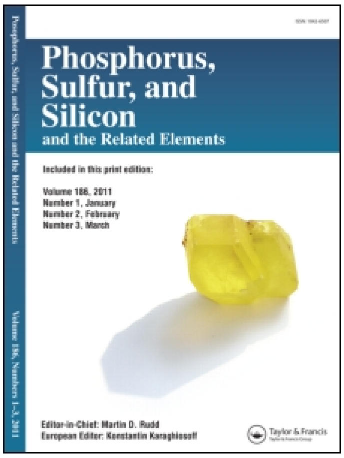

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

THE REACTION OF ALKANEPHOSPHONIC ACID ESTERS WITH METALS

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To cite this Article Koch, P. , Rumpel, H. , Sutter, P. and Weis, C. D.(1989) 'THE REACTION OF ALKANEPHOSPHONIC ACID ESTERS WITH METALS', Phosphorus, Sulfur, and Silicon and the Related Elements, 44: 1, 75 — 85
To link to this Article: DOI: 10.1080/10426508908043709
URL: http://dx.doi.org/10.1080/10426508908043709

Phosphorus, Sulfur, and Silicon, 1989, Vol. 44, pp. 75–85
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THE REACTION OF ALKANEPHOSPHONIC ACID ESTERS WITH METALS

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(Received September 6, 1988)

The reaction of dialkyl alkanephosphonates (methyl, ethyl, isopropyl) with alkali and earth alkali metals, respectively, has been investigated. These metals reacted with phosphonates yielding the corresponding salts of monoalkyl alkanephosphonates with the evolution of a mixture of low molecular weight gaseous products the composition of which was quantitatively determined by gas chromatographic methods. The gaseous products could be traced to the primary formation of radical fragments originating from cleavage of either the carbon–oxygen or the phosphorus–oxygen bonds. Lower alkanes were formed predominantly, but there were also traces of acetylene and also of benzene. Diisopropyl methylphosphonate showed to a large extent cleavage of the carbon–phosphorus bond, yielding a mixture of the salts of isopropylphosphonite and isopropyl methylphosphonate. Reaction mechanisms were advanced to explain some of the results.

Key words: Dialkyl alkanephosphonates; metal salts of alkyl alkanephosphonates; GC of gas mixtures; P—C bond cleavage; P—O bond cleavage; reaction mechanism.

INTRODUCTION

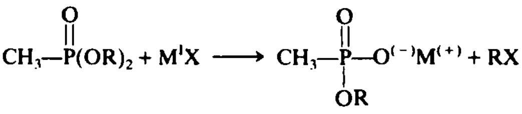
The esters of phosphonic acids are composed of fragments with carbon atoms bonded to phosphorus which strongly resist any attack by strong base or acid under hydrolytic conditions. On the other hand, the hydrolysis of the ester part of the molecule by either one of these reagents proceeds readily with the formation of the half esters of the alkylphosphonic acid and the corresponding alkylphosphonic acid, respectively. A smooth carbon-phosphorus cleavage of the alkylphosphonic acids occurred also in the presence of eccherицia coli bacteria.[1]

Phosphonic acid esters that undergo cleavage of the carbon-phosphorus bond bear a carbonyl or a hydroxyl function on the carbon next to the phosphorus atom.[2]

The cleavage of the alkyl esters of phosphonates is not restricted to their reaction with acids or with bases, but was also observed to occur with metal salts. Typical examples of these reactions were realized by heating dialkylphosphonates with halides of the alkali, earth alkali, rare earth and the heavy metals yielding the corresponding salts of monoalkyl alkanephosphonates.[3,4,5]

The reaction of dimethyl methylphosphonate (DMMP) and its higher alkyl analogues with alkali chlorides or bromides[6] is known to proceed spontaneously with the expulsion of one mole of alkyl halide as exemplified below (Scheme 1).

Dimethyl methylphosphonate in particular has often served as a model compound in studies which dealt with the interaction of monomolecular layers of dialkyl alkanephosphonates with metal oxides. There are some recent papers



$$CH_3-\overset{O}{\overset{\|}{P}}(OR)_2 + M^{I}X \longrightarrow CH_3-\underset{OR}{\overset{O}{\overset{\|}{P}}}-O^{(-)}M^{(+)} + RX$$

R = Alkyl, X = Br, Cl, J, M^I = Li, Na, K

SCHEME 1

which describe the interaction of DMMP with the surface of metals or metal oxides.[7–10] These investigations have largely been designed to study the surface chemistry of alkane phosphonates (and especially with DMMP as a model compound), their adsorption–desorption processes, and their bonding configuration on those surfaces which ultimately revealed then a pattern of their thermal degradation. A number of other reports are concerned with the decomposition of DMMP in high voltage discharges or in laser induced photo destruction.[11,12]

These reports, however, are concerned with the interaction of metals with DMMP and ultimately also with reactions leading towards the total destruction of the DMMP molecule, thus producing carbon, phosphorus and small fragments thereof combined with oxygen or with hydrogen.

However, scarcely any attention has been directed towards the reaction of these metals with alkane phosphonates occurring with retention of the phosphonate structure. It seemed to be limited to a solitary report[13] dealing with reactions of sodium metal with several phosphonates either in toluene as diluent or in an excess of the respective phosphonate. Some evolution of alkanes (0.1 mole or less) was noticed the composition of which indicating the ester part of the molecule to be their origin. The solid products formed were presumed to have a composition corresponding to the salts of the esters of the respective phosphonates.

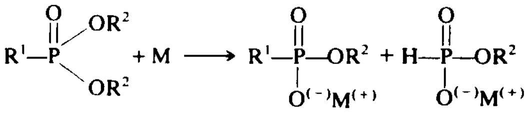
We deemed it of interest to investigate this unprecedented cleavage of aliphatic phosphonic acid esters by a metal, and also to gain some insight and mechanistic understanding into the formation and the composition of the evolved gaseous reaction products. The purpose of this paper is to report some of our recent findings concerning the interaction of representative examples of dialkyl alkanephosphonates with alkali and with earth alkali metals.

However, in this paper, the emphasis will be primarily synthetic, rather than mechanistic.

RESULTS

At the commencement of these investigations, the reactions of metals with phosphonates were carried out in the presence of air. However, mass spectrometric determinations of the gaseous fragments formed revealed that this procedure led, aside from a mixture of alkanes and alkenes, to a number of additional products such as carbon monoxide, carbon dioxide, water and phosphine. Therefore, all the subsequent reactions were performed in an atmosphere of argon, thus reducing the number of unwanted by-products. Similar observations were also quoted by Fraser *et al.*[11,12], however, in a different connotation.

The reactions of different phosphonates with alkali metals are collected in Scheme 2.



1–3 **4–7, 9,** **8, 10**

No	R^1	R^2	M	No	R^1	R^2	% yield
1[a)]	CH_3	CH_3	Li	**4**	CH_3	CH_3	95
1	CH_3	CH_3	Na	**5**	CH_3	CH_3	94.5
2[b)]	CH_3	C_2H_5	Li	**6**	CH_3	C_2H_5	98.2
3[c)]	CH_3	$CH(CH_3)_2$	Li	**7**	CH_3	$CH(CH_3)_2$	64[d]
				8		$CH(CH_3)_2$	36[d]
3[c)]	CH_3	$CH(CH_3)_2$	Na	**9**	CH_3	$CH(CH_3)_2$	25[d]
	CH_3	$CH(CH_3)_2$		**10**		$CH(CH_3)_2$	75[d]

[a)] Dimethyl methylphosphonate (DMMP), [b)] Diethyl methylphosphonate (DEMP), [c)] Diisopropyl methylphosphonate (DIMP), [d)] % Composition calcd. from NMR-spectral data.

SCHEME 2

The addition of lithium (0.02 g atom) having a clean surface to an excess of DMMP(**1**) under an atmosphere of argon at room temperature resulted at the outset in no appreciable gas evolution which, however, commenced vigorously on warming the suspension to 80–90°C. The large excess of DMMP (and likewise also of other dialkylphosphonates) was used to moderate the rather violent exothermic reaction which started as soon as the metal had melted. The total volume of gases evolved was 2.9 liter. A representative sample of the mixture of the gaseous products was collected in a gas trap, the components identified by their mass spectra, and then analyzed by gas chromatography comparing them with known samples. The results are detailed in Table I.

The reaction of sodium with DMMP (Scheme 2) followed essentially the same course, and also the pattern of the percentage distribution of gases was superficially identical, although neither ethane nor any of the C_4-gas fragments were formed, and also benzene proved to be absent. However, 1.08% of ethene was found. The total volume of gases evolved was 4.4 liters per 0.3 g atom of sodium (or 2.92 liters/0.2 g atom) which correlated well with the result obtained with lithium metal.

The lithium (**4**) and the sodium (**5**) salts, respectively, which were formed in these reactions were isolated after having distilled the excess of DMMP from the solutions, and their structures were ascertained by the elemental analysis and their ^1H and ^{13}C NMR spectra, but if already known by comparison of their infrared spectra with known specimen.[6]

A comparison of the gases formed in the reaction of lithium with DMMP and with Diethyl methylphosphonate (DEMP)(**2**), respectively, showed significant differences. Whereas in DMMP the bulk of gases consisted of methane, ethane and of dimethyl ether, in DEMP 96.98% of the gas mixture proved to be ethane

TABLE I

Reaction of alkali and earth alkali metals with dialkyl alkanephosphonates, product distribution (Vol%) of the gaseous products

Product	Lithium DMMP	Sodium DMMP	Lithium DEMP	Magnesium DMMP	Lithium DIMP	Sodium DIMP
Methane	82.44	87.88	1.46	30.58	4.16	0.54
Acetylene	0.04	0.09	0.13			
Ethylene	0.04	1.08	0.10	0.02		
Ethane	8.05		96.98	1.56	0.06	0.036
Unknown[1]					0.4	0.054
Propene	0.04	0.05		0.02	8.9	0.7
Propane	0.04		0.07	0.17	81.5	95.96
2-Propanol					4.16	2.16
Unknown[1]	0.27	0.05		0.02	0.23	0.36
Methanol	0.87					
Dimethylether	8.82	10.37	0.07	67.57		
n-Butane			1.13			
2-Butene			0.07			
i-Butane	0.04			0.17		
i-Butene	0.04			0.03		
Unknown[1]	0.04	0.14				
Unknown[1]	0.04	0.09				
Unknown[1]		0.05				
n-Pentane		0.05				
1-Pentene	0.04					
Benzene	0.04			0.04		
2,3-Dimethylbutane					0.47	0.12
n-Hexane						0.02

[1] The percentage of unknown compounds was calculated using the response factor of propane (FID); DMMP = Dimethyl methylphosphonate, DEMP = Diethyl methylphosphonate, DIMP = Diisopropyl methylphosphonate

and only 1.46% of methane was observed. There was no formation of ether. The small amount of 2-butene is believed to be due to the disproportionation of ethyl radicals, $2C_2H_5 \rightarrow C_4H_8 + 2H$.

Strong evidence for a carbon–phosphorus fission was supplied from the results of the reactions of lithium and sodium, respectively, with diisopropyl methylphosphonate (DIMP) (**3**).

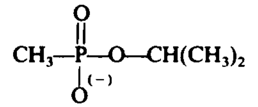
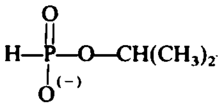
Lithium and DIMP yielded predominantly propane (81.50%), propene (8.90%), methane (4.16%), and 2-propanol (4.16%), together with minor quantities of other products (see Table 1).

Inspection of the ^{1}H-NMR spectra of the remaining metal salt showed that a mixture of the lithium salts of methyl isopropylphosphonate and isopropylphosphonite had been formed in a ratio of 1.8:1 (Table II). This was indicated by the presence of two sets of resonances for the isopropyl group and only one for the P—CH_3 and P—H, respectively. The ratio of the composition of the two components was determined from the integrals of the signals.

The structure of the two compounds could be ascertained from their ^{1}H- and ^{13}C NMR spectra. The relative composition of the mixture of compounds **7**, **8** and **9**, **10**, respectively, was determined from the integrals of the signals in the ^{1}H NMR spectra. The methyl groups of the isopropyl and of the CH_3—P groups

TABLE II

Composition (%) of alkali salts formed in the reactions of DIMP with lithium and with sodium[a]

$M^{(+)}$	 $CH_3-P(=O)(O^{(-)})-O-CH(CH_3)_2$	 $H-P(=O)(O^{(-)})-O-CH(CH_3)_2$
Li	64 (**7**)	36 (**8**)
Na	25 (**9**)	75 (**10**)

[a] Determined from the integrals of the signals in the ^1H NMR spectra.

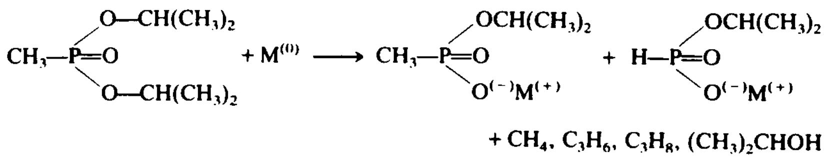
in **7** appeared at 1.08 ppm and at 0.92 ppm. The signal of the $-O-C\underline{H}(CH_3)_2$ group absorbed as a multiplet at 4.21 ppm, and is superimposed with the corresponding signal of **8**.

The signal for the methyl groups of the isopropyl structural element of **8** is superimposed with that of **7** at 1.08 ppm, a further doublet at 6.57 ppm was assigned to P—H with a coupling constant of $J_{HP} = 570$ Hz. Also in the ^{13}C NMR spectra, the presence of two sets of resonances for the isopropyl group and only one for the $P-CH_3$ group indicated the presence of **7** and **8**, respectively (for details see the experimental part).

The reaction of DIMP with sodium furnished again mainly propane (95.96%) and 2-propanol (2.16%). The total volume of the gases evolved was 3.02 liters per 0.2 g atom of sodium. However, the ratio of the mixture of the sodium salts of methyl isopropylphosphonate (**9**) and of isopropylphosphonite (**10**) was now 1 : 3, e.g. the reverse composition of the results obtained with lithium.

The ratio in which the two salts were formed varied considerably with the age, respectively the purity of the lithium metal used and this also heavily effected the reactivity, and the exothermic violence of the ensueing reaction.

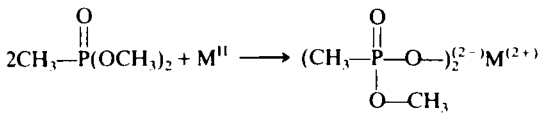
Thus cleavage of the carbon–phosphorus bond had readily occurred, and even became the favored route when sodium was caused to react with a phosphonate. The overall reaction is represented in Scheme 3.



SCHEME 3

No ether was detected, yet there are minor quantities of higher alkanes, such as 2,3-dimethylbutane and *n*-hexane.

The reaction of magnesium turnings with DMMP was initiated by heating DMMP to reflux (Scheme 4). The reaction started after an induction period of 4–8 minutes and then proceeded exothermally. The rate of reflux was moderated by a large excess of DMMP. There were 25 liters of gas evolved per mole of

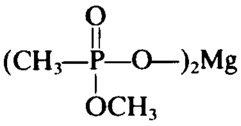


$$2CH_3-\overset{\overset{O}{\|}}{P}(OCH_3)_2 + M^{II} \longrightarrow (CH_3-\underset{\underset{O-CH_3}{|}}{\overset{\overset{O}{\|}}{P}}-O-)_2^{(2-)}M^{(2+)}$$

11 M = Mg
12 M = Ca
13 M = Ba

SCHEME 4

magnesium, thus only half the amount to be expected. The largest part of the gas consisted of dimethyl ether (67.5%), followed by 30.6% of methane, 1.5% of ethane and very minor amounts of ethene, propane, propene and isobutane. The viscous residue was induced to crystallize and furnished the magnesium salt of methyl methylphosphonic acid (**9**) in 95.4% yield. The structure and the composition of the salt (**11**) was ascertained by the ^{1}H NMR spectrum and the analytical results.



$$(CH_3-\underset{\underset{OCH_3}{|}}{\overset{\overset{O}{\|}}{P}}-O-)_2Mg$$

11

The acetone washing of the salt were concentrated yielding a viscous oil which consisted of differing compounds. Distillation under reduced pressure yielded a small fraction of trimethylphosphine oxyde. The ^{13}C NMR investigation of the residue showed signals for CH_2-groups at 18–25 ppm indicating fragments displaying the structural moiety of $-CH_2-PO_3^{(2-)}$.

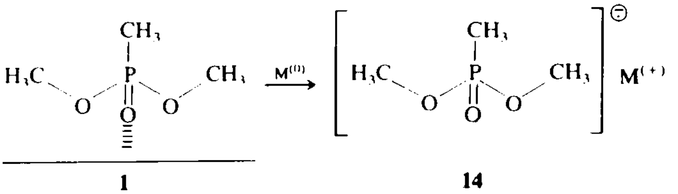
Calcium and barium reacted very slowly with rather a sluggish evolution of gases (Scheme 4). The reaction with calcium went to completion after 19 hours, and furnished the calcium salt of methyl methylphosphonate. A reaction time of 90 hours was required to convert barium into the methyl methylphosphonate salt.

Higher dialkyl alkanephosphonates proved unreactive with earth alkali metals.

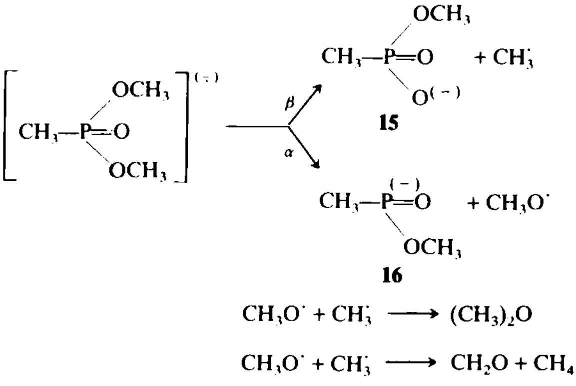
DISCUSSION

The adsorption of dialkyl alkylphosphonates onto the surface of alkali or earth alkali metals may be envisaged as following a pattern similar to their adsorption on carbon, aluminum, heavy metals or iron oxide surfaces.[7-10] The bonding of DMMP on clean surfaces of rhodium was assigned to interaction through the lone pair of electrons of the oxygen of the P=O part of the molecule. A stepwise decomposition of the chemisorbed DMMP to methyl methylphosphonic acid was observed above 295 K and to methylphosphonic acid above 573 K, each step resulting in the loss of a methoxy group. The remainder decomposed to small molecules including hydrogen, water, carbon monoxide, carbon dioxide, methane, methanol and formic acid.

The way in which molecular DMMP might be bonded to a metal surface was discussed and the bonding geometry shown was consistent with all the results obtained.[7-10] (Scheme 5). The subsequent steps may involve a one electron transfer from the metal to the phosphorus atom yielding the radical anion **14.** The breakdown of the radical anion follows the known pattern of the α- and the β-fission of the P—O—CH_3 moiety, forming methyl and/or methoxy radicals (Scheme 6), both of which can be traced as methane or as dimethyl ether, respectively. Since the radicals are assumed to be generated in a solvent cage of DMMP molecules further collisions with those lead in the high concentrations which had been used to the formation of methane. The relatively minor amounts of C_3–C_5-fragments attested to further collisions of radicals which may have been build up from other small fragments. The formation of benzene is believed to be due to the presence of acetylene which then underwent trimerization to some extent. Similar schemes may also be realized for other alkanephosphonates in their reaction with metals.



SCHEME 5

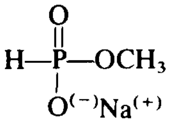


SCHEME 6

That the methane evolved stems from the methyl ester group and not from the methyl group bonded to phosphorus was strongly supported by the reaction of lithium with DEMP which produced ethane in 97% yield, and thus showed that only the alkyl part attached to oxygen is responsible for the formation of the evolved gas, as otherwise large quantities of methane should have been formed. The small amount of methane (1.46%), however, may well be due to a cleavage of the carbon-phosphorus bond. There was virtually no formation of dimethyl ether.

The number of alkanes formed was greatly reduced in the reaction of diisopropyl methylphosphonate with alkali metals, and there was no formation of diisopropyl ether.

While the formation of the lithium or the sodium salt of isopropyl methylphosphonate fitted into the common fragmentation pattern, the presence of large amounts of the salts of isopropylphosphonite showed that a fission of the carbon-phosphorus bond might not be so unusual as one was let to assume. Also the ^{13}C NMR spectrum of the sodium salt of methyl methylphosphonate (**5**) displayed signals (J_{PH}: 563.5 Hz) which clearly indicated that the crude sample contained a very small amount of the sodium salt of methylphosphonite.



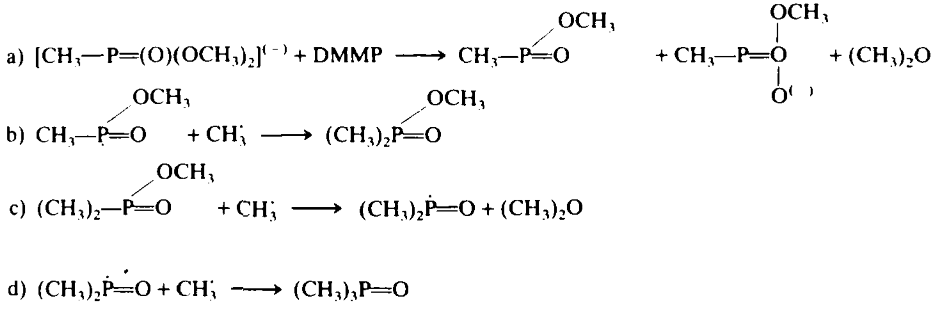
$$H-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^{(-)}Na^{(+)}}{|}}{P}}-OCH_3$$

The source of hydrogen required for the formation of the P—H bond and for the formation of the alkanes is still unknown but very likely is to be found in the large excess of phosphonate molecules surrounding the reactive species.

The absence of olefins in general and in particular in this process is a striking difference to the thermal fragmentation pattern of dialkyl alkylphosphonates which yielded mainly unsaturated hydrocarbons. Therefore it seems unlikely that a cleavage of the carbon-phosphorus bond will be preceeded by an alkyl interchange which is known to be a thermally induced, although, a very slow process yielding alkenes in high yield.[14]

The reaction of DMMP with magnesium (Scheme 7) brought about an extensive evolution of dimethyl ether. Since also trimethylphosphine oxide had been identified among the reaction products, its formation might partially account for the fate of methyl radicals which were not manifested otherwise among the gaseous products. The following reaction sequence postulates the formation of the trimethylphosphine oxide, and also the large amount of dimethyl ether found.

The presence of compounds possessing structural units such as $—CH_2—PO_3^{(2-)}$ supported the surmise that a rather indiscriminate attack of radicals occurs on the metal surface which leads finally to a strip-down of all the phosphorus oxygen ester bonds in the molecule.



SCHEME 7

About 50–60% of the alkyl radicals formed in these reactions are not accounted for, since they do not appear as one of the alkanes. Presumably, they have been used in multiple alkylation processes yielding ultimately trialkylphosphine oxides.

EXPERIMENTAL SECTION

Dimethyl methylphosphonate (DMMP) was distilled over a fractionating column (bp 178°C/760 mm) and stored over a desiccant. Diethyl methylphosphonate (DEMP)[15] and diisopropyl methylphosphonate (DIMP)[16] were prepared according to the literature.

Gas chromatographic analysis were performed on a Hewlett-Packard model 5890, equipped with a split-/splitless injection port, a flame ionization detector (FID) and a cryogenic system. Separation was achieved by using a 10 m 0.32 mm Pora-Plot Q fused-silica capillary (Chrompack). The following gas chromatographic conditions were applied: Injection: 100 μL, split 1:60, carrier gas: helium, 50 kPa, oven temperature: 10°C (2 minutes), 10°C/min. to 90°C, 5°C/min. to 170°C, 20°C/min. to 250°C, 250°C (2 min.).

The infrared spectra were recorded on a Perkin Elmer Model 157 either in potassium bromide pellets or in nujol mull. Detailed assignments for the characteristic bands in the infrared spectra of the metal salts have been made earlier,[17,18] and our assignments are referred to the data given by these authors. The P=O stretch at about 1245 cm^{-1}(vs) is absent in all the infrared spectra of the metal salts of the alkyl methylphosphonates which appears otherwise as a very strong band in DMMP and its analogues.

Proton (^{1}H), carbon (^{13}C) and ^{31}P NMR spectra were recorded on a Brucker WM-400 Fourier transform spectrometer (^{1}H at 400.13 MHZ) equipped with a 5 mm sample lead. The concentration of the sample solution was approximately 10–40 mmoles in CD_3SOCD_3 or D_2O at 25°C. Chemical shifts are referred to the proton signal of CD_3SOCHD_2 (2.49 ppm), and the ^{13}C signal of $CD_3SOC^{13}D_3$ (39.5 ppm) as internal standard. With D_2O the chemical shifts were related to $(CH_3)_3Si(CH_2)_3—SO_3^-$ (DDS) as external standard.

General procedure for the reaction of dialkyl alkanephosphonates with metals. The reactions of alkali, and of earth alkali metals were carried out under an atmosphere of argon. They were performed in a 3-necked flask provided with an efficient stirrer, gas inlet tube and a condensor having a gas outlet at the top. This was connected to a first trap filled with glass wool, followed by a second, so as to condense any unwanted traces of phosphonate. The gases evolved were then led into an evacuated gas trap of a volume of 250–500 mL.

Lithium Methyl methylphosphonate (**4**). Lithium (2.1 g, 0.3 g atom) was added under an atmosphere of argon to DMMP (300 mL) and the stirred suspension heated to 120°C. The reaction commenced with gas evolution and the temperature rose to 155°C. A sample of the gas was withdrawn for analysis. A white suspension was formed as the metal reacted with the DMMP. After gas evolution had ceased (4.4 liters), the mixture was stirred for 3 hours at 160°C. The excess of DMMP was distilled at 12 torr, and 300 mL of acetone added to the residual salt. Filtration and subsequent washing with acetone and ether (200 mL each) yielded the lithium salt of methyl methylphosphonate (33.1 g, 95%) mp > 300°C; IR(nujol) ν 1310 (CH_3P), 1184 (P—O—C stretch), 1109(PO_2^-), 1063 (OC of POC), 805 (CH_3P); ^{1}H NMR (D_2O) δ 1.25, $J_{HP} = 16.3$ Hz (CH_3P), 3.52 $J_{HP} = 10.7$ Hz ($POCH_3$); ^{13}C NMR (D_2O) δ 53.7, $J_{CP} = 4.9$ Hz ($POCH_3$), 13.1, $J_{CP} = 137.3$ Hz (CH_3P). Anal. Calcd. for $C_2H_6O_3PLi$: C, 20.71; H, 5.21; P, 26.70; Li, 5.98. Found: C, 20.54; H, 5.18; P, 26.56; Li, 6.03.

Sodium Methyl methylphosphonate (**5**). Sodium (4.6 g, 0.2 g atom) was added to DMMP (200 mL) and the suspension heated to 95°C whereupon an exothermic reaction commenced and evolved 2.93 L of gas. Work-up was accomplished following the previous procedure yielding the sodium salt of methyl methylphosphonate (24.9 g, 94.5%) mp > 300°C; IR (nujol): ν 1308 (CH_3P), 1197 (P—O—C), 1122 (PO_2^-), 1049 (POC), 891 (CH_3P); H^1 NMR (DMSO-d_6) δ3.25, $J_{HP} = 10.1$ Hz ($POCH_3$), 0.86, $J_{HP} = 15.5$ Hz (PCH_3); ^{13}C NMR (DMSO-d_6) δ50.0, $J_{CP} = 5.5$ Hz ($POCH_3$), 12.6 $J_{CP} = 133$ Hz (P—CH_3). Anal. Calcd for $C_2H_6O_3PNa$: C, 18.19; H, 4.58; P, 23.46; Na, 17.41. Found: C, 18.24; H, 4.61; P, 23.58; Na, 17.48.

Lithium Ethyl methylphosphonate (**6**). The salt was prepared by adding lithium (0.35 g, 0.05 g atom) to diethyl methylphosphonate (38 g). The temperature rose without external heating to 140°C. The work-up followed the procedure detailed for **4**, yielding the lithium salt of ethyl methylphosphonate (5.8 g, 98.2%) mp > 350°C; IR (nujol) ν1309, (CH_3P), 1180 (POC), 1120 (PO_2^-), 1079 (POC), 889 (CH_3P). Analysis Calcd. for $C_3H_8O_3PLi$: C, 27.72; H, 6.20; P, 23.82; Li, 5.34. Found: C, 27.50; H, 6.31; P, 23.72; Li, 5.48.

Lithium Isopropyl methylphosphonate (**7**) and isopropyl–phosphonite (**8**). Lithium (1.4 g, 0.2 g atom) was added to diisopropyl methylphosphonate (140 g). The temperature increased slowly to 130°C without applying an external source of heating. After gas evolution (3.02 L) had ceased, the mixture was evaporated to dryness at 13 torr. Work-up yielded a mixture of the lithium salts of isopropyl methyl-phosphonate (64%) and isopropylphosphonite (36%) (total: 26.65 g) mp > 300°C; $^{1\mathrm{H}}$ NMR (DMSO-d_6) for **7**: δ 4.21 (—O—C$\underline{\mathrm{H}}$(CH$_3$)$_2$), 1.08 (CH$_3$ of CH(CH$_3$)$_2$), 0.92, $J_{\mathrm{HP}} = 16$ Hz (PCH$_3$); ^{13}C NMR (DMSO-d_6) for **7**: δ 71.2 $J_{\mathrm{CP}} = 5.5$ Hz (O—$\underline{\mathrm{C}}$H(CH$_3$)$_2$, 26.1, $J_{\mathrm{CP}} = 3.5$ Hz (CH$_3$ of (CH$_3$)$_2$CH) 14.9 $J_{\mathrm{CP}} = 137$ Hz (CH$_3$P); ^{1}H NMR (DMSO-d_6) for **8**: δ6.57 $J_{\mathrm{HP}} = 570$ Hz (PH), 4.21 (O—C$\underline{\mathrm{H}}$(CH$_3$)$_2$, 1.08 (CH$_3$ of CH(CH$_3$)$_2$; ^{13}C NMR DMSO-d_6 for **8**: 71.6 $J_{\mathrm{CP}} = 5.5$ Hz (—O—$\underline{\mathrm{C}}$H(CH$_3$)$_2$, 25.9 $J_{\mathrm{CP}} = 3.5$ Hz (CH$_3$ of CH(CH$_3$)$_2$).

Sodium Isopropyl methylphosphonate (**9**) and sodium isopropyl-phosphonite (**10**). Sodium (4.6 g, 0.2 g atom) was added in small pieces to diisopropyl methylphosphonate (140 g) and heated to 120°C, when gas evolution commenced. Work-up was accomplished following the procedure detailed for **4**, yielding 30 g of a mixture of the sodium salt of isopropyl methylphosphonate (25%) and isopropylphosphonite (75%), mp 166–180°C; ^{1}H NMR (DMSO-d_6) for **9**: δ 4.19 (O—C$\underline{\mathrm{H}}$(CH$_3$)$_2$), 1.1 (CH$_3$ of CH(CH$_3$)$_2$, 0.93 $J_{\mathrm{HP}} = 16$ Hz (CH$_3$P); **10** δ 6.58 $J_{\mathrm{HP}} = 569$ Hz (HP), 4.19 (—O—C$\underline{\mathrm{H}}$(CH$_3$)$_2$, 1.1 (CH$_3$ of CH(CH$_3$)$_2$).

Magnesium Bis(Methyl methylphosphonate) (**11**). Magnesium turnings (24.3 g, 1 g atom) were added to DMMP (600 mL) and the stirred suspension heated to 140°C. The reaction started after approximately 8 minutes with violent reflux and gas evolution. The temperature rose rapidly to 175°C and the source of heating was removed since the exothermic reaction proceeded by itself. External heating was again applied when the reaction slowly subsided and the temperature had decreased to 165°C. Reflux temperature was maintained for another 1.5 hours until all traces of metal had been consumed. The total volume of gas evolved was 25.6 liters. Stirring was discontinued and the temperature allowed to fall to 80°C, whereupon two layers resulted. The upper one which consisted of DMMP was removed by suction. The oil was transferred to a beaker and stirred consecutively 4–6 times with 100 mL of acetone. The oil became crystalline, and crystals were filtered and washed on the filter with acetone (200 ml) followed by anhydrous ether (200 ml), yielding magnesium bis(methyl methylphosphonate) (230 g, 95%) mp 128°C (dec); IR (nujol) ν1317, 1199 (POCH$_3$), 1117 (PO$_2^-$), 1049 (OC of POC), 1317 (CH$_3$P), 900 (CH$_3$P); ^{1}H NMR (D$_2$O) δ 3.45 $J_{\mathrm{HP}} = 11$ Hz (POCH$_3$), 1.19 $J_{\mathrm{HP}} = 16$ Hz (PCH$_3$); ^{13}C NMR (D$_2$O) δ53.73 $J_{\mathrm{CP}} = 5.5$ Hz (POCH$_3$), 12.92 $J_{\mathrm{CP}} = 136.7$ Hz (PCH$_3$). Anal Calcd for $C_4H_{12}O_6P_2Mg$: C, 19.82; H, 4.99; P, 25.56; Mg, 10.03. Found: C, 20.20; H, 5.02; P, 25.54; Mg, 9.83.

The acetone and ether washing were combined and the volatile solvents distilled off in a rotary evaporator yielding a viscous oil. This was again extracted with 200 mL of anhydrous ether, the ether layer decanted from the insoluble oil and concentrated under reduced pressure, leaving 32 g of liquid. Distillation at 70°C/12 mm yielded 4.8 g of trimethylphosphine oxide, IR (liquid) ν 1208 (P═O), 1115 (P═O), 950,887 (CH$_3$—P); ^{1}H NMR (D$_2$O) δ 1.56, $J_{\mathrm{H—P}} = 13.5$ Hz; ^{13}C NMR δ 18.6, $J_{\mathrm{C—P}} = 70$ Hz.

Calcium Bis(Methyl methylphosphonate) (**12**). A slurry of calcium (20 g 0.5 g atom) in DMMP (500 mL) was heated to reflux for 19 hours. Excess of DMMP was distilled from the solution under vacuum (1 mm), acetone (300 mL) added to the viscous residue and stirred. Crystals were filtered and washed consecutively with acetone (200 mL) and ether (200 mL), yielding calcium methyl methylphosphonate (121.4 g, 94%) mp > 300°C; IR (nujol) ν 1191 (P—O—CH$_3$), 1053 (OC), 1309 (CH$_3$P), 894 (CH$_3$P); Anal. Calcd for $C_4H_{12}O_6P_2Ca$: C, 18.61; H, 4.69; P, 24.00; Ca, 15.52. Found: C, 19.08; H, 5.01; P, 23.94; Ca, 15.20.

Barium Bis(Methyl methylphosphonate) (**13**). A slurry of barium (4.12 g, 0.03 g atom) in DMMP (40 mL) was heated under reflux for 91 hours. The supernatant white suspension was decanted from the unreacted barium (2.4 g) and the excess of DMMP distilled under vacuum (1 torr). Acetone was added to the residue and the suspension was filtered. The white product was washed with acetone (20 mL), followed by ether (20 mL), yielding barium bis(methyl methylphosphonate) (3.62 g, 34%), mp > 300°C; IR (nujol) ν 1179 (P—O—CH$_3$), 1111 (PO$_2^-$), 1055 (OC of POC), 1304 (CH$_3$P), 883 (CH$_3$P). Anal. Calcd. for $C_4H_{12}O_6P_2Ba$: C, 13.52; H, 3.40; P, 17.43; Ba, 38.64. Found: C, 13.60; H, 3.21; P, 17.41; Ba, 38.7.

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