# Surface mediated synthesis of unsymmetrical *O,O*-dialkyl alkyl pyrophosphonates using neutral alumina: potential Chemical Weapons Convention related compounds

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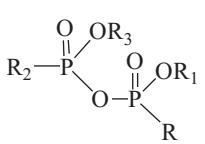
The surface mediated synthesis of unsymmetrical *O,O'*- dialkyl alkyl pyrophosphonates from *O*-alkyl alkylphosphonic acid is described. These pyrophosphonates are listed in schedule 2B4 of Chemical Weapon Convention (CWC). The effect of the presence of chromatographic grade of $Al_2O_3$ on the phosphorylation of a series of alkyl phosphonic acids has also been investigated. For phosphonic acids having different alkyl groups, it was observed that higher yields of the more hindered pyrophosphonates were formed in the presence of $Al_2O_3$. This method has an advantage over the conventional methods in terms of easy work-up, reduced reaction time and high yields.

**Keywords:** O-alkyl, alkyl phosphonic chloride, O-alkyl alkyl phosphonic acid, O,O'-dialkyl alkyl pyrophosphonates, chemical weapon convention

The development of new efficient synthetic procedures for the retrospective detection and identification of chemical warfare agents (CWAs) and related compounds is a prominent area of contemporary research. This field of synthesis and analysis has attracted the attention of several workers because of the strict verification program of Chemical Weapons Convention (CWC).[1-6] Consequently, work has been devoted to building spectral libraries of CRCs.[7-12] In such analysis, final structures of analytes are confirmed by synthesising the reference compounds and matching the finger prints of their spectra (mostly GC/MS and $^{31}$P NMR). *O,O'*-Dialkyl alkyl pyrophosphonates are one such class of compounds which are often produced when highly toxic chemical warfare agents such as Sarin, Soman, Vx and their analogues are prepared in any laboratory or plant. These pyrophosphonates can also arise from environmental samples if any laboratory is involved in synthesising more than one kind of agents. Thus, both symmetrical and unsymmetrical pyrophosphonates may serve as important forensic markers for the verification of these agents. They are also covered in the list of CWC text under schedule 2 B4.[13] This is probably the reason that these compounds were also spiked in one of the official proficiency test conducted by Organisation for Prohibition of Chemical Weapons (OPCW).[14] Thus, the generation of spectral data base of pyrophosphonates is one of the important objective of the verification regime of the CWC. The general structure of such pyrophosphonates is given below. There was a need to develop an efficient synthetic procedure which can be used to prepare several *O,O'*-dialkyl alkyl pyrophosphonates.



Several methods have been reported in the literature for the synthesis of symmetrical pyrophosphates.[15-18] However the synthesis of symmetrical and unsymmetrical pyrophosphonates has not been fully explored. There have been only few reports on the synthesis of unsymmetrical pyrophosphonates, which have several drawbacks such as use of carcinogenic solvent, long reaction time, and formation of several by-products. Surface-mediated solid phase reaction are of growing interest[19-25] essentially because of their ease of execution and work-up, mild reaction conditions, fast rate of reaction, selectivity, high yields, solvents-less reaction conditions and low cost in comparison with their homogeneous counter parts.[26-28] This prompted us to explore the utility of surface-mediated reaction for the synthesis of the title compounds.

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## Result and discussion

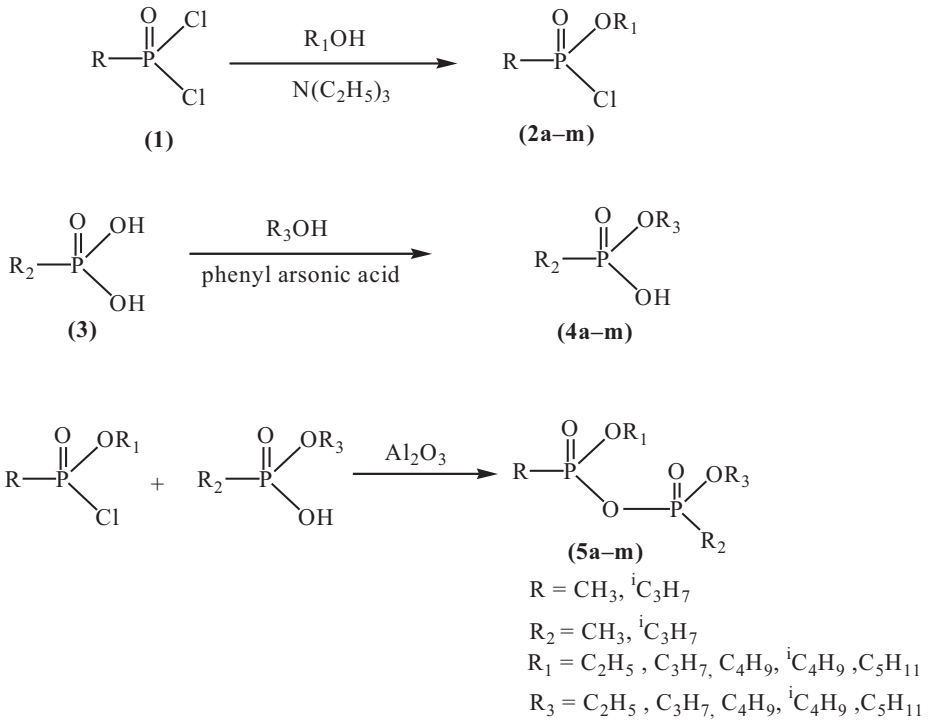
Chromatographic grade $Al_2O_3$ has many applications as a heterogeneous catalyst either by itself, or (more commonly) as a support for other reagents.[19-25] There have been only few reports, however, on the use of $Al_2O_3$ as a support for substrates, despite the fact that novel, synthetically useful, reactivities have been observed under these conditions. Unsymmetrical functional substrates adsorb to the surface of $Al_2O_3$ via a functional group. Adsorption of a group to the surface creates a sterically congested environment about that group which shields it from added reagents leaving only the non-adsorbed group available for the reaction. We anticipate that unsymmetrical substituted functional group would be adsorbed to the surface of $Al_2O_3$ primarily via the less sterically hindered functional group. This would allow selective reaction at the more sterically hindered, non-adsorbed, site. Such selectivity would conveniently complement the corresponding reactions in solution in which the less sterically hindered site is typically the more reactive.

In order to test the above proposition, we carried out the reaction of alkyl phosphonic dichloride **1**[29] with various alcohols in presence of triethylamine at 0°C followed by heating at 50°C. It gave *O*-alkyl alkylphosphonic chloride **2a–m**.[30] *O*-Alkyl alkyl phosphonic acids **3a–m** which were also synthesised by reported method[31] were condensed with various *O*-alkyl alkyl phosphonic chloride **2a–m** in the presence of neutral alumina [(Brockmann I activated standard grade, particle size 150 mesh) was purchased from Sigma-Aldrich, US] to give the corresponding *O,O'*-dialkyl alkyl pyrophosphonates **5a–m**.

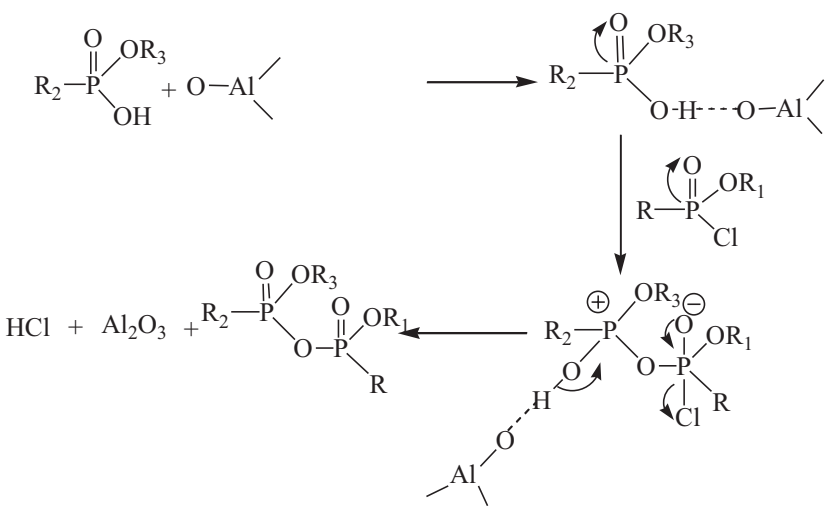
The results of the synthesis of various pyrophosphonates **5a–m** are summarised in Table 1. All the compounds **5a–m** were characterised by spectroscopic techniques such as FT–IR, NMR and GC–MS. The FT–IR results showed the appearance of strong and broad bands in the range of 975–965 $cm^{-1}$, due to the unsymmetrical stretching of the P–O–P linkage.[32] The other frequencies assigned for the P–O–C, P–C and P = O linkage were compared with literature values and found within the range.[33] The results of other analysis **5a–m** are presented in experimental section.

## Conclusion

In conclusion, we have synthesised various, *O,O'*-dialkylalkyl pyrophosphonates with excellent yields. The main advantage




**Scheme 1**




**Scheme 2** Proposed mechanism for the formation of pyrophosphonates on alumina as a solid support.

of this method is that reactions were found clean and had operational simplicity. Since, column chromatography was not required to obtain the pure products, the method is attractive for organic chemists.

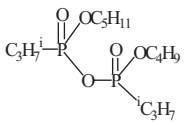
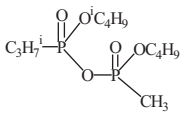
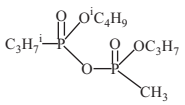
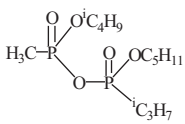
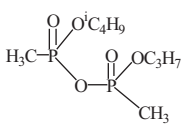
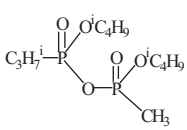
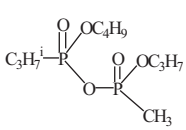
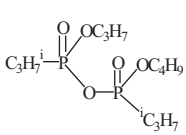
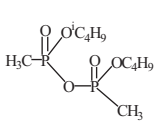
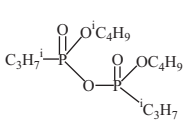
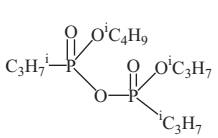
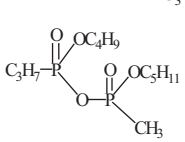
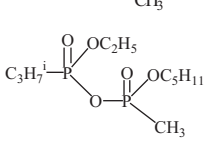
## Experimental

*General*

Boiling points are uncorrected. IR spectra were recorded on Bruker FT–IR spectrometer model Tensor 27 on KBr disk. $^1$H NMR spectra were recorded in $CDCl_3$ on Bruker DPX Avance FT-NMR at 400 using tetramethylsilane as an internal standard for $^1$H NMR. A Chemito GC model 1000 instrument was used with flame ionisation detector (FID). A capillary column (30 m × 0.25 mm I.D-BP5) packed with 5% phenyl- and 95% dimethyl-polysiloxane (SGE) coated on fused silica was employed. The injection port and detector block were maintained at 280 and 260°C respectively and the column oven was at programmed temperature profile starting at 50°C, and ramped up to 280°C at 25°C/min. Nitrogen was used as carrier gas (at a flow rate of 30 ml/min). Air for FID was supplied at 300 ml/min and hydrogen at 30 ml/min. In all analysis, 0.1 µl sample was injected and peaks recorded on Iris32 data acquisition station. The GC–MS analyses were performed in EI (70 eV) in full scan mode with an Agilent 6890 GC equipped with a model 5973 mass selective detector (Agilent Technologies, USA). An SGE BPX5 capillary column with 30 m length × 0.32 mm internal diameter × 0.25 µm film thickness was used at temperature program of 80ºC (2 min)–20°C/min–280°C (3 min). Helium was used as the carrier gas at a constant flow rate of 1.2 ml/min. The samples were analysed in split less mode at injection temperature. Elemental analyses were performed on elemental analyser Carlo Erba Instrumentazione Model NOD1106 using benzanilide as a reference compound.

*General procedure for the preparation of O-pentyl O'-butyl diisopropyl pyro phosphonate* (**5a**): In a typical experimental procedure, neutral activated alumina (1.0 g, 0.01M) was mixed to *O*-butyl isopropylphosphonic acid (1.80 g, 0.01M) in a pestle and mortar. It was ground for 5 min at room temperature. After grinding,

**Table 1** Synthesis of *O,O'*- dialkyl alkyl pyrophosphonates **5a–m** using neutral alumina

| Entry | Product | Reaction time[a]/min | Yield/%[b] | B.p./°C/mmHg |
|---|---|---|---|---|
| **5a** |  | 20 | 85.3 | 155/1 |
| **5b** |  | 15 | 91.5 | 120/1 |
| **5c** |  | 15 | 94.5 | 140/1.5 |
| **5d** |  | 15 | 95.8 | 127/1.5 |
| **5e** |  | 15 | 96.5 | 141/1.5 |
| **5f** |  | 15 | 89.5 | 125/1 |
| **5g** |  | 30 | 83.7 | 118/1 |
| **5h** |  | 20 | 93.5 | 158/1 |
| **5i** |  | 10 | 92.8 | 115/1 |
| **5j** |  | 20 | 91.7 | 160/1 |
| **5k** |  | 30 | 94.6 | 148/1 |
| **5l** |  | 15 | 88.5 | 119/1 |
| **5m** |  | 15 | 85.7 | 120/1 |

[a]Reactions were performed at 60°C and monitored on TLC and GC. [b]Isolated yield.

the mixture was transferred to a single neck flask. This was sealed with rubber septum and then *O*-pentyl isopropylphosphonic chloride (2.12 g, 0.01M) was added through a syringe at 0°C. The resultant dispersion was shaken occasionally at room temperature followed by heating at 60°C for 20 minutes. The reaction mixture was monitored by TLC and GC by drawing few milligrams of mixture and suspending in 1 ml of diethyl ether. After completion of the reaction, the reaction mixture was extracted with n-pentane (4 × 25 ml) and filtered. The solvent was evaporated and residue was distilled under vacuum to afford the pure product. Yield: 85.3%, b.p. 155°C/1 mmHg.

IR: (KBr) $\upsilon_{max}$/cm$^{-1}$ 2888 (C–H), 1228 (P = O), 1065 (P–O–C), 970 (P–O–P), 685 (P–C). Analyses: Calcd. for $C_{15}H_{34}O_5P_2$: C, 50.55; H, 9.6%. Found: C, 50.6; H, 9.75%. H$^1$ NMR (δppm, 400 MHz; $CDCl_3$; $Me_4Si$): 0.90 (t, $J_{HH}$ = 6.35 Hz, 6H, $CH_3$), 1.05 (dd, $^3J_{PH}$ = 21.43 Hz, 12H, $CH_3$), 1.25(m, 4H, $CH_2$), 1.36(m, 4H, $CH_2$), 1.67(m, 2H, $CH_2$), 2.05(m, 2H, CH), 4.10(m, 4H, $CH_2$); GC–MS (EI) *m/z* (%): 356 (10.53), 287(12.05), 273(15.73), 231(100), 213(28.58), 187 (45.23), 171(45.28), 125(86.28), 65(15.36), 43(40.23).

*O-Butyl O'-isobutyl P-isopropyl P'-methyl pyrophosphonate* (**5b**): IR: (KBr) $\upsilon_{max}$/cm$^{-1}$ 2889 (C–H), 1233 (P = O), 1093 (P–O–C), 965 (P–O–P), 690 (P–C) cm$^{-1}$. Analyses: Calcd. for $C_{12}H_{28}O_5P_2$: C, 45.9; H, 9.0%. Found: C, 45.95; H, 9.10%. H$^1$ NMR (δppm, 400 MHz; $CDCl_3$; $Me_4Si$): 0.92 (t, $J_{HH}$ = 6.5 Hz, 3H, $CH_3$), 0.94 (d, $J_{HH}$ = 6.3 Hz, 6H, $CH_3$), 1.12 (dd, $^3J_{PH}$ = 21.2 Hz, 6H, $CH_3$), 1.22(m, 2H, $CH_2$), 1.33(m, 2H, $CH_2$), 1.63(d, $^2J_{PH}$ = 18.6 Hz, 3H, $CH_3$), 1.81(m, 1H, CH), 2.05(m, 1H, CH), 3.78(m, 2H, $CH_2$), 4.05(m, 2H, $CH_2$); GC–MS (EI) *m/z* (%): 314 (8.50), 231(100), 213(27.29), 187(27.50), 171(29.30), 125(54.54), 57(18.18), 43(43.63).

*O-Isobutyl O'-propyl P-isopropyl P'-methyl pyrophosphonate* (**5c**): IR: (KBr) $\upsilon_{max}$/cm$^{-1}$ 2885 (C–H), 1230 (P = O), 1090 (P–O–C), 970 (P–O–P), 695 (P–C). Analyses: Calcd. for $C_{11}H_{26}O_5P_2$: C, 44.0; H, 8.7%. Found: C, 44.1; H, 8.67%. H$^1$ NMR (δppm, 400 MHz; $CDCl_3$; $Me_4Si$): 0.90 (t, $J_{HH}$ = 7.1 Hz, 3H, $CH_3$), 0.98 (d, $J_{HH}$ = 6.6 Hz, 6H, $CH_3$), 1.07 (dd, $^3J_{PH}$ = 21.3 Hz, 6H, $CH_3$), 1.30(m, 2H, $CH_2$), 1.60(d, $^2J_{PH}$ = 18.6 Hz, 3H, $CH_3$), 1.83(m, 1H, CH), 2.08(m, 1H, CH), 3.79(m, 2H, $CH_2$) 3.99(m, 2H, $CH_2$); GC–MS (EI) *m/z* (%): 300 (5.76), 299, 231(100), 213(72.72), 188(73.05), 171(54.54), 145(34.54), 128(73.10), 65(27.30), 43(75.06).

*O-isobutyl O'-pentyl P-isopropyl P'-methyl pyrophosphonate* (**5d**): IR: (KBr) $\upsilon_{max}$/cm$^{-1}$ 2880 (C–H), 1235 (P = O), 1094 (P–O–C), 965 (P–O–P), 685 (P–C). Analyses: Calcd. for $C_{13}H_{30}O_5P_2$: C, 47.6; H, 9.2%. Found: C, 47.45; H, 9.1%. H$^1$ NMR (δppm, 400 MHz; $CDCl_3$; $Me_4Si$): 0.92 (t, $J_{HH}$ = 6.48 Hz, 3H, $CH_3$), 0.95 (d, $J_{HH}$ = 6.9 Hz, 6H, $CH_3$), 1.08 (dd, $^3J_{PH}$ = 21.2 Hz, 6H, $CH_3$), 1.20(m, 4H, $CH_2$), 1.33(m, 2H, $CH_2$), 1.60(d, $^2J_{PH}$ = 18.5 Hz, 3H, $CH_3$), 1.80(m, 1H, CH), 2.03(m, 1H, CH), 3.81(m, 2H, $CH_2$), 4.03(m, 2H, $CH_2$); GC–MS (EI) *m/z* (%): 329 (M + H$^+$), 287, 231(100), 213(26.31), 188 (15.26), 171(28.45), 125(57.63), 57(10.10), 43(48.16).

*O-Isobutyl O'-propyl dimethyl pyrophosphonate* (**5e**): IR: (KBr) $\upsilon_{max}$/cm$^{-1}$ 2889 (C–H), 1233 (P = O), 1090 (P–O–C), 970 (P–O–P), 695 (P–C). Analyses: Calcd. for $C_9H_{22}O_5P_2$: C, 39.7; H, 8.15%. Found: C, 39.7; H, 8.1%. H$^1$ NMR (δppm, 400 MHz; $CDCl_3$; $Me_4Si$): 0.92 (t, $J_{HH}$ = 7.1 Hz, 3H, $CH_3$), 0.98 (d, $J_{HH}$ = 6.8 Hz, 6H, $CH_3$), 1.30(m, 2H, $CH_2$), 1.65(d, $^2J_{PH}$ = 18.3 Hz, 6H, $CH_3$), 1.85 (m, 1H, CH), 3.88(m, 2H, $CH_2$), 4.15(m, 2H, $CH_2$); GC–MS (EI) *m/z* (%): 315 (7.34), 215(10.52), 175(100), 157 (46.93), 143 (20.40), 125(13.10), 97(32.65), 79(20.40), 41(24.45).

*O, O'-Diisobutyl P-isopropyl P'-methyl pyrophosphonate* (**5f**): IR: (KBr) $\upsilon_{max}$/cm$^{-1}$ 2888 (C–H) 1230 (P = O), 1085 (P–O–C), 970 (P–O–P), 695 (P–C). Analyses: Calcd. for $C_{12}H_{28}O_5P_2$: C, 45.9; H, 9.0%. Found: C, 45.9; H, 9.0%. H$^1$ NMR (δppm, 400 MHz; $CDCl_3$; $Me_4Si$): 0.98 (d, $J_{HH}$ = 6.9 Hz, 12H, $CH_3$), 1.05 (dd, $^3J_{PH}$ = 21.2 Hz, 6H, $CH_3$), 1.63(d, $^2J_{PH}$ = 18.2 Hz, 3H, $CH_3$), 1.88(m, 2H, CH), 2.05(m, 1H, CH), 3.78(m, 2H, $CH_2$), 3.99(m, 2H, $CH_2$); GC–MS(EI) *m/z* (%): 313 (5.23) 4.06), 287, 243, 231(100), 213 (23.80), 187(23.80), 171 (28.57), 145(18.23), 128(73.10), 125(571.25), 57(23.29), 43(36.75).

*O-Butyl O'-propyl P-isopropyl P'-methylpyrophosphonate* (**5g**): IR: (KBr) $\upsilon_{max}$/cm$^{-1}$ 2889 (C–H), 1233 (P = O), 1089 (P–O–C), 970 (P–O–P), 695 (P–C). Analyses: Calcd. for $C_{11}H_{26}O_5P_2$: C, 44.0; H, 8.7%. Found: C, 44.0; H, 8.7%. H$^1$ NMR (δppm, 400 MHz; $CDCl_3$; $Me_4Si$): 0.95 (t, $J_{HH}$ = 6.8 Hz, 6H, $CH_3$), 1.05 (dd, $^3J_{PH}$ = 21.3 Hz, 6H, $CH_3$), 1.15(m, 2H, $CH_2$), 1.21(m, 2H, $CH_2$), 1.38(m, 2H, $CH_2$), 1.60(d, $^2J_{PH}$ = 18.4 Hz, 3H, $CH_3$), 2.05(m, 1H, CH), 3.70(m, 2H, $CH_2$), 4.05(m, 2H, $CH_2$); GC–MS (EI) *m/z* (%): 300 (4.06),287(18.18), 231(100), 213(27.27), 187 (36.37), 171(27.35), 145(15.10), 125(81.18), 65(10.95), 43(40.90).

*O-Propyl O'-butyl diisopropyl pyrophosphonate* (**5h**): IR: (KBr) $\upsilon_{max}$/cm$^{-1}$ 2887 (C–H), 1225 (P = O), 1080 (P–O–C), 972 (P–O–P), 690 (P–C). Analyses: Calcd. for $C_{13}H_{30}O_5P_2$: C, 47.6; H, 9.2%. Found: C, 47.5; H, 9.2%. H$^1$ NMR (δppm, 400 MHz; $CDCl_3$; $Me_4Si$): 0.90 (t, $J_{HH}$ = 7.0 Hz, 6H, $CH_3$), 1.05 (dd, $^3J_{PH}$ = 21.4 Hz, 12H, $CH_3$), 1.25(m, 4H, $CH_2$), 1.36(m, 2H, $CH_2$), 1.67(m, 2H, $CH_2$), 2.05(m, 2H, CH), 4.10(m, 4H, $CH_2$); GC–MS (EI) *m/z* (%): 329 (6.56), 287 (18.18), 273(10.73), 231(100), 213(28.25), 187 (40.23), 171(32.56), 145(18.10), 125(86.28), 65(16.35), 43(50.20).

*O-Butyl O'-isobutyl dimethylpyrophosphonate* (**5i**): IR: (KBr) $\upsilon_{max}$/cm$^{-1}$ 2889 (C–H), 1245 (P = O),1088 (P–O–C), 975 (P–O–P), 687 (P–C). Analyses: Calcd. for $C_{10}H_{24}O_5P_2$: C, 41.96; H, 8.45%. Found: C, 41.95; H, 8.46%. H$^1$ NMR (δppm, 400 MHz; $CDCl_3$; $Me_4Si$): 0.90 (t, $J_{HH}$ = 6.5 Hz, 3H, $CH_3$), 0.95 (d, $J_{HH}$ = 6.9 Hz, 6H, $CH_3$), 1.21(m, 2H, $CH_2$), 1.35(m, 2H, $CH_2$), 1.65(d, $^2J_{PH}$ = 18.3 Hz, 6H, $CH_3$), 1.90(m, 1H, CH), 3.75(m, 2H, $CH_2$), 3.99(m, 2H, $CH_2$); GC–MS (EI) *m/z* (%):285 (M + H$^+$), 211(9.12), 199(12.85), 156 (60.23), 142(35.26), 118(18.25), 100(30), 83(28), 57 (100), 41(78.23).

*O-Isobutyl O'-butyl diisopropyl pyrophosphonate* (**5j**): IR: (KBr) $\upsilon_{max}$/cm$^{-1}$ 2865 (C–H), 1225 (P = O),1093 (P–O–C), 975 (P–O–P), 685 (P–C). Analyses: Calcd. for $C_{14}H_{32}O_5P_2$: C, 49.1; H, 9.4%. Found: C, 49.1; H, 9.40%. H$^1$ NMR (δppm, 400 MHz; $CDCl_3$; $Me_4Si$): 0.90 (dd, $^3J_{PH}$ = 21.5 Hz, 12H, $CH_3$), 0.95 (t, $J_{HH}$ = 6.5 Hz, 3H, $CH_3$), 1.05 (d, $J_{HH}$ = 7.1 Hz, 6H, $CH_3$), 1.15(m, 2H, $CH_2$), 1.31(m, 2H, $CH_2$),1.74(m, 1H, CH), 2.05(m, 2H, CH), 4.19(m, 4H, $CH_2$); GC–MS (EI) *m/z* (%): 343 (M + H$^+$), 287(14.19), 243(10.46), 231(100), 213(24.65), 187 (26.21), 171(23.89), 145(11.52), 125(50.15), 43(17.25).

*O-Isobutyl O'-isopropyl diisopropyl pyrophosphonate* (**5k**): IR: (KBr) $\upsilon_{max}$/cm$^{-1}$ 2885 (C–H), 1235 (P = O), 1096 (P–O–C), 972 (P–O–P), 692 (P–C). Analyses: Calcd. for $C_{13}H_{30}O_5P_2$: C, 47.6; H, 9.2%. Found: C, 47.5; H, 9.2%. H$^1$ NMR (δppm, 400 MHz; $CDCl_3$; $Me_4Si$): 0.95 (dd, $^3J_{PH}$ = 21.3 Hz, 12H, $CH_3$), 1.05 (d, $J_{HH}$ = 6.9 Hz, 6H, $CH_3$), 1.15 (d, $J_{HH}$ = 7.2 Hz, 6H, $CH_3$), 1.65(m, 1H, CH), 2.07(m, 2H, CH), 3.75(m, 1H, CH), 4.07(m, 2H, $CH_2$); GC–MS (EI) *m/z* (%): 329 (M + H$^+$), 287(15.11), 243(5.69), 231(100), 213(40.28), 187 (51.26), 171(44.23), 145(21.32), 125(76.13), 65(22.14), 43(74.12).

*O-Butyl O'-pentyl P-isopropyl P'-methylpyrophosphonate* (**5l**): IR: (KBr) $\upsilon_{max}$/cm$^{-1}$ 2889 (C–H), 1233 (P = O), 1090 (P–O–C), 970 (P–O–P), 695 (P–C). Analyses: Calcd. for $C_{13}H_{30}O_5P_2$: C, 47.6; H, 9.2%. Found: C, 47.5; H, 9.2%. H$^1$ NMR (δppm, 400 MHz; $CDCl_3$; $Me_4Si$): 0.92 (dd, $^3J_{PH}$ = 21.2 Hz, 6H, $CH_3$), 1.05 (t, $J_{HH}$ = 6.6 Hz, 6H, $CH_3$), 1.10 (m, 2H, $CH_2$), 1.22 (m, 4H, $CH_2$), 1.35(m, 4H, $CH_2$), 1.65(d, $^2J_{PH}$ = 18.5 Hz, 3H, $CH_3$), 2.08(m, 1H, CH), 3.70(m, 2H, $CH_2$), 4.05(m, 2H, $CH_2$); GC–MS (EI) *m/z* (%): 329 (M + H$^+$), 231(15.23), 203(100) 185 (27.13), 159(16.23), 125(14.25), 97(58.97), 41(28.36).

*O-Ethyl O'-pentyl P-isopropyl P'-methylpyrophosphonate* (**5m**): IR: (KBr) $\upsilon_{max}$/cm$^{-1}$ 2890(C–H), 1230 (P = O), 1085 (P–O–C), 975 (P–O–P), 693 (P–C). Analyses: Calcd. for $C_{11}H_{26}O_5P_2$: C, 44.0; H, 8.7%. Found: C, 44.0; H, 8.7%. H$^1$ NMR (δppm, 400 MHz; $CDCl_3$; $Me_4Si$): 0.92 (t, $J_{HH}$ = 6.7 Hz, 3H, $CH_3$), 0.94 (t, $J_{HH}$ = 6.7 Hz, 3H, $CH_3$), 1.05 (dd, $^3J_{PH}$ = 21.2 Hz, 6H, $CH_3$), 1.30(m, 4H, $CH_2$), 1.63 (d, $^2J_{PH}$ = 18.6 Hz, 3H, $CH_3$), 1.88(m, 1H, $CH_2$), 2.10(m, 1H, CH), 3.75(m, 2H, $CH_2$), 4.05(m, 2H, $CH_2$); GC–MS (EI) *m/z* (%):301 (M + H$^+$), 231(100),213(17.56), 187(24.45), 171(17.19), 145 (13.48), 125(71.52), 41(50.22).

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