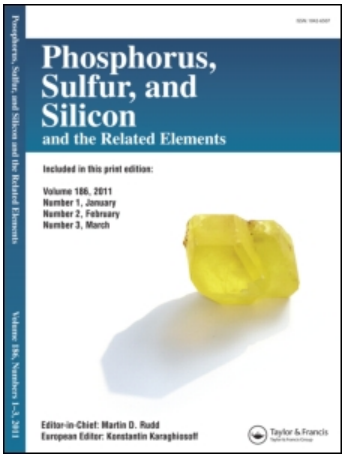

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Surface-Mediated Synthesis of *O*-Alkyl 2-Methoxyethyl Alkylphosphonates Under Solvent Free Conditions: Potential Marker of Nerve Agents

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SURFACE-MEDIATED SYNTHESIS OF *O-A*LKYL 2-METHOXYETHYL ALKYLPHOSPHONATES UNDER SOLVENT FREE CONDITIONS: POTENTIAL MARKER OF NERVE AGENTS

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This article describes rapid and efficient surface mediated synthesis of O-alkyl 2-methoxyethyl alkylphosphonates from alkylphosphonic acids and alcohols using dicyclohexyl carbodiimide (DCC)-Celite as a solid support. These compounds are markers of nerve agents. 2-Methoxyethyl methylphosphonic acids (2a–d) were reacted with various alcohols to yield O-alkyl 2-methoxyethyl alkylphosphonates (AMEAPs, 3a–m). This synthetic method has advantages over other methods in terms of selectivity, shorter reaction time, high yield, and easy work-up.

Keywords Chemical warfare agents; Chemical Weapons Convention; DCC-Celite; nerve agents; phosphonates

INTRODUCTION

Chemical Weapons Convention (CWC) is an international disarmament treaty that came into force in 1997, to which more than 183 countries including India are parties. The treaty prohibits development, stockpiling, and alleged use of chemical weapons.[1] However after the incident of September 11, 2001, the threat from chemical weapons of mass destruction has evolved into a serious matter of concern to both military as well as civilian people. An international organization, known as Organization for Prohibition of Chemical Weapons (OPCW), is responsible for implementation of the treaty by executing its strict verification program.[1–7] The OPCW is maintaining a network of designated laboratories to verify the presence of CWC-related chemicals and their markers in the samples collected by the inspectors from suspected and declared sites.[8] Due to the internationally sensitive nature of the verification process, the analytical performance of designated laboratories and laboratories seeking designation is periodically evaluated by OPCW by conducting the official proficiency tests (OPTs).[9,10]

Thus for successful performance in PTs and for off-site analysis of real samples, the availability of spectral data is a primary requirement. Consequently, a great deal of work

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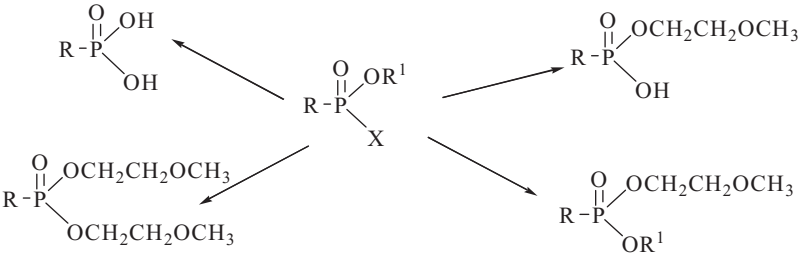


R= CH_3, R^1= $(CH_3)_2CHO$, X=F (Sarin); R= CH_3, R^1= $(CH_3)_3CCH(CH_3)$ O, X=F(Soman);
R= CH_3, R^1= C_2H_5O, X= SC_2H_4N ($^{i}C_3H_7)_2$ (VX)

Figure 1 Major neutralized products of sarin, soman, and VX by DS-2 solution.

is devoted to developing the spectral database of CRCs.[11–13] In spite of global efforts, only limited spectra of scheduled chemicals are available in various libraries.[14] The chemicals relevant to the convention (CRCs) not only include the popular chemical warfare agents, but precursors and degradation products are also included in CWC text, which makes the list of CRCs very exhaustive.

Among the various chemical warfare agents (CWAs), nerve agents such as sarin, soman, VX, tabun, and their homologues are extremely toxic in nature. In general, DS-2 solution (diethylene tetra amine 78%, methoxy ethanol 20%, and NaOH 2%) is accepted for their detoxification from the contaminated surfaces. However, when nerve agents (sarin, soman, VX, and their homologues) are neutralized with DS-2 solution, the major products of decontamination have been identified as *O*-alkyl 2-methoxyethyl alkylphosphonates (AMEAPs), 2-methoxyethyl alkylphosphonic acids (MEAPs), bis(2-methoxyethyl) alkylphosphonates (BMEAPs), and their alkylphosphonic acids (APAs) (Figure 1).

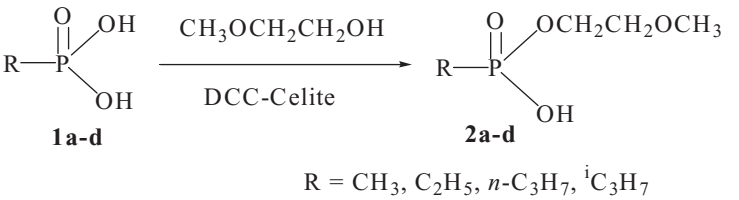
Since the inception of the project, 24,000 compounds from the sarin and soman family and 40,000 compounds from the VX family have been estimated for the list of CWC text.[15] Hence, these nerve agents will also give more or less same number of AMEAPs. Because of this reason, AMEAPs have been considered as important markers of these nerve agents and are listed in scheduled 2B4 class of the CWC text.[1] Probably this is the reason that they have been spiked quite often in OPTs. The synthesis of their degradation products (in pure form) by reported methods and including their spectroscopic data in the database will be a difficult task. In order to resolve such problems, there is a need to develop efficient and rapid synthetic procedures, which should provide the pure compounds with minimum effort and time. Rapid synthesis of AMEAPs in pure form is essential to confirm the structures of analytes revealed by their spectroscopic (e.g., GC-MS, ^{31}P NMR, and GC-FTIR) data. The perfect match of spectra with synthesized compounds is one of the unique ways to report the results of analysis, as it does not require much expertise to interpret the spectra. Furthermore, the spectra and chromatographic data collected by synthesis of pure compounds are also helpful in on-site and off-site analysis of real samples.[7–9]

Several methods are reported in the literature for the synthesis of phosphonates; however the reported methods have several drawbacks such as long reaction times, use of carcinogenic solvents, harsh reaction conditions, tedious work-up, and the use of chromatographic techniques to obtain the pure compounds.[16–32]

In recent years, the use of organic–inorganic hybrid immobilized solid support reagents has received great interest. Such reagents not only simplify the purification process but are also environmentally friendly.[33–40] However, reactions under solvent-free conditions are some of the more promising alternatives and have recently attracted attention due to legislative enforcement.[41,42] The main advantages of such reactions are that they are simpler in operation and they save energy. The absence of solvent in organic synthesis also makes the reactions cleaner, prevents solvent wastes, and reduces hazards and toxicity. Furthermore, from the synthetic viewpoint, these reactions significantly reduce the reaction time, and workup is also easy.[42–48] Efficiency of dicyclohexyl carbodilmide (DCC) and Celite under operationally simple conditions has prompted us to explore the possibility of this reagent for the synthesis of AMEAPs.[49]

RESULTS AND DISCUSSION

In continuation of our ongoing program to develop new reagents and synthetic procedures for the synthesis of organophosphorus compounds,[28,50,51] we report in this article a convenient method for the synthesis of *O*-alkyl 2-methoxyethyl alkylphosphonates (AMEAPs) by exploiting surface-mediated synthesis at the appropriate temperature. Initially 2-methoxyethyl alkylphosphonic acids **2a–d** were synthesized by DCC-Celite (molar ratio 1:2)–mediated condensation reaction of the corresponding alkylphosphonic acid and 2-methoxyethanol in a molar ratio of 1:1 at 50–80 °C for 60–90 min. The reaction was monitored by ^{31}P NMR spectroscopy. The ^{31}P NMR results showed quantitative conversion of the alkylphosphonic acids to the corresponding 2-methoxyethyl alkylphosphonic acids (MEAPs). After completion of the reaction, the mixture was extracted with ether to yield crude **2a–d** product (Scheme 1).

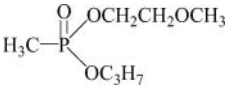
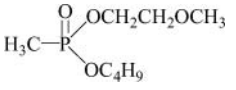
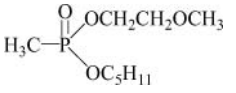
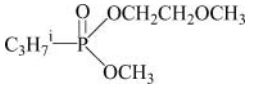
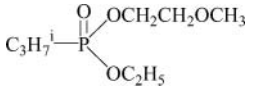
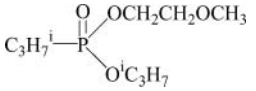
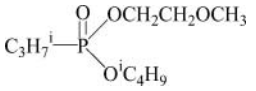
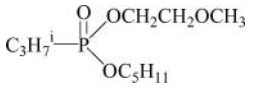
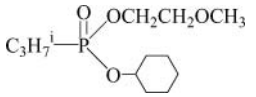
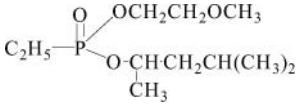
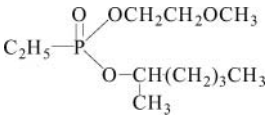
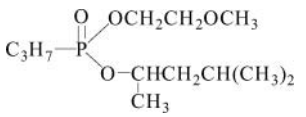
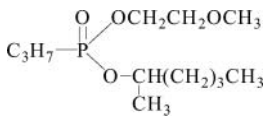


Scheme 1

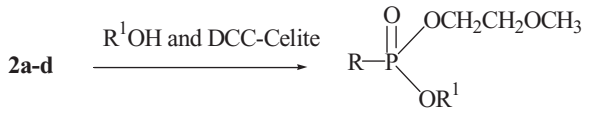
Compounds **2a–d** were reacted with various alcohols in the presence of fresh DCC-celite by following the same molar ratio and at 100°C. The reactions were monitored by TLC and ^{31}P NMR spectroscopy. After completion of the reaction, the reaction mixture was extracted with ether, and the ether layer was washed with dilute aqueous solution of sodium carbonate to remove traces of unreacted acid. AMEAPs (**3a–m**) were obtained in very good yield (68–80%) (Scheme 2).

The purity of the compounds was checked on silica TLC plate using a chloroform/acetone mixture (8:2). Compounds **3a–m** were distilled under vacuum and characterized by IR, NMR spectroscopy, GC-MS, and elemental analysis. The results are summarized in Table I.

Table I Synthesis of *O*-alkyl 2-methoxyethyl alkylphosphonates **3a–m**

3	Product	Reaction time (min.)	Yield (%)[a]	Bp (°C/mm Hg)	^{31}P NMR (δ ppm)[b]
a		70	76.5	145/0.5	31.4
b		85	73.4	147/0.5	31.2
c		90	72.5	160/0.5	31.2
d		45	80.5	142/0.5	35.8
e		55	77.6	145/0.5	35.3
f		60	69.7	150/0.5	34.7
g		85	70.8	150/0.5	34.9
h		95	73.5	162/0.5	34.3
i		100	77.3	165/0.5	35.6
j		110	71.6	Oil	33.0
k		110	68.4	Oil	32.7
l		120	70.5	Oil	32.3
m		120	70.3	Oil	32.2

[a]Isolated yield.
[b]^{31}P NMR spectra were recorded in $CDCl_3$ at 162 MHz.



3a-m

$R = CH_3, C_2H_5, n\text{-}C_3H_7, {}^{i}C_3H_7$

$R^1 = CH_3, C_2H_5, n\text{-}C_3H_7, {}^{i}C_3H_7, C_4H_9,$
${}^{i}C_4H_9, C_5H_{11}, C_6H_{11}, C_6H_{13}$

Scheme 2

CONCLUSION

In conclusion, we have developed a rapid and efficient method for the synthesis of *O*-alkyl 2-methoxyethyl alkylphosphonates **3a–m** with excellent yields. The main advantage of this method is that reactions were found to be clean and had operational simplicity. Column chromatography was not required to get the pure products, which makes the method more attractive for organic chemists.

EXPERIMENTAL

Melting points were determined on a hot stage microscope and are uncorrected. IR spectra were recorded with a Bruker FT-IR spectrometer model Tensor 27 on KBr disk, and solid compounds were analyzed by making KBr pellets. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded in $CDCl_3$ with Bruker DPX Avance FT-NMR spectrometer at 400, 100, and 162 MHz, respectively, using tetramethylsilane as internal standard for ^{1}H, ^{13}C, and 85% H_3PO_4 as external standard for ^{31}P NMR. A Chemito GC model 1000 instrument was used with a flame ionization detector (FID). A capillary column (30 m × 0.25 mm LD-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°C 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 analyses, 0.1 μL sample was injected, and peaks were recorded on an 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 with temperature program of 80°C (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 analyzed in splitless mode at injection temperature.

Synthesis of 2-Methoxyethyl Alkylphosphonic Acids (2): General Procedure

Alkylphosphonic acid (0.1 mol), DCC (20.6 g, 0.1 mol), 2-methoxyethanol (7.6 g, 0.1 mol), and celite (6.4 g, 0.2 mol) were ground with a pestle in a mortar at room temperature followed by heating 50–80°C for a period of 60–90 min. The progress of the reaction

was monitored by ^{31}P NMR after drawing a few milligrams of the reaction mixture and extracting with ether. After the disappearance of the signal of the alkylphosphonic acid in the ^{31}P NMR spectrum, the reaction mass was washed with ether, and the solvent was evaporated. The residue afforded the crude 2-methoxyethyl alkylphosphonic acid, which was used for the next step without further purification.

2-Methoxyethyl methylphosphonic acid (2a). IR (KBr): 695 (P—C), 1090, 1150 (P—O—C), 1230 (P=O), 2890 (C—H) cm^{-1}; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 31.8; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.54 (d, $^2J_{PH}$ = 17.6 Hz, 3H, CH_3), 3.39 (s, 3H, CH_3), 3.62 (t, J = 4.9 Hz, 2H, CH_2), 4.10 (dt, $^3J_{PH}$ = 8.1 Hz, J_{HH} = 6.4 Hz, 2H, CH_2), 8.53 (s, 1H, OH); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 11.5 (d, $^1J_{PC}$ = 146 Hz, CH_3), 58.9 (CH_3), 64.4 (d, $^3J_{PC}$ = 6.3 Hz, CH_2), 71.8 (d, $^2J_{PC}$ = 5.8 Hz, CH_2).

2-Methoxyethyl ethylphosphonic acid (2b). IR (KBr): 693 (P—C), 1085, 1150 (P—O—C), 1240 (P=O), 2883 (C—H) cm^{-1}; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 33.6; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.05 (dt, $^3J_{PH}$ = 19.4 Hz, J_{HH} = 8.3 Hz, 3H, CH_3), 1.59 (dq, $^2J_{PH}$ = 17.9 Hz, J_{HH} = 6.9 Hz, 2H, CH_2), 3.26 (s, 3H, CH_3), 3.48 (t, J = 7.3 Hz, 2H, CH_2), 3.95 (dt, $^3J_{PH}$ = 7.3 Hz, J_{HH} = 5.8 Hz, 2H, CH_2), 8.53 (s, 1H, OH); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 9.5 (d, $^2J_{PC}$ = 6.5 Hz, CH_3), 18.6 (d, $^1J_{PC}$ = 139 Hz, CH_2), 58.0 (CH_3), 63.1 (d, $^3J_{PC}$ = 6.3 Hz, CH_2), 71.3 (d, $^2J_{PC}$ = 5.8 Hz, CH_2).

2-Methoxyethyl propylphosphonic acid (2c). IR (KBr): 702 (P-C), 1090, 1153 (P—O—C), 1235 (P=O), 2880 (C—H) cm^{-1}; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 34.2; ^1H NMR (400 MHz, $CDCl_3$): δ = 0.95 (t, J = 7.4 Hz, 3H, CH_3), 1.21 (dq, $^3J_{PH}$ = 15.6 Hz, J_{HH} = 7.1 Hz, 2H, CH_2), 1.55 (dt, $^2J_{PH}$ = 17.9 Hz, J_{HH} = 6.7 Hz, 2H, CH_2), 3.23 (s, 3H, CH_3), 3.45 (t, J = 7.3 Hz, 2H, CH_2), 4.05 (dt, $^3J_{PH}$ = 7.3 Hz, J_{HH} = 6.2 Hz, 2H, CH_2), 8.50 (s, 1H, OH); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 9.5 (d, $^3J_{PC}$ = 6.5 Hz, CH_3), 11.3 (d, $^2J_{PC}$ = 7.3 Hz, CH_2), 18.7 (d, $^1J_{PC}$ = 139.8 Hz, CH_3), 57.9 (CH_3), 63.0 (d, $^3J_{PC}$ = 6.4 Hz, CH_2), 71.2 (d, $^2J_{PC}$ = 5.9 Hz, CH_2).

2-Methoxyethyl isopropylphosphonic acid (2d). IR (KBr): 698 (P—C), 1093, 1150 (P—O—C), 1245 (P=O), 2865 (C—H) cm^{-1}; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 34.9; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.17 (dd, $^3J_{PH}$ = 21.4 Hz, J_{HH} = 7.5 Hz, 6H, CH_3), 2.05 (d of septets, $^2J_{PH}$ = 17.6 Hz, J_{HH} = 6.9 Hz, 1H, CH), 3.20 (s, 3H, CH_3), 3.42 (t, J = 7.3 Hz, 2H, CH_2), 3.95 (dt, $^3J_{PH}$ = 7.3 Hz, J_{HH} = 5.4 Hz, 2H, CH_2), 8.53 (s, 1H, OH); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 14.4 (d, $^2J_{PC}$ = 10.0 Hz, CH_3), 21.1 (d, $^1J_{PC}$ = 144.2 Hz, CH), 58.0 (CH_3), 63.1 (d, $^3J_{PC}$ = 6.3 Hz, CH_2), 71.3 (d, $^2J_{PC}$ = 5.8 Hz, CH_2).

Synthesis of *O*-Alkyl 2-Methoxyethyl Alkylphosphonates (3): General Procedure

2-Methoxyethyl alkylphosphonic acid (0.03 mol), DCC (6.18 g, 0.03 mol), alcohol (0.03 mol), and Celite (1.924 g, 0.06 mol) were ground with a pestle in a mortar at 50–100°C for 45–120 min (Table I). The progress of the reaction was monitored by TLC and ^{31}P NMR spectroscopy after drawing a few milligrams of the reaction mixture and extracting with ether. After the disappearance of the signal of the 2-methoxyethyl alkylphosphonic acid in the ^{31}P NMR spectrum, the reaction mass was extracted with ether (3 × 25 mL). The ether layer was washed with dilute aqueous sodium carbonate solution to remove the traces of free acids. The ether layer was collected and dried over anhydrous Na_2SO_4. It was filtered and washed with ether. The filtrate and washings were collected, and the solvent

was evaporated. The residue was distilled under vacuum to afford the pure compound **3a–m** (68.4–80.5%) (Table I).

***O*-Propyl 2-methoxyethyl methylphosphonate (3a).** Anal. Calcd. $C_7H_{17}O_4P$: C, 42.86; H, 8.73. Found: C, 42.85; H, 8.70%. IR (KBr): 703 (P—C), 1085, 1156 (P—O—C), 1229 (P=O), 2870 (C—H) cm^{-1}; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): $\delta = 31.4$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.96$ (t, $J = 7.4$ Hz, 3H, CH_3), 1.51 (d, $^2J_{PH} = 17.6$ Hz, 3H, CH_3), 1.70 (sextet, $J = 7.4$ Hz, 2H, CH_2), 3.40 (s, 3H, CH_3), 3.60 (t, $J = 7.6$ Hz, 2H, CH_2), 4.02 (dt, $^3J_{PH} = 9.9$ Hz, $J_{HH} = 6.4$ Hz, 2H, CH_2), 4.20 (dt, $^3J_{PH} = 8.4$ Hz, $J_{HH} = 5.9$ Hz, 2H, CH_2); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 10.1$ (CH_3), 11.1 (d, $^1J_{PC} = 145.0$ Hz, CH_3), 23.8 (d, $^3J_{PC} = 5.2$ Hz, CH_2), 58.7 (CH_3), 64.4 (d, $^3J_{PC} = 6.1$ Hz, CH_2), 67.1 (d, $^2J_{PC} = 6.4$ Hz, CH_2), 71.8 (d, $^2J_{PC} = 5.8$ Hz, CH_2); GC-MS (EI,%): 197 ($M+H^+$), 166, 155 (3.5), 139 (27.4), 125 (30.5), 111 (15.3), 97 (100), 79 (43.7), 58 (88.5), 45 (51.3).

***O*-Butyl 2-methoxyethyl methylphosphonate (3b).** Anal. Calcd. $C_8H_{19}O_4P$: C, 45.79; H, 9.11. Found: C, 45.76; H, 9.10%. IR (KBr): 696 (P—C), 1083, 1155 (P—O—C), 1235 (P=O), 2880 (C—H) cm^{-1}; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): $\delta = 31.2$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.96$ (t, $J = 7.3$ Hz, 3H, CH_3), 1.50 (d, $^2J_{PH} = 17.6$ Hz, 3H, CH_3), 1.75 (t, $J = 7.1$ Hz, 4H, CH_2), 3.35 (s, 3H, CH_3), 3.61 (t, $J = 7.5$ Hz, 2H, CH_2), 4.0 (dt, $^3J_{PH} = 9.8$ Hz, $J_{HH} = 5.8$ Hz, 2H, CH_2), 4.25 (dt, $^3J_{PH} = 8.3$ Hz, $J_{HH} = 5.5$ Hz, 2H, CH_2); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 10.1$ (CH_3), 11.1 (d, $^1J_{PC} = 145.0$ Hz, CH_3), 21.4 (CH_2), 23.8 (d, $^3J_{PC} = 5.5$ Hz, CH_2), 58.7 (CH_3), 64.3 (d, $^3J_{PC} = 6.1$ Hz, CH_2), 67.2 (d, $^2J_{PC} = 6.4$ Hz, CH_2), 71.7 (d, $^2J_{PC} = 5.9$ Hz, CH_2); GC-MS (EI,%): 211 ($M+H^+$), 165 (9.4), 155 (11.7), 137 (17.6), 125 (28.7), 111 (11.7), 97 (100), 79 (21.6), 58 (73.7), 45 (39.5).

***O*-Pentyl 2-methoxyethyl methylphosphonate (3c).** Anal. Calcd. $C_9H_{21}O_4P$: C, 48.21; H, 9.44. Found: C, 48.20; H, 9.45%. IR (KBr): 694 (P—C), 1089, 1152 (P—O—C), 1237 (P=O), 2885 (C—H) cm^{-1}; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): $\delta = 31.2$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.93$ (t, $J = 7.3$ Hz, 3H, CH_3), 1.39 (dt, $J = 7.2$ Hz, $J_{HH} = 8.1$ Hz, 2H, CH_2), 1.52 (d, $^2J_{PH} = 17.5$ Hz, 3H, CH_3), 1.70 (quintet, $J = 7.2$ Hz, 4H, CH_2), 3.38 (s, 3H, CH_3), 3.61 (t, $J = 7.6$ Hz, 2H, CH_2), 4.00 (dt, $^3J_{PH} = 9.8$ Hz, $J_{HH} = 6.4$ Hz, 2H, CH_2), 4.25 (dt, $^3J_{PH} = 8.3$ Hz, $J_{HH} = 6.7$ Hz, 2H, CH_2); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 10.2$ (CH_3), 11.2 (d, $^1J_{PC} = 145$ Hz, CH_3), 21.3 (CH_2), 22.8 (CH_2), 23.9 (d, $^3J_{PC} = 6.2$ Hz, CH_2), 58.4 (CH_3), 64.3 (d, $^3J_{PC} = 6.1$ Hz, CH_2), 66.9 (d, $^2J_{PC} = 6.4$ Hz, CH_2), 71.7 (d, $^2J_{PC} = 5.9$ Hz, CH_2); GC-MS (EI,%): 225 ($M+H^+$), 181(3.1) 167(8.9), 155 (18.5), 137 (8.45), 125 (35.3), 111 (10.8), 97 (100), 79 (15.8), 71 (9.6) 58 (73.8), 45 (40.3).

***O*-Methyl 2-methoxyethyl isopropylphosphonate (3d).** Anal. Calcd. $C_7H_{17}O_4P$: C, 42.86; H, 8.73. Found: C, 42.85; H, 8.70%. IR (KBr): 698 (P—C), 1085, 1155 (P—O—C), 1245 (P=O), 2875 (C—H) cm^{-1}; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): $\delta = 35.8$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.17$ (dd, $^3J_{PH} = 21.4$ Hz, $J_{HH} = 7.8$ Hz, 6H, CH_3), 2.05 (d of septets, $^2J_{PH} = 17.9$ Hz, $J_{HH} = 7.1$ Hz, 1H, CH), 3.40 (s, 3H, CH_3), 3.60 (t, $J = 7.6$ Hz, 2H, CH_2), 4.02 (dt, $^3J_{PH} = 9.9$ Hz, $J_{HH} = 6.6$ Hz, 3H, CH_3), 4.12 (dt, $^3J_{PH} = 8.4$ Hz, $J_{HH} = 5.7$ Hz, 2H, CH_2); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 14.4$ (d, $^2J_{PC} = 10.0$ Hz, CH_3), 21.2 (d, $^1J_{PC} = 144.2$ Hz, CH), 58.3 (CH_3), 64.3 (d, $^3J_{PC} = 6.1$ Hz, CH_2), 66.9 (d, $^2J_{PC} = 6.5$ Hz, CH_3), 71.5 (d, $^2J_{PC} = 6.0$ Hz, CH_2); GC-MS (EI,%): 195 ($M+H^+$), 181 (3.5), 166 (11.8), 155 (35.9), 139 (87.3), 125 (21.9), 109 (15.3), 96 (10.0), 79 (83.1), 58 (100), 45 (41.3).

***O*-Ethyl 2-methoxyethyl isopropylphosphonate (3e).** Anal. Calcd. $C_8H_{19}O_4P$: C, 45.79; H, 9.11. Found: C, 45.76; H, 9.10%. IR (KBr): 705 (P—C), 1085, 1153 (P—O—C), 1235 (P=O), 2855 (C—H) cm^{-1}; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): $\delta =$ 35.3; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.15$ (dd, $^3J_{PH} = 21.5$, $J_{HH} = 9.3$ Hz, 6H, CH_3), 1.21 (t, $J = 7.5$ Hz, 3H, CH_3), 2.02 (d of septets, $^2J_{PH} = 17.8$ Hz, $J_{HH} = 7.4$ Hz, 1H, CH), 3.45 (s, 3H, CH_3), 3.70 (t, $J = 7.6$ Hz, 2H, CH_2), 4.07 (dt, $^3J_{PH} = 10.3$ Hz, $J_{HH} = 6.3$ Hz, 2H, CH_2), 4.12 (dq, $^3J_{PH} = 8.5$ Hz, $J_{HH} = 5.4$ Hz, 3H, CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 14.3$ (d, $^2J_{PC} = 10.0$ Hz, CH_3), 16.4 (d, $^3J_{PC} = 5.4$ Hz, CH_3), 21.1 (d, $^1J_{PC} = 144.2$ Hz, CH), 58.6 (CH_3), 64.3 (d, $^3J_{PC} = 6.1$ Hz, CH_2), 67.0 (d, $^3J_{PC} = 6.4$ Hz, CH_2), 71.7 (d, $^2J_{PC} = 5.8$ Hz, CH_2); GC-MS (EI,%): 211 ($M+H^+$), 180 (13.5), 167 (27.8), 155 (61.5), 139 (25.1), 125 (65.4), 107 (17.3), 93 (11.9), 79 (8.1), 58 (100), 45 (44.7), 43 (43.6).

***O*-Isopropyl 2-methoxyethyl isopropylphosphonate (3f).** Anal. Calcd. $C_9H_{21}O_4P$: C, 48.21; H, 9.44. Found: C, 48.20; H, 9.44%. IR (KBr): 695 (P—C), 1085, 1150 (P—O—C), 1235 (P=O), 2855 (C—H) cm^{-1}; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): $\delta =$ 34.7; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.10$ (dd, $^3J_{PH} = 21.2$, $J_{HH} = 7.1$ Hz, 6H, CH_3), 1.20 (d, $J = 8.0$ Hz, 6H, CH_3), 2.05 (d of septets, $^2J_{PH} = 17.7$ Hz, $J_{HH} = 6.8$ Hz, 1H, CH), 3.40 (s, 3H, CH_3), 3.75 (t, $J = 7.6$ Hz, 2H, CH_2), 4.00 (d of septets, $^3J_{PH} = 10.1$ Hz, $J_{HH} = 6.4$ Hz, 1H, CH), 4.15 (dt, $^3J_{PH} = 8.7$ Hz, $J_{HH} = 7.3$ Hz, 2H, CH_2); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 14.3$ (d, $^2J_{PC} = 10.0$ Hz, CH_3), 17.3 (CH_3), 21.1 (d, $^1J_{PC} = 144.2$ Hz, CH), 58.6 (CH_3), 64.3 (d, $^3J_{PC} = 6.1$ Hz, CH_2), 67.3 (d, $^2J_{PC} = 6.4$ Hz, CH), 71.7 (d, $^2J_{PC} = 5.8$ Hz, CH_2); GC-MS (EI,%): 225 ($M + H^+$), 194 (5.8), 183 (7.6), 165 (21.7), 152 (10.2), 139 (30.6), 125 (100), 113 (11.7), 107 (10.3), 79 (8.3), 65 (15.6), 58 (63.9), 43 (44.6).

***O*-Isobutyl 2-methoxyethyl isopropylphosphonate (3g).** Anal. Calcd. $C_{10}H_{23}O_4P$: C, 50.41; H, 9.73. Found: C, 50.40; H, 9.75%. IR (KBr): 702 (P—C), 1075, 1150 (P—O—C), 1245 (P=O), 2848 (C—H) cm^{-1}; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): $\delta = 34.9$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.10$ (d, $J = 8.0$ Hz, 6H, CH_3), 1.15 (dd, $^3J_{PH} =$ 21.5, $J_{HH} = 6.8$ Hz, 6H, CH_3), 1.73 (quintet, $J = 7.6$ Hz, 1H, CH), 2.10 (d of septets, $^2J_{PH} = 17.6$ Hz, $J_{HH} = 6.1$ Hz, 1H, CH), 3.45 (s, 3H, CH_3), 3.70 (t, $J = 7.3$ Hz, 2H, CH_2), 4.05 (dt, $^3J_{PH} = 10.3$ Hz, $J_{HH} = 6.9$ Hz, 2H, CH_2), 4.12 (dt, $^3J_{PH} = 8.7$ Hz, $J_{HH} = 5.6$ Hz, 2H, CH_2); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 11.5$ (CH_3), 14.3 (d, $^2J_{PC} = 10.0$ Hz, CH_3), 18.2 (d, $^3J_{PC} = 4.2$ Hz, CH), 21.1 (d, $^1J_{PC} = 144.2$ Hz, CH), 58.6 (CH_3), 64.3 (d, $^3J_{PC} = 6.1$ Hz, CH_2), 67.0 (d, $^2J_{PC} = 6.4$ Hz, CH_2), 71.7 (d, $^2J_{PC} = 5.8$ Hz, CH_2); GC-MS (EI,%): 239 ($M+H^+$), 223 (3.7), 208 (2.9), 195 (5.3), 183 (10.4), 165 (11.2), 153 (11.3), 139 (22.7), 125 (100), 113 (7.5), 79 (8.3), 65 (10.2), 58 (43.7), 43(25.4).

***O*-Pentyl 2-methoxyethyl isopropylphosphonate (3h).** Anal. Calcd. $C_{11}H_{25}O_4P$: C, 52.37; H, 9.99. Found: C, 52.35; H, 10.00%. IR (KBr): 698 (P—C), 1080, 1155 (P—O—C), 1235 (P=O), 2865 (C—H) cm^{-1}; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ $= 34.3$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.95$ (t, $J = 7.4$ Hz, 3H, CH_3), 1.15 (dd, $^3J_{PH}$ $= 21.4$, $J_{HH} = 7.7$ Hz, 6H, CH_3), 1.20 (t, $J = 7.3$ Hz, 2H, CH_2), 1.39 (q, $J = 7.0$ Hz, 2H, CH_2), 1.75 (q, $J = 7.4$ Hz, 2H, CH_2), 2.05 (d of septets, $^2J_{PH} = 17.8$ Hz, $J_{HH} = 6.2$ Hz, 1H, CH), 3.38 (s, 3H, CH_3), 3.61 (t, $J = 7.6$ Hz, 2H, CH_2), 4.03 (dt, $^3J_{PH} = 9.8$ Hz, $J_{HH} =$ 7.2 Hz, 2H, CH_2), 4.25 (dt, $^3J_{PH} = 8.3$ Hz, $J_{HH} = 5.7$ Hz, 2H, CH_2); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 10.1$ (CH_3), 11.1 (d, $^2J_{PC} = 10.1$ Hz, CH_3), 18.8 (CH_2), 21.1 (d, $^1J_{PC} =$ 144.2 Hz, CH), 22.8 (CH_2), 23.8 (d, $^3J_{PC} = 5.4$ Hz, CH_2), 58.6 (CH_3), 64.5 (d, $^3J_{PC} = 6.1$ Hz, CH_2), 67.1 (d, $^2J_{PC} = 6.4$ Hz, CH_2), 71.6 (d, $^2J_{PC} = 5.9$ Hz, CH_2); GC-MS (EI,%):

253 ($M+H^+$), 237 (2.8), 222 (5.7), 209 (10.5), 183 (20.3) 165 (7.3), 139 (25.4), 125 (100), 113 (8.3), 79 (6.4), 58 (9.4), 43 (44.7).

***O*-Cyclohexyl 2-methoxyethyl isopropylphosphonate (3i).** Anal. Calcd. $C_{12}H_{25}O_4P$: C, 54.53; H, 9.53. Found: C, 54.50; H, 9.50%. IR (KBr): 694 (P—C), 1089, 1152 (P—O—C), 1237 (P=O), 2885 (C—H) cm^{-1}; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): $\delta =$ 35.6; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.12$ (dd, $J = 7.4$ Hz, $J_{HH} = 6.7$ Hz, 2H, CH_2), 1.15 (dd, $^3J_{PH} = 21.4$, $J_{HH} = 7.4$ Hz, 6H, CH_3), 1.25 (dt, $J = 7.5$ Hz, $J_{HH} = 7.8$ Hz, 4H, CH_2), 1.85 (dt, $J = 7.5$ Hz, $J_{HH} = 7.8$ Hz, 4H, CH_2), 2.10 (d of septets, $^2J_{PH} = 17.8$ Hz, $J_{HH} = 6.1$ Hz, 1H, CH), 3.39 (s, 3H, CH_3), 3.60 (t, $J = 7.6$ Hz, 2H, CH_2), 4.12 (dt, $^3J_{PH} = 8.3$ Hz, $J_{HH} = 8.1$ Hz, 2H, CH_2), 4.42 (dd, $^3J_{PH} = 7.3$ Hz, $J_{HH} = 5.4$ Hz, 1H, CH); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 14.3$ (d, $^2J_{PC} = 10.0$ Hz, CH_3), 21.1 (d, $^1J_{PC} =$ 144.2 Hz, CH), 23.6 (CH_2), 25.2 (CH_2), 33.4 (d, $^3J_{PC} = 5.5$ Hz, CH_2), 58.9 (CH_3), 64.2 (d, $^3J_{PC} = 6.1$ Hz, CH_2), 71.1 (d, $^2J_{PC} = 6.4$ Hz, CH_2), 75.0 (d, $^2J_{PC} = 5.9$ Hz, CH); GC-MS (EI,%): 265 ($M+H^+$), 235 (3.6), 221 (6.9), 207 (2.5), 183 (28.3) 165 (5.2), 139 (15.3), 125 (100), 113 (5.8), 83 (10.2), 59 (30.1), 41 (19.7).

***O*-1,3-Dimethylbutyl 2-methoxyethyl ethylphosphonate (3j).** Anal. Calcd. $C_{11}H_{25}O_4P$: C, 52.37; H, 9.99. Found: C, 52.40; H, 9.98%. IR (KBr): 695 (P—C), 1089, 1150 (P—O—C), 1238 (P=O), 2845 (C—H) cm^{-1}; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): $\delta =$ 33.0; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.95$ (d, $J = 7.4$ Hz, 6H, CH_3), 1.05 (sextet, $J =$ 7.2 Hz, 1H, CH), 1.17 (dt, $^3J_{PH} = 20.2$ Hz, $J_{HH} = 6.7$ Hz, 3H, CH_3), 1.20 (dd, $J = 7.4$ Hz, $J_{HH} = 6.6$ Hz, 2H, CH_2), 1.77 (dq, $^2J_{PH} = 17.6$ Hz, $J_{HH} = 7.5$ Hz, 2H, CH_2), 2.11 (dd, $J_{HH} = 6.3$ Hz, 3H, CH_3), 3.38 (s, 3H, CH_3), 3.61 (t, $J = 7.6$ Hz, 2H, CH_2), 4.0 (dt, $^3J_{PH} =$ 9.8 Hz, $J_{HH} = 7.4$ Hz, 2H, CH_2), 4.25 (dt, $^3J_{PH} = 8.3$ Hz, $J_{HH} = 6.7$ Hz, 1H, CH); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 9.9$ (CH_3), 10.4 (CH), 10.6 (d, $^2J_{PC} = 7.0$ Hz, CH_3), 19.5 (d, $^1J_{PC} = 143.6$ Hz, CH_2), 21.4 (CH_2), 23.8 (d, $^3J_{PC} = 5.8$ Hz, CH_3), 58.6 (CH_3), 64.3 (d, $^3J_{PC} = 6.1$ Hz, CH_2), 67.9 (d, $^2J_{PC} = 6.4$ Hz, CH_2), 71.6 (d, $^2J_{PC} = 5.9$ Hz, CH); GC-MS (EI,%): 253 ($M+H^+$), 169 (19.4), 151 (71.5), 138 (11.6), 125 (7.5), 111 (100), 93 (7.9), 79 (4.5), 58 (33.7), 43 (26.5).

***O*-1-Methylpentyl 2-methoxyethyl ethylphosphonate (3k).** Anal. Calcd. $C_{11}H_{25}O_4P$: C, 52.37; H, 9.99. Found: C, 52.35; H, 10.00%. IR (KBr): 703 (P—C), 1085, 1150 (P—O—C), 1250 (P=O), 2867 (C—H) cm^{-1}; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): $\delta =$ 32.7; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.96$ (t, $J = 7.3$ Hz, 3H, CH_3), 1.17 (dt, $^3J_{PH} =$ 20.2 Hz, $J_{HH} = 8.3$ Hz, 3H, CH_3), 1.38 (q, $J = 7.4$ Hz, 2H, CH_2), 1.75 (t, $J = 7.4$ Hz, 4H, CH_2), 1.77 (dq, $^2J_{PH} = 17.6$ Hz, $J_{HH} = 7.8$ Hz, 2H, CH_2), 2.05 (q, $J = 6.2$ Hz, 3H, CH_3), 3.38 (s, 3H, CH_3), 3.61 (t, $J = 7.6$ Hz, 2H, CH_2), 4.12 (dt, $^3J_{PH} = 9.8$ Hz, $J_{HH} = 5.9$ Hz, 2H, CH_2), 4.25 (dq, $^3J_{PH} = 8.3$ Hz, $J_{HH} = 5.3$ Hz, 1H, CH); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 10.1$ (CH_3), 11.7 (d, $^2J_{PC} = 7.0$ Hz, CH_3), 19.5 (d, $^1J_{PC} = 143.6$ Hz, CH_2), 21.4 (CH_2), 22.8 (CH_2), 23.8 (CH_2), 39.2 (d, $^3J_{PC} = 7.6$ Hz, CH_3), 58.7 (CH_3), 64.4 (d, $^3J_{PC} = 6.1$ Hz, CH_2), 67.1 (d, $^2J_{PC} = 6.4$ Hz, CH_2), 71.8 (d, $^2J_{PC} = 5.9$ Hz, CH); GC-MS (EI,%): 253 ($M+H^+$), 181 (3.1) 169 (18.3), 151 (88.5), 138 (8.45), 125 (7.3), 111 (100), 93 (10.2), 79 (5.8), 71 (9.6) 58 (33.7), 45 (20.3).

***O*-1,3-Dimethylbutyl 2-methoxyethyl propylphosphonate (3l).** Anal. Calcd. $C_{12}H_{27}O_4P$: C, 54.12; H, 10.22. Found: C, 54.10; H, 10.20%. IR (KBr): 695 (P—C), 1090, 1155 (P—O—C), 1235 (P=O), 2865 (C—H) cm^{-1}; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): $\delta = 32.3$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.96$ (d, $J = 7.2$ Hz, 6H, CH_3), 1.05 (sextet, $J = 7.2$ Hz, 1H, CH), 1.07 (t, $J = 7.2$ Hz, 3H, CH_3), 1.18 (dq, $^3J_{PH} = 20.2$ Hz, $J_{HH} = 7.3$ Hz, 2H, CH_2), 1.20 (q, $J = 7.4$ Hz, 2H, CH_2), 1.77 (dt, $^2J_{PH} = 17.6$ Hz,

J_{HH} = 6.9 Hz, 2H, CH_2), 2.11 (q, J_{HH} = 8.1 Hz, 3H, CH_3), 3.38 (s, 3H, CH_3), 3.60 (t, J = 7.6 Hz, 2H, CH_2), 4.05 (dt, $^3J_{PH}$ = 9.8 Hz, J_{HH} = 7.2 Hz, 2H, CH_2), 4.25 (dt, $^3J_{PH}$ = 8.3 Hz, J_{HH} = 6.8 Hz, 1H, CH); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 9.9 (CH_3), 10.4 (CH), 11.1 (d, $^3J_{PC}$ = 6.2 Hz, CH_3), 12.4 (d, $^2J_{PC}$ = 7.0 Hz, CH_2), 19.5 (d, $^1J_{PC}$ = 143.6 Hz, CH_3), 21.4 (CH_2), 33.3 (d, $^3J_{PC}$ = 7.0 Hz, CH_3), 58.7 (CH_3), 64.4 (d, $^3J_{PC}$ = 6.1 Hz, CH_2), 70.2 (d, $^2J_{PC}$ = 6.4 Hz, CH_2), 73.1 (d, $^2J_{PC}$ = 5.9 Hz, CH); GC-MS (EI,%): 267 ($M+H^+$), 183 (15.3), 165 (55.3), 152 (11.5), 139 (9.6), 125 (100), 110 (3.7), 96 (7.9), 69 (4.5), 58 (33.7), 43 (26.5).

***O*-1-Methylpentyl 2-methoxyethyl propylphosphonate (3m).** Anal. Calcd. $C_{12}H_{27}O_4P$: C, 54.12; H, 10.22. Found: C, 54.10; H, 10.20%. IR (KBr): 697(P—C), 1085, 1140 (P—O—C), 1254 (P=O), 2875 (C—H) cm^{-1}; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 32.2; ^1H NMR (400 MHz, $CDCl_3$): δ = 0.95 (t, J = 7.2 Hz, 3H, CH_3), 1.07 (t, J = 7.2 Hz, 3H, CH_3), 1.17 (dq, $^3J_{PH}$ = 20.2 Hz, J_{HH} = 7.4 Hz, 2H, CH_2), 1.39 (q, J = 7.4 Hz, 2H, CH_2), 1.75 (sextet, J = 7.4 Hz, 4H, CH_2), 1.77 (dt, $^2J_{PH}$ = 17.6 Hz, J_{HH} = 6.6 Hz, 2H, CH_2), 2.15 (q, J = 8.2 Hz, 3H, CH_3), 3.38 (s, 3H, CH_3), 3.61 (t, J = 7.6 Hz, 2H, CH_2), 4.0 (dt, $^3J_{PH}$ = 8.8 Hz, J_{HH} = 5.8 Hz, 2H, CH_2), 4.25 (dq, $^3J_{PH}$ = 7.3 Hz, J_{HH} = 6.1 Hz, 1H, CH); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 10.1 (CH_3), 11.1 (d, $^3J_{PC}$ = 6.0 Hz, CH_3), 17.6 (d, $^2J_{PC}$ = 7.0 Hz, CH_2), 19.5 (d, $^1J_{PC}$ = 143.6 Hz, CH_2), 21.4 (CH_2), 22.8 (CH_2), 23.8 (CH_2), 39.6 (d, $^3J_{PC}$ = 6.0 Hz, CH_3), 58.7 (CH_3), 64.4 (d, $^3J_{PC}$ = 6.1 Hz, CH_2), 69.0 (d, $^2J_{PC}$ = 6.4 Hz, CH_2), 73.3 (d, $^2J_{PC}$ = 5.9 Hz, CH); GC-MS (EI,%): 267 ($M+H^+$), 183 (13.1) 165 (68.3), 152 (8.5), 139 (8.4), 125 (100), 107 (4.7), 93 (10.2), 79 (5.8), 69 (5.6) 58 (35.3), 45 (28.6).

REFERENCES

1. Convention on the Prohibition of the Development, Production, Stockpiling, and Use of Chemical Weapons and their Destruction, Technical Secretariat of the Organization for Prohibition of Chemical Weapons. The Hague (1997). Available at: http://www.opcw.nl.
2. W. Krutzsch and R. Trapp, *A Commentary of CWC* (Martinus Nijhoff, The Netherlands, 1994).
3. M. Mesilaakso and M. Rautio, *Encyclopedia of Analytical Chemistry* (Wiley, Chichester, UK, 2000), p. 899.
4. O. Kostiainen, In M. J. Bogusz, *Forensic Science, Handbook of Analytical Separations* (Elsevier, Amsterdam, 2000), vol. 2, p. 405.
5. Convention on the Prohibition of the Development, Production, Stockpiling and Use of Chemical Warfare and on their Destruction CD/1170, Geneva (August, 1992).
6. Conference on Disarmament: *The Convention on the Prohibition of the Development, Production, Stockpiling and Use of Chemical Warfare and on Their Destruction*. Organization for the Prohibition of Chemical Weapons (OPCW), The Hague (1994).
7. Committee on Review and Evaluation of the Army Chemical Stockpiles Disposal Program, National Research Council, *Recommendations for Disposal of Chemical Agents and Munitions* (National Academy Press, Washington, DC, 1994).
8. Criteria for Designation of Laboratories by OPCW-C-I/DEC.61 (22 May 1997).
9. J. Hendrikkse, In *A Comprehensive Review of the Official OPCW Proficiency Test in Chemical Weapons Chemical Analysis: Sample Collection, Preparation, and Analytical Methods*, M. Mesilaakso, Ed. (Wiley, Chichester, UK, 2005), p. 89.
10. E. W. J. Hooijshuur, A. G. Hulst, A. L. De Jong, L. P. De Reuver, S. H. Van Krimpen, B. L. M. Van Baar, E. R. J. Wils, C. E. Kientz, and U. A. Th. Brinkman, *Trends Anal. Chem.*, **21,** 116 (2002).
11. E. R. J. Wils, *Fresenius J. Anal. Chem.*, **22,** 338 (1990).

12. A. K. Gupta, P. D. Shakya, D. Pardasani, M. Palit, and D. K. Dubey, *Rapid Commun. Mass Spectrom.*, **19,** 975 (2005).
13. A. K. Gupta, M. Palit, P. D. Shakya, D. Pardasani, R. K. Srivastava, and D. K. Dubey, *Eur. J. Mass Spectrom.*, **12,** 271 (2006).
14. Central OPCW Analytical Database, Version 6, released June 2004, Technical Secretariat of OPCW, The Hague.
15. M. Mesilaakso, In *Chemical Weapons Chemical Analysis: Sample Collection, Preparation, and Analytical Methods*, M. Mesilaakso, Ed. (Wiley, Chichester, UK, 2005), p. 151.
16. A. K. Bhattacharya and G. Thyagarajan, *Chem. Rev.*, **81,** 415 (1981).
17. A. Michaelis and R. Kaehne, *Ber. Dtsch. Chem. Ges.*, **31,** 1048 (1898).
18. B. A. Arbusov, *Pure Appl. Chem.*, **9,** 315 (1964).
19. R. G. Harvey and E. R. Sombre, In *Topics in Phosphorus Chemistry* (Interscience, New York, 1964), vol. 1, p. 57.
20. E. Muller, Ed., *Methoden der Organischen Chemie (Houben-Weyl)* (Thieme, Stuttgart, Germany, 1964), vol. XIIXII, p. 433.
21. A. Michaelis and T. Becker, *Chem. Ber.*, **30,** 1003 (1897).
22. Q. Yao and S. Levchik, *Tetrahedron Lett.*, **47,** 277 (2006).
23. S. Samanta and N. K. Roy, *Ind. J. Chem.*, **37B,** 564 (1998).
24. K. C. Nicolaou, Z. Yang, M. Ouellette, G. O. Shi, P. Gaertner, J. L. Gunzner, C. Agrios, R. Huber, R. Chadha, and D. H. Huang, *J. Am. Chem. Soc.*, **119,** 8105 (1997).
25. E. A. Dennis and F. H. Westheimer, *J. Am. Chem. Soc.*, **88,** 3432 (1966).
26. A. C. Poshkus and J. E. Herweh, *J. Am. Chem. Soc.*, **84,** 555 (1962).
27. (a) Q. Yao and S. Levchik, *Tetrahedron Lett.*, **47,** 277 (2006); (b) V. Roussis and D. F. Wiemer, *J. Org. Chem.*, **54,** 627 (1989).
28. M. Sathe, A. K. Gupta, and M. P. Kaushik, *Tetrahedron Lett.*, **47,** 3107 (2006).
29. M. Kabachnik, Ed., *Reactions and Methods of Organic Compound Investigation*, (Goskhimizdat, Moscow, 1953), vol. 13, p. 427.
30. (a) L. D. Quin, *A Guide to Organophosphorus Chemistry* (Wiley, New York, 2000); (b) A. F. Grapov, *Reakts. Metody Issled. Org. Soedin.*, **15,** 41 (1966); (c) F. R. Hartley, Ed., In *The Chemistry of Organophosphorus Compounds*, (Wiley, New York, 1996), vol. 4, p. 495.
31. G. M. Kosolapoff, *J. Am. Chem. Soc.*, **67,** 1180 (1945).
32. M. R. M. D. Charandabi, M. L. Ettel, M. P. Kaushik, J. H. Huffman, and K. W. Morse, *Phosphorus, Sulfur, and Silicon*, **44,** 233 (1989), and references therein.
33. A. P. Wight and M. E. Davis, *Chem. Rev.*, **102,** 3589 (2002).
34. A. Fadel, R. Yefash, and J. Saluan, *Synthesis*, 37 (1987).
35. G. Rosini, R. Falarini, E. Marotta, and R. Righi, *J. Org. Chem.*, **55,** 781 (1990).
36. M. Kodomari, T. Sakamoto, and S. Yoshitomi, *J. Chem. Soc., Chem. Commun.*, 701 (1990).
37. P. J. Kropp, K. A. Daus, S. D. Crawford, M. W. Tubergren, K. D. Kepler, S. L. Craig, and V. P. Wilson, *J. Am. Chem. Soc.*, **112,** 7433 (1990).
38. G. Hondrogiannis, R. M. Pagni, G. W. Kabalka, P. Anisoki, and R. Kurt, *Tetrahedron Lett.*, **31,** 5433 (1990).
39. H. K. Pantney, *Tetrahedron Lett.*, **32,** 2259 (1991).
40. G. Schotter, *Chem. Mater.*, **13,** 3422 (2001).
41. K. Tanaka, *Solvent-Free Organic Synthesis* (Wiley, Weinheim, Germany, 2003).
42. R. J. Gedye, K. Westaway, H. Ali, L. Baldisera, L. Laberge, and J. Rousell, *Tetrahedron Lett.*, **27,** 279 (1986).
43. R. J. Giguere, T. L. Bray, S. M. Duncan, and G. Majetich, *Tetrahedron Lett.*, **27,** 4945 (1986).
44. A. Abramovitch, *Org. Prep. Proc. Int.*, **23,** 685 (1991).
45. D. M. P. Migos and D. R. Baghurst, *Chem. Soc. Rev.*, **20,** 1 (1991).
46. S. Caddick, *Tetrahedron*, **51,** 10403 (1995).
47. A. Loupy, A. Petit, M. Ramdiani, C. Yvanaeff, M. Majdoub, B. Labiad, and D. Villemin, *Can. J. Chem.*, **71,** 90 (1993).

48. A. Baezza, C. Najera, R. Gracia, and J. M. Sansano, *Synthesis*, 2787 (2005).
49. (a) A. R. Hajipour, A. R. Halahati, and A. E. Ruoho, *Tetrahedron Lett.*, **47,** 2719 (2006); (b) A. K. Gupta, R. Kumar, H. K. Gupta, and D. K. Dubey, *Tetrahedron Lett.*, **49,** 1656 (2008).
50. J. Acharya, A. K. Gupta, and M. P. Kaushik, *Tetrahedron Lett.*, **46,** 5293 (2005).
51. J. Acharya, P. D. Shakya, D. Pardasani, M. Palit, D. K. Dubey, and A. K. Gupta, *J. Chem. Res.*, **3,** 194 (2005).