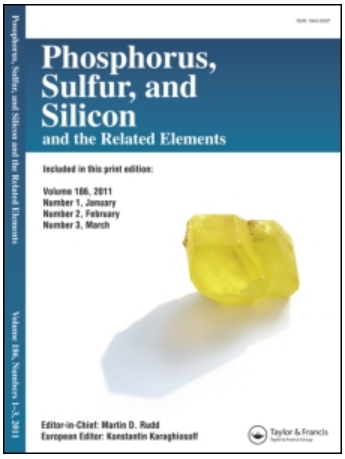

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PREPARATION, DERIVATIZATION WITH TRIMETHYLSILYLDIAZOMETHANE, AND GC/MS ANALYSIS OF A "POOL" OF ALKYL METHYLPHOSPHONIC ACIDS FOR USE AS QUALITATIVE STANDARDS IN SUPPORT OF COUNTERTERRORISM AND THE CHEMICAL WEAPONS CONVENTION

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There are hundreds of nerve agents in the class of alkyl methylphosphonofluoridates covered by Schedule 1 of the CWC (Chemical Weapons Convention). Hydrolysis of these sarin-like nerve agents results in an equal number of alkyl methylphosphonic acids. These alkyl methylphosphonic acids are persistent and provide good evidence of specific agent production or use. In order to support the CWC and counterterrorism activities, it is desirable to have ready access to each of these hydrolysis products for use as qualitative standards. A means for simultaneously producing multiple alkyl methylphosphonates from methylphosphonic acid and the corresponding alcohols was developed. Derivatization of these alkyl methylphosphonic acids with trimethylsilyldiazomethane yields the corresponding methyl esters which are suitable for GC/MS analysis.

Keywords: Alkyl methylphosphonic acid; chemical warfare agents; counterterrorism; esterification; mass spectra; trimethylsilyldiazomethane

The ability to detect a greater variety of chemical weapons and related chemicals has become more urgent as information that was once privy to the military becomes increasingly available. The large number of potential chemical warfare agents as described in the CWC (Chemical Weapons Convention) adds to the complexity of this problem.

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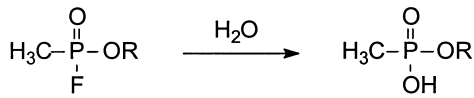
The CWC prohibits the production, storage, and use of chemical weapons.* Signatory countries that possess chemical weapons also agree to dispose of their stockpiles. Schedule 1 of the CWC lists specific as well as classes of highly toxic chemicals that are highly toxic with no known licit use. Included in Schedule 1 are the neurotoxic chemicals of the type RP(O)F(OR') where R may be C_{1-3} and R′ may be C_{1-10}. Sarin (isopropyl methylphosphonofluoridate) and soman (pinacolyl methylphosphonofluoridate) are two specific examples of this class of compounds of which there are 3652 possibilities.[1] Verification of compliance with the CWC allows for on-site inspections and the use of chemical analyses, including gas chromatography-mass spectrometry for definitive identification as required by the OPCW (Organization for the Prohibition of Chemical Weapons).** However, terrorist may produce and use one or more of these nerve agents. Such an event occurred in the Tokyo subway on March 20, 1995.

Sarin, **1a**, and soman, **1b**, are known to hydrolyze to isopropyl methylphosphonic acid, **2a**, and pinacolyl methylphosphonic acid, **2b** respectively (Scheme 1).[2] The remaining alkyl methylphosphonofluoridates covered by the CWC are expected to hydrolyze in the same manner. These alkyl methylphosphonic acids are persistent and provide good evidence of specific agent production or use. Reported here are simple and convenient methods for preparing a "pool" of alkyl methylphosphonic acid standards that would be necessary to identify specific nerve agent hydrolysis products.***



1 2

a: R = $CH(CH_3)_2$
b: R= $CH(CH_3)C(CH_3)_3$

SCHEME 1 Hydrolysis reaction of alkyl methylphosphonofluoridate nerve agents.

For the preparation of monoesters of methylphosphonic acid, a method was sought that would be applicable to the simultaneous

*_Convention on the Prohibition of the Development, Stockpiling, and Use of Chemical Weapons and on their Destruction_, United States Arms Control and Disarmament Agency, Washington, D.C., 1993. As of December 31, 2001 there were 145 State Parties to the CWC, www.opc.org.

**The OPCW is responsible for monitoring the CWC.

***Prof. Hoffmann, while suggesting alternatives for the term "library," noted that "pool" was initially used by combinatorial chemists.[3]

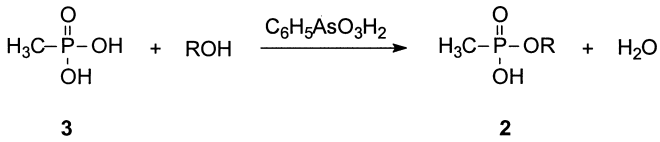
preparation of a large number of these monoesters such as a reaction analogous to the acid-catalyzed esterification of carboxylic acids with alcohols. Such a method would provide a means for obtaining the mass spectra of a large number of hydrolysis products from sarin-like chemical warfare agents. However, no such method for the esterification of methylphosphonic acid has been reported. Previously reported methods for synthesizing alkyl methylphosphonic acids include the reaction of an alcohol with methylphosphonic anhydride,[4,5] partial hydrolysis of the dialkyl ester of methylphosphonic acid,[6,7] hydrolysis of the monochloro monoester[8,9] and hydrogenation of the benzyl alkyl ester.[10]

Derivatization of alkyl methylphosphonic acids prior to analysis by gas chromatography has been used for forensic analyses from the sarin attack at the Tokyo subway.[8,11,12] The methods for derivatizing alkyl methylphosphonic acids include silylation,[13–17] methylation with diazomethane[18–20] or trimethylphenylammonium hydroxide,[21,22] and other alkylations.[23–25]

RESULTS AND DISCUSSION

Reported here is a new method for preparing alkyl methylphosphonic acids. Heating a mixture of methylphosphonic acid (**3**), 1-butanol, and an aqueous solution of arsenic(V) acid in toluene for 48 h with azeotropic removal of the water gave the dibutyl ester of methylphosphonic acid as indicated by analysis of the reaction mixture. Further analysis of the reaction mixture showed that dibutyl methylphosphonate was present only in very small amounts and that the predominant product was the monoester, butyl methylphosphonic acid.

Subsequently, phenylarsonic acid was substituted for arsenic acid to reduce the loss of lower boiling alcohols through azeotropic distillation. This method for preparing monoalkyl esters of methylphosphonic acid was found to be successful with primary and secondary alcohols, including cyclic alcohols and alcohols containing an ether group (Scheme 2). The alcohols used, in order of increasing number of carbons, are: ethanol, propanol, 2-propanol, 2-methoxyethanol, butanol, 2-butanol, 2-methyl-1-propanol, cyclopropanemethanol, 2-ethoxyethanol, pentanol,

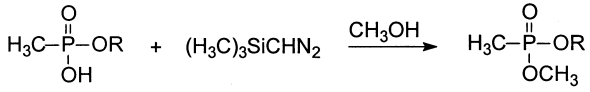


SCHEME 2 Preparation of alkyl methylphosphonates, **2**.

cyclobutanemethanol, 3-methylbutanol, 2-isopropoxyethanol, hexanol, pinacolyl alcohol, cyclohexanol, 2-methylcyclohexanol, octanol, 2-ethylhexanol, decanol, and (−)-borneol. With cyclopentanol, the product initially was formed during the reaction but decomposed prior to completion.

Substitution of *p*-toluenesulfonic acid for phenylarsonic acid did not result in the esterification of methylphosphonic acid. This observation has led us to speculate that the mechanism involves the formation of an arsonic acid ester followed by transesterification to produce the phosphonic acid ester.

Trimethylsilyldiazomethane, a stable and commercially-available reagent, has been shown to readily form the methyl esters of carboxylic acids.[26] The suitability of trimethylsilyldiazomethane for the methylation of alkyl methylphosphonic acids was demonstrated by us.[27] Addition of a 2.0 M solution of trimethylsilyldiazomethane in THF to a mixture of benzene, chloroform, or MTBE with methanol (or other alcohol) containing a portion of the reaction mixture of alkyl methylphosphonic acids provides the corresponding alkyl methyl methylphosphonates, **4** (Scheme 3). These alkyl methyl methylphosphonates are readily analyzed by GC/MS. In this way, an alkyl methylphosphonic acid or a group of isomeric alkyl methylphosphonic acids suspected of being present in a sample can be readily prepared and used as qualitative standards. Other techniques, such as the retention index method[28,29] and a computer algorithm for determining the type of phosphorus ester[1] also can be used to assist in this determination.



2 **4**

SCHEME 3 Derivatization of **2** to yield the methyl esters, **4**.

During the derivatization, the methanol acts as a hydrogen source and other alcohols (e.g., ethanol and 1-hexanol) may be substituted for it and still provide the methyl ester with no apparent impact on efficiency. Omission of an alcohol or addition of the trimethylsilyldiazomethane to the phosphonic acid prior to the addition of the alcohol results in a mixture of esters being formed, specifically the methyl ester, the (trimethylsilyl)methyl ester, and the trimethylsilyl ester.[27]

Figure 1 shows the chromatogram from derivatization and GC/MS analysis of the reaction mixture when methylphosphonic acid was simultaneously esterified with seven straight-chain alcohols. Figure 2

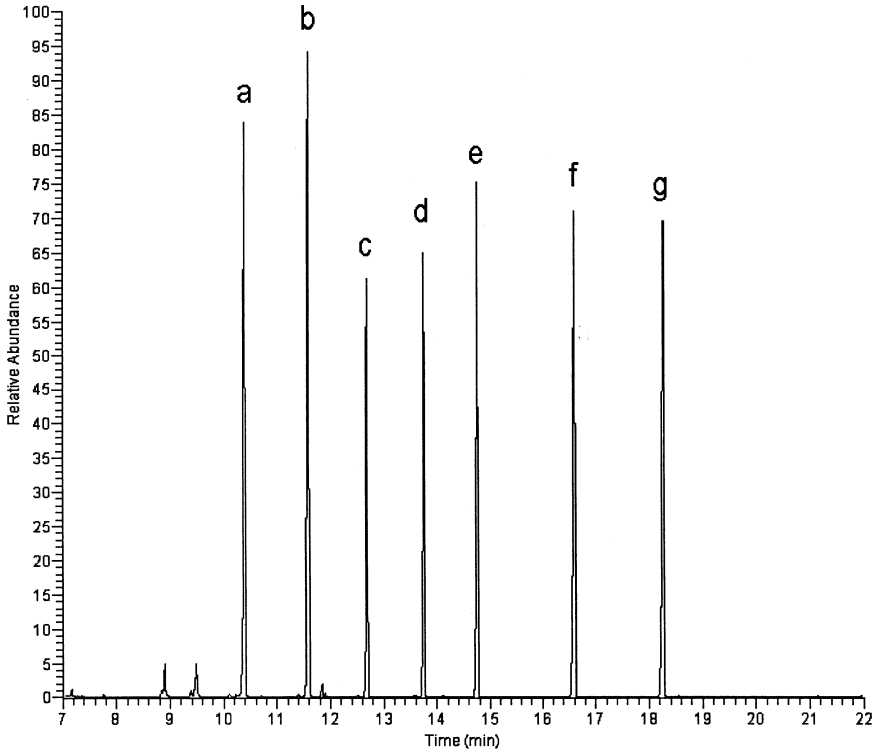


FIGURE 1 Total ion current chromatogram from derivatization and GC/MS analysis of a reaction mixture containing: (a) ethyl methylphosphonic acid; (b) propyl methylphosphonic acid; (c) butyl methylphosphonic acid; (d) pentyl methylphosphonic acid; (e) hexyl methylphosphonic acid; (f) octyl methylphosphonic acid; (g) decyl methylphosphonic acid.

shows the chromatogram from derivatization and GC/MS analysis of the reaction mixture when methylphosphonic acid was esterified with 11 additional alcohols, including secondary alcohols and branched-chain alcohols. Methylphosphonic acid appears to react less readily with the sterically hindered alcohols, pinacolyl alcohol, 2-methylcyclohexanol, (−)-borneol, based on the relative chromatographic peak intensities. It is not known if the efficiency of the derivatization is affected by the presence of bulky ester groups. Alcohols with an asymmetric center give rise to diastereomers that can be separated on the GC column. In most cases this resolution is complete, but it is less than 20% for the diastereomers of *sec*-butyl methyl methylphosphonate and less than 5% for the diastereomers of 2-ethylhexyl methyl methylphosphonate.

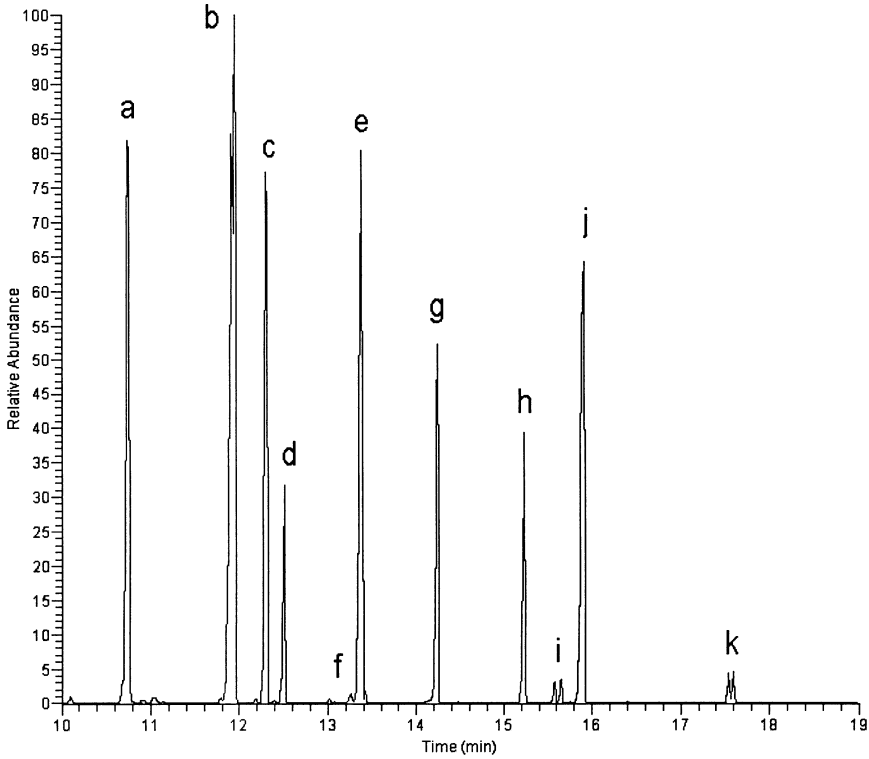


FIGURE 2 Total ion current chromatogram from derivatization and GC/MS analysis of a reaction mixture containing: (a) isopropyl methylphosphonic acid; (b) *sec*-butyl methylphosphonic acid; (c) isobutyl methylphosphonic acid; (d) cyclopropanemethyl methylphosphonic acid; (e) isoamyl methylphosphonic acid; (f) pinacolyl methylphosphonic acid; (g) cyclobutanemethyl methylphosphonic acid; (h) cyclohexyl methylphosphonic acid; (i) 2-methylcyclohexyl methylphosphonic acid; (j) 2-ethylhexyl methylphosphonic acid; (k) bornyl methylphosphonic acid.

For each alkyl methyl methylphosphonate listed in the text, a tabular listing of those ions with a relative abundance equal to or greater than three per cent are presented in Tables I–III. For those that give diastereomers, relative abundances for both are listed. Because an ion trap was used to acquire the spectra, an ion corresponding to m/z M + 1 is generally observed, resulting from self-chemical ionization within the ion trap.[30] Often the most abundant ion in each of the spectra is that with m/z 111 resulting from loss of the alkyl ester group (Figure 3).

Continuing studies involve the application of these methods to the preparation of multigram quantities of alkyl esters of phosphorus acids

TABLE I Relative Ion Abundances of Derivatized *n*-Alkyl Methylphosphonic Acid Monoesters shown in Figure 1

Phosphonate	*m/z* (relative abundance)
Ethyl methyl methylphosphonate (MW 138)	63 (11.2), 65 (8.0), 79 (18.8), 80 (6.6), 93 (39.4), 94 (12.1), 95 (9.8), 111 (76.0), 112 (18.4), 113 (3.9), 139 (100.0)
Methyl *n*-propyl methylphosphonate (MW 152)	63 (18.9), 65 (5.0), 66 (3.3), 79 (15.2), 81 (4.2), 93 (38.2), 94 (71.5), 111 (100.0), 112 (47.0), 123 (9.1), 137 (8.8), 151 (3.0), 153 (78.0)
n-Butyl methyl methylphosphonate (MW 166)	63 (8.6), 79 (5.4), 93 (32.0), 94 (26.7), 111 (100.0), 112 (4.0), 137 (9.4), 167 (24.6)
Methyl *n*-pentyl methylphosphonate (MW 180)	63 (6.6), 79 (4.8), 93 (43.4), 94 (6.2), 95 (6.7), 111 (100.0), 112 (3.2), 137 (6.0), 181 (14.4)
n-Hexyl methyl methylphosphonate (MW 194)	63 (5.2), 79 (4.1), 93 (35.1), 94 (9.8), 95 (4.4), 111 (100.0), 112 (3.5), 137 (3.3), 195 (11.4)
Methyl *n*-octyl methylphosphonate (MW 222)	63 (3.3), 79 (3.2), 93 (25.2), 94 (14.1), 111 (100.0), 112 (3.7), 223 (6.1)
n-Decyl methyl methylphosphonate (MW 250)	93 (20.7), 94 (10.5), 111 (100.0), 112 (3.9), 251 (4.0)

and to the analysis of monoesters of alkylphosphonic acids in matrices relevant to the support of the CWC and counterterrorism activities.

EXPERIMENTAL

All chemicals were purchased from Aldrich, Pfaltz & Baur, or Lancaster.

Typical procedure for the esterification of methylphosphonic acid with multiple alcohols: methylphosphonic acid (1.6 g), ethanol (1.5 mL), propanol (0.61 mL), butanol (0.22 mL), pentanol (0.26 mL), hexanol (0.31 mL), octanol (0.38 mL), decanol (0.47 mL), phenylarsonic acid (0.13 g) were heated under an atmosphere of dry nitrogen in 80 mL of toluene for 28 h with continuous azeotropic removal of the water formed. Upon cooling, a portion of the reaction mixture is derivatized as described below.

Typical procedure for the methylation of alkyl methylphosphonic acids: 20 μL of 2.0 M trimethylsilyldiazomethane in THF is added to a mixture of 800 μL of benzene, 200 μL of methanol, and 40 μL

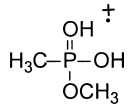


FIGURE 3 Representation of characteristic ion *m/z* 111.

TABLE II Relative Ion Abundances of Derivatized *Iso*- and Cyclo-alkyl Methylphosphonic Acid Monoesters shown in Figure 2

Phosphonate	*m/z* (relative abundance)
Isopropyl methyl methylphosphonate (MW 152)	63 (15.9), 65 (5.2), 79 (9.7), 80 (5.1), 93 (79.3), 94 (8.4), 95 (7.9), 111 (91.9), 112 (9.6), 137 (36.8), 138 (3.7), 151 (3.3), 153 (100.0)
sec-Butyl methyl methylphosphonate (MW 166)	63 (14.7, 16.1), 79 (5.5, 7.0), 93 (67.2, 83.9), 94 (26.4, 8.2), 111 (100.0, 94.5), 112 (17.2, 18.6), 137 (66.3, 57.4), 138 (9.6, 5.2), 151 (19.9, 14.2), 167 (71.6, 100.0)
Isobutyl methyl methylphosphonate (MW 166)	63 (9.1), 79 (17.9), 93 (43.8), 94 (23.9), 111 (100.0), 112 (9.5), 124 (4.1), 151 (8.2), 167 (58.0)
Cyclopropanemethyl methyl methylphosphonate (MW 164)	54 (7.0), 55 (3.8), 63 (22.3), 79 (4.9), 93 (78.6), 94 (12.1), 111 (100.0), 112 (6.4), 123 (11.8), 165 (29.5)
Isoamyl methyl methylphosphonate (MW 180)	63 (5.8), 79 (4.7), 93 (40.8), 94 (8.4), 111 (100.0), 112 (3.2), 137 (11.7), 181 (27.4)
Methyl pinacolyl methylphosphonate (MW 194)	63 (7.4, 6.7), 79 (11.5, 15.0), 93 (35.8, 29.6), 94 (9.1, 12.7), 111 (100.0, 100.0), 137 (20.1, 21.2), 138 (19.8, 26.9)
Cyclobutanemethyl methyl methylphosphonate (MW 178)	63 (7.8), 67 (3.4), 79 (16.0), 93 (34.7), 94 (12.8), 96 (8.1), 97 (4.8), 111 (100.0), 149 (5.9), 150 (13.8), 179 (20.5)
Cyclohexyl methyl methylphosphonate (MW 192)	63 (5.2), 79 (8.3), 93 (32.2), 94 (13.3), 110 (3.7), 111 (100.0), 163 (4.3), 193 (10.4)
Methyl 2-methylcyclohexyl methylphosphonate (MW 206)	63 (5.3, 4.9), 79 (7.1, 7.0), 81 (4.4, 4.6), 93 (27.9, 27.7), 111 (100.0, 100.0)
2-Ethylhexyl methyl methylphosphonate (MW 222)	55 (3.6, 3.8), 63 (3.1, 3.0), 79 (10.1, 9.7), 93 (23.8, 20.2), 94 (20.4, 17.2), 111 (100.0, 100.0), 124 (10.0, 7.3), 223 (6.4, 7.9)
Bornyl methyl methylphosphonate (MW 246)	63 (7.6, 7.3), 65 (5.3, 4.8), 67 (8.7, 8.5), 77 (14.3, 13.8), 78 (6.8, 6.1), 79 (18.3, 18.4), 80 (6.5, 7.5), 91 (34.2, 33.4), 92 (27.7, 28.5), 93 (100.0, 100.0), 94 (9.2, 9.8), 95 (11.9, 11.6), 105 (6.6, 6.3), 107 (9.0, 8.7), 108 (12.0, 12.9), 111 (60.3, 57.2), 121 (33.7, 32.5), 122 (3.3, 3.0), 136 (33.9, 35.3), 137 (40.8, 42.8)

TABLE III Relative Ion Abundances of Derivatized Alkoxyalkyl Methylphosphonic Acid Monoesters

Phosphonate	*m/z* (relative abundance)
2-Methoxyethyl methyl methylphosphonate (MW 168)	58 (5.6), 63 (16.7), 79 (4.7), 93 (52.4), 94 (8.4), 108 (7.4), 111 (100.0), 125 (9.6), 137 (4.1), 138 (16.6), 169 (17.9)
2-Ethoxyethyl methyl methylphosphonate (MW 182)	63 (11.5), 79 (24.2), 93 (42.0), 94 (26.1), 108 (3.3), 111 (100.0), 124 (3.1), 125 (18.4), 137 (14.5), 138 (15.0), 139 (3.5), 169 (4.2), 183 (22.2)
2-Isopropoxyethyl methyl methylphosphonate (MW 196)	58 (11.9), 63 (12.0), 79 (44.8), 93 (55.0), 94 (81.4), 111 (100.0), 112 (3.4), 124 (42.6), 125 (10.4), 137 (55.6), 138 (12.0), 155 (4.8), 183 (5.7), 197 (46.7)

TABLE IV GC/MS Parameters

Instrument: Finnigan GCQ (ion trap)
GC Injector Temp: 260°C
Injection Volume: 1 μL, splitless
Carrier Gas: He, 1 mL/min
GC Column: Restek Rtx-200, 30 m × 0.25 mm, 25 μm film thickness
Oven Temp.: 45°C for 4.3 min; 12°C/min to 270°C; hold 270°C 5 min.
Transfer Line: 270°C
MS: + EI, scan 50–440 amu

of the reaction mixture containing the alkyl methylphosphonic acid in toluene at ambient temperature. The esterification is complete in less than 30 min and this derivatized mixture is injected directly into the gas chromatograph-mass spectrometer without any further work-up. GC/MS instrument conditions are described in Table IV.

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