

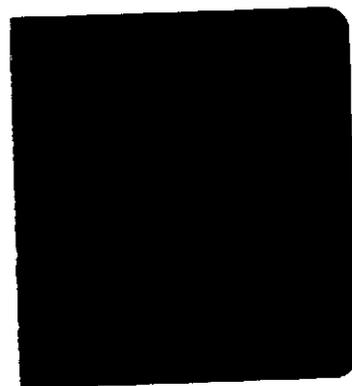
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U. S. Army

Chemical Research and Development Laboratories

Technical Report

CRDIR 3148

Preparation of O-Alkyl Alkylphosphonoazidothioates  
of the Type  $\text{MeP(S)(OR)N}_3$  (U)

by

B. Kagan

R. R. Irino

F. W. Hoffmann

September 1962



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Chemical Research Division

Recommending Approval:

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Director of Research

Approved:

*S. D. Silver*  
S. D. SILVER  
Scientific Director

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Chemical Corps Research and Development Command  
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## FOREWORD

This work was conducted under Task 4C08-03-016-07, New Agents Research (U). The experimental data are contained in notebooks 6531, 6643, and 6664. The work was started in June 1960 and completed in October 1961.

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**DIGEST**

The preparation of a series of O-alkyl methylphosphonoazidothioates is described, as well as the preparation of a representative sample of an S-alkyl analog.

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(C) PREPARATION OF O-ALKYL ALKYLPHOSPHONOAZIDOTHIOATES  
OF THE TYPE  $\text{MeP(S)(OR)N}_3$  (U)

I. (C) INTRODUCTION.

(C) As part of a continuing research program attempting to improve the effectiveness of candidate CW agents, substituted methylphosphonoazido-

thioates of the type  $\begin{array}{c} \text{RO} \quad \text{S} \\ \diagdown \quad / \\ \text{P} \\ / \quad \diagdown \\ \text{Me} \quad \text{N}_3 \end{array}$  where R = alkyl or cycloalkyl, were investigated.

These azides were expected to be more volatile than V agents and possibly retain the high mammalian toxicity of these agents.

(U) The preparation of a series of O-alkyl methylphosphonoazidothioates, as well as a representative sample of an S-alkyl methylphosphonoazidothioate, is described in this report.

II. (C) EXPERIMENTATION.

A. (U) Materials.

Standard laboratory equipment was used throughout this work. The methylphosphonothioic dichloride was prepared according to the procedure of Hoffmann, Wadsworth, and Weiss<sup>1</sup> from methyldichlorophosphine and sulfur. The alcohols used were commercial products

B. (C) Procedures.

1. (C) Preparation of O-Alkyl Methylphosphonochloridothioates.

a. (C) General Method.

(U) The O-alkyl methylphosphonochloridothioates were prepared according to the procedure of Hoffmann, Wadsworth, and Weiss from methylphosphonothioic dichloride and the appropriate alcohol. They are listed in table I. A similar procedure was also used for the preparation of S-cyclohexyl methylphosphonochloridothioate, which is described later.

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1. Hoffmann, F. W., Wadsworth, D. H., and Weiss, H. D. Organic Phosphorus Compounds. III. O, O'-Dialkyl Alkylphosphonothioates and O-Alkyl Alkylphosphonochloridothioates. J. Am. Chem. Soc. 80, 3245 (1958).

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TABLE 1

LIST OF O-ALKYL METHYLPHOSPHONOCHLORIDO-



R	Boiling Range		$n_D^{25}$
	Temperature	Pressure	
	deg	mm	
Et	57-8	9.75	1.4921
n-Pr	71	9.5	1.4881
i-Pr	46-8	4.5	1.4865
n-Bu	46-7	0.6	1.4861
n-Am	64-5	1.25	1.4850
n-Hex	70-1	0.5	1.4805
Pinacolyl	52-5	0.25	1.4839
Cyclopentyl	66-8	0.9	1.5144
Cyclohexyl	70-2	0.35	1.5161

b. (U) Preparation of O-Methyl Methylphosphonochloridothioate.

A mixture of 96 gm (3 moles) of methanol and 303.6 gm (3 moles) of triethylamine was added dropwise over a 3-hr period to a solution of 445.8 gm (3 moles) of methylphosphonodichloridothioate in ether. The heat of reaction was sufficient to keep the ether refluxing during the addition. After standing overnight, the mixture was filtered, the filter cake was washed with ether, and the combined filtrate and washings were dried over calcium sulfate. After removal of the solvent, the residual light-yellow oil was kept under 15 to 20 mm pressure at room temperature for 7 hr, then distilled twice in vacuo

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to give a crude yield of 260.4 gm (60%) of O-methyl methylphosphonochloridothioate, bp 50° to 51° (13 mm),  $n_D^{25}$  1.5036. A center cut was submitted for analysis.

Calcd for  $C_2H_6OPSCl$ : C, 16.61; H, 4.18; P, 21.43; S, 22.18; Cl, 24.53

Found: C, 16.2; H, 4.0; P, 21.68; S, 22.32; Cl, 25.00

c. (C) Preparation of S-Cyclohexyl Methylphosphonochloridodithioate.

A mixture of 58.1 gm (0.5 mole) of cyclohexylthiol and 51 gm (0.5 mole) of triethylamine was added over a 45-min period to a solution of 74 gm (0.5 mole) of methylphosphonothioic dichloride in 100 ml of ether. The reaction mixture was kept at 15° ± 3° during the addition and then stirred at room temperature for 4 hr. Water was then added, with cooling, until all the triethylamine hydrochloride dissolved. The layers were separated. The aqueous layer was extracted several times with ether, the combined organic layer and extracts were dried, the solvent was removed under reduced pressure, and the residual oil was distilled in vacuo to give 59.2 gm (52% yield) of S-cyclohexyl methylphosphonochloridodithioate, bp 92° to 95° (0.15 mm),  $n_D^{25}$  1.5781.

Calcd for  $C_7H_{14}PS_2Cl$ : C, 36.75; H, 6.17; P, 13.54; S, 28.04; Cl, 15.50

Found: C, 37.02; H, 6.18; P, 13.48; S, 28.83; Cl, 15.52

2. (C) Preparation of O-Alkyl Methylphosphonoazidothioates.

a. (U) The preparation of O-isopropyl methylphosphonoazidothioate is described below as a general example of this method.

A solution of 94.1 gm (0.55 mole) of O-isopropyl methylphosphonochloridothioate in 300 ml of dioxane was added over 1 hr, with stirring, to a solution of 71 gm (1.09 moles) of sodium azide in 200 ml of water. The temperature of the reaction mixture rose to 37° during the addition and an oily upper layer formed. After it was stirred for 3 hr, the mixture was extracted

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several times with chloroform, the combined extracts were dried over anhydrous calcium sulfate, the solvent was removed at reduced pressure, and the crude product was distilled twice *in vacuo* to give 75.4 gm of O-isopropyl methylphosphonoazidothioate. Physical and analytical data for this and other azides are reported in table 2.

b. (U) A similar procedure was used to prepare S-cyclohexyl methylphosphonoazidodithioate from the chloridothioate; however, the crude material was not distillable. From 55 gm (0.24 mole) of the appropriate chloridothioate compound, 49 gm (87%) of a light-yellow oil were obtained that turned red-brown on standing.

Calcd for  $C_7H_{14}N_3PS_2$ : C, 35.73; H, 6.00; N, 17.86; P, 13.16;  
S, 27.25

Found: C, 36.2; H, 5.7; N, 17.4; P, 13.28;  
S, 28.18

### III. (U) DISCUSSION.

In the preparation of compounds of the phosphonoazidothioate series, the addition of a chloridothioate to the sodium azide solution, described in the experimental part, seemed to give somewhat better yields than the reverse addition of the azide to the chloridothioate. For example, the yields of the n-propyl and isopropyl compounds were higher than the yields of the ethyl, butyl, or amyl homologs.

All the products, however, were contaminated with a chlorine-containing impurity, even though excess azide was used and the materials were redistilled. In fact, the pinacolyl azide showed an increase in chlorine content with repeated distillation. The complete removal of the final traces of chlorine-containing impurity was made difficult by the close similarity between the boiling point of the phosphonochloridothioates and their corresponding azides. Attempts to prepare O-methyl methylphosphonoazidothioate from the corresponding phosphonochloridothioate gave only small amounts of mixtures that could not be separated.

This is a part of a continuing research program. No conclusions were reached.

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**TABLE 2**

**PHYSICAL AND ANALYTICAL DATA FOR**  
 $\begin{matrix} \text{RO} & \text{S} \\ \diagdown & / \\ & \text{P} \\ / & \diagdown \\ \text{Me} & \text{N}_3 \end{matrix}$  (U)

R	Boiling range		Yield %	C		N		N		P		S		Cl	
	Temp deg	Pressure mm		Calcd	Found										
$\text{C}_2\text{H}_5$	57-8	5	71.5	21.82	22.85	4.80	4.94	25.44	25.04	16.75	18.05	19.42	19.7	0.34	0.34
$\text{C}_3\text{H}_7$	53-8	1.5	88	26.81	27.6	5.63	5.7	23.55	23.5	17.39	16.95	17.90	18.14	0.31	0.31
$\text{CH}_3$ CH	61-3	5.5	77.5	26.81	25.9	5.63	5.8	23.45	23.1	17.29	16.38	17.90	18.14	0.23	0.23
$\text{C}_2\text{H}_5$	67-9	1.8	70	31.08	31.3	6.26	6.4	21.75	21.6	16.01	15.17	16.40	16.62	0.52	0.52
$\text{C}_3\text{H}_7$	63-7	0.7	71.5	34.77	35.9	6.81	6.9	20.28	19.4	14.95	15.54	15.49	15.64	1.26	1.26
$\text{C}_2\text{H}_5$	74.6	0.55	66.5	30.00	30.55	7.29	7.34	19.00	16.6	14.00	13.18	14.99	14.97	2.24	2.24
	59	0.25	71.5	35.11	34.5	5.89	5.6	20.48	19.8	15.09	15.22	15.63	15.67	0.95	0.95
	78.80	0.7	68.3	38.34	38.6	6.44	6.5	19.17	15.1	14.33	13.36	14.63	14.73	3.28	3.28
$\begin{matrix} \text{CH}_3 & \text{CH} \\   &   \\ \text{CH}_2 & \text{CH}_2 \\   &   \\ \text{CH}_3 & \text{H}_3 \end{matrix}$	61-3	0.9	49	38.00	38.22	7.25	7.23	19.00	16.35	14.00	13.93	14.49	15.04	3.39	3.39

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Irvine, and F. W. Hoffmann

CRDLR 3148, September 1962  
Task 4C08-03-016-07, CONFIDENTIAL REPORT

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alkylphosphonazidothioates are given. S-Cyclohexyl methyl-  
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tory equipment was used throughout.

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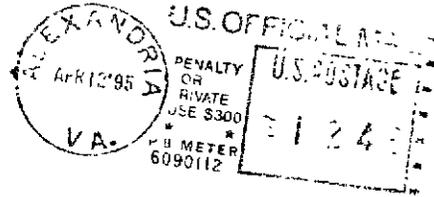
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