

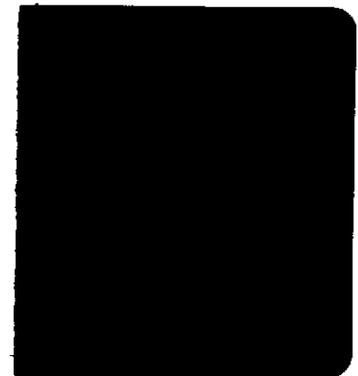
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CHEMICAL WARFARE LABORATORIES
TECHNICAL REPORT

114826

CWLR 2048

**PREPARATION OF V AGENTS IN
AQUEOUS MEDIUM (U)**

by

J. H. Canfield
Benjamin Kagan
F. W. Hoffmann

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24 August 1956

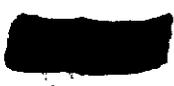
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CHEMICAL WARFARE LABORATORIES
Army Chemical Center, Maryland

Chemical Warfare Laboratories Report No. 2048

Directorate of Research

PREPARATION OF V AGENTS IN AQUEOUS MEDIUM (U)

by

J.H. Canfield
Benjamin Kagan
F.W. Hoffmann


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Chemical Warfare Laboratories
Report No. 2048

APPROVED:

PREPARATION OF V AGENTS
IN AQUEOUS MEDIUM (U)

William H. Summerson
WILLIAM H. SUMMERSON, Ph.D.
Director of Research

Project No. 4-08-03-016-04
Notebook No. 4594

Date Started: 10 October 1955
Date Completed: 29 December 1955

S. D. Silver
S.D. SILVER
Deputy Commander for
Scientific Activities

[REDACTED]

ABSTRACT

(S) Object.

(S) The object of project 4-08-03-016-04 is to study and investigate V agents as candidates for further development and type classification. V agents are high-boiling compounds having a high order of percutaneous toxicity.

(C) The object of the work described in this report was to investigate the synthesis of various V agents in aqueous medium.

(C) Results.

EA 1517 (VE), EA 1664 (VM), EA 1677, and EA 1701 have been prepared in aqueous medium in 55% to 65% yields and a high degree of purity. An 84% yield was obtained in one run of EA 1701 using a 38% excess of N-(2-chloroethyl)diisopropylamine but the purity was not quite as high as in previous runs where no such excess was used.

(C) Conclusions.

1. The V agents of the general type I can be obtained in reasonably good yield and a high degree of purity by the aqueous extraction method.

2. If purities higher than 95% are not required, yields of 90% of the theoretical can readily be obtained by this method using a large excess of the dialkylaziridinium chloride solution.

(U) Recommendations.

None, since work under the project is continuing.

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PREPARATION OF V AGENTS IN AQUEOUS MEDIUM (U)

I. (S) INTRODUCTION.

A. (S) Object.

(S) The object of project 4-08-03-016-04 is to study and investigate V agents as candidates for further development and type classification. V agents are high-boiling compounds having a high order of percutaneous toxicity.

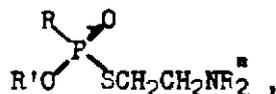
(C) The object of the work described in this report was to investigate the synthesis of various V agents in aqueous medium.

B. (U) Authority.

Authority for this work was the 1956 project program, Project 4-08-03-016-04, V-Agents.

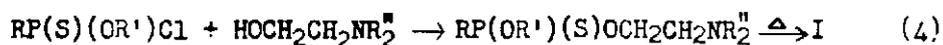
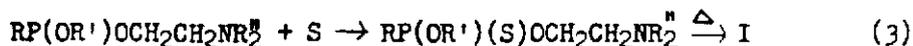
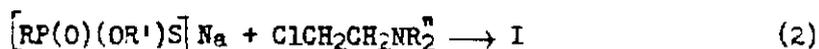
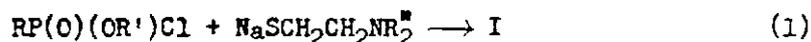
II. (S) HISTORICAL AND THEORETICAL.

(S) The final steps of the various methods used in the preparation of V agents of the general type I,



(I)

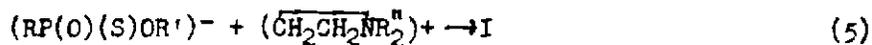
where R, R', and R'' are the same or different alkyl groups, are illustrated by the following equations:



(S) Methods 3 and 4 involve both the formation and subsequent isomerization of the corresponding thiono isomers which had been shown previously in the case of O,O-diethyl O-(2-diethylaminoethyl) phosphorothioate to EA 1508 (VG) to proceed through an intermediate cyclic aziridinium(ethylenimonium) ion (1). While method 2 can be regarded as a simple metathetical reaction when carried out in an inert anhydrous medium, such as benzene, it was demonstrated

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by Epstein, Michel, and Levy (2) that the formation of compounds of the type I (EA 1508 and EA 1517 (VE)) in aqueous reaction medium from the thiol acid salts and the dialkyl-N-(2-chloroethyl)amine proceeds as an ionic reaction according to equation 5.



(S) Epstein et al. (2) prepared EA 1508 and EA 1517 in aqueous reaction medium on a 0.02-molar scale by mixing aqueous solutions of the sodium salt of the appropriate thiol acid with an alkaline aqueous solution of 2-chlorotriethylamine. The product was extracted as formed by continuous liquid-liquid extraction. This convenient method which yields products of a high degree of purity was subsequently adapted by Ford-Moore (3) to the preparation of EA 1508, EA 1517, and EA 1664 (VM) on a 0.2- to 0.4-molar scale. However, agents of the type I with $\text{R}_2^+ = \text{Me}$ could not be prepared in this manner because of almost complete dimerization in the aqueous medium.

(C) The results of a study of the aqueous preparation of four representative V agents in 1-mole batches are described in detail in this report.

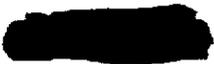
III. (S) EXPERIMENTAL.

A. (U) Materials.

O-Ethyl methylphosphonothioate and O-ethyl ethylphosphonothioate were prepared by the procedure described by Canfield, Kagan, and Hoffmann (4).

2-Chlorotriethylamine was prepared from commercially available 2-chlorotriethylamine hydrochloride (Michigan Chemical Co.) by treatment with excess alkali and purified by distillation. The physical constants for the free base are b.p. 47-49°/15mm., n_D^{25} 1.4344.

N-(2-Chloroethyl)diisopropylamine was prepared as follows: To a stirred solution of 580 g. (4 moles) of 2-diisopropylaminoethanol in 600 ml. of chloroform, cooled to 10°, was added 561 g. (4.7 moles) of thionyl chloride, keeping the pot temperature by a cooling bath between 10° and 20°C. The first half of the thionyl chloride was added dropwise at a very slow rate; the remainder could be added much more rapidly. The entire reaction mixture was refluxed for 7 hr., during which time the pot temperature rose from 59° to 76°. The excess thionyl chloride and solvent were removed under reduced pressure, leaving a solid residue. This residue was dissolved in 500 ml. of water, filtered, and made basic by the addition of a solution of 180 g. of sodium hydroxide in 300 ml. of water. The organic layer was separated and distilled to give the following fractions:



Fraction	Boiling range	Amount	n_D^{25}
	°C./mm.	g.	
1	To 52/6.2	8.0	1.4401
2	52/6.2 - 53.5/6	193.0	1.4404
3	53.5/6 - 52.5/5	154.0	1.4404
4	52.5/5 - 55/5.8	166.5	1.4404
Residue		5.5	

The combined fractions 2, 3, and 4 gave 513.5 g. (78% yield) of N-(2-chloroethyl)-diisopropylamine.

B. (U) Equipment.

The distillations of the compounds described in this report were carried out in conventional glass equipment. The reduced pressures noted were attained with either a Welch Duo-seal pump, series 1400, or a Welch Duo-seal pump, series 1404. No diffusion pumps were used at any time. The syntheses and extractions were carried out in a continuous liquid-liquid extractor built to specifications as shown in the accompanying drawing.

The removable reaction flasks (A) were made in several capacities, from 300 ml. to 1 liter, to suit the size run being made. The most used size was a 1-liter flask.

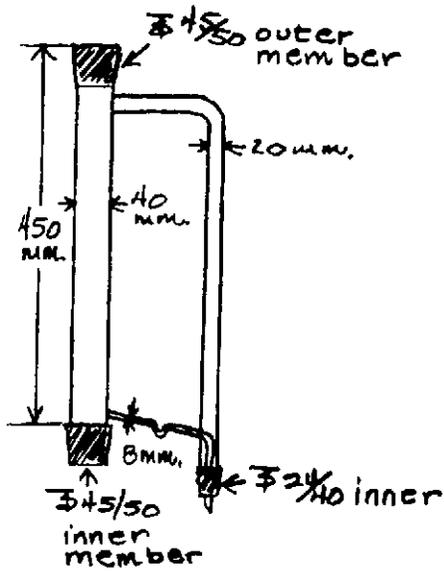
The center return tube for fresh solvent had a fritted glass tip which served to break up the solvent flow into small droplets in order to offer a greater surface area for extraction.

In order to minimize overheating of the product in the solvent recovery flask, the external tube (B) was heated with Glas-col electrical heating tape avoiding condensation of the solvent in the side-arm.

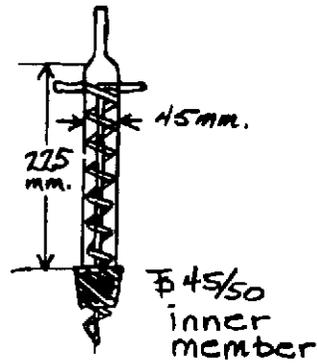
C. (S) Preparation of EA 1517.

A mixture of 203.2 g. (1.5 moles) of 2-chlorotriethylamine (50% excess) and 250 ml. of water adjusted to pH 13 with 7 to 8 sodium hydroxide pellets was stirred at room temperature until the organic layer had dissolved completely (about 1.5 hr.). At the same time, a solution of 40 g. (1 mole) of sodium hydroxide and 154.1 g. (1 mole) of ethyl ethylphosphonothioate was

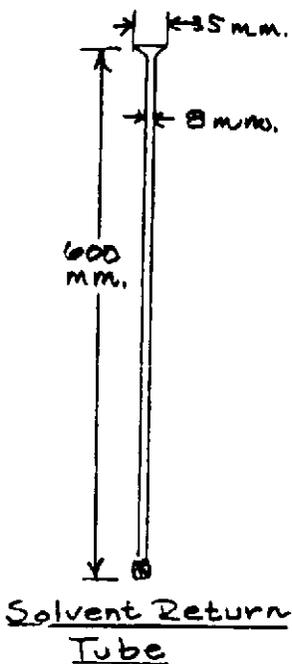
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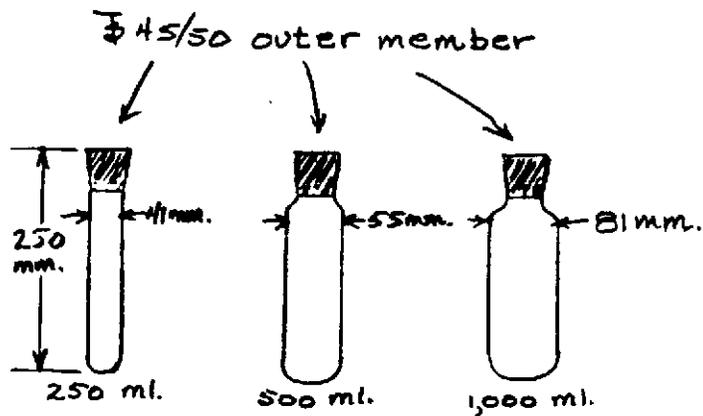
Extractor (B)



Condenser



Solvent Return Tube



Reaction Flasks
to fit Extractor (A)

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prepared in 80 ml. of water. The solutions were mixed in the extractor, diluted to 800 ml. with water, and extracted continuously with benzene for 4 hr. under nitrogen. After stripping off the solvent 243 g. of crude product, n_D^{25} 1.4790, was obtained.

The first distillation yielded the following fractions:

Fraction	Boiling range	Amount	n_D^{25}
	$^{\circ}\text{C./mm.}$	g.	
1	80/0.1 - 75/0.05	70.0	1.4774
2	75/0.05 - 71/0.03	101.9	1.4774
3	71/0.03	34.0	1.4774

The combined fractions weighed 205.9 g. (81% yield). The following fractions were obtained on redistillation of the combined fractions 1 to 3:

Fraction	Boiling range	Amount	n_D^{25}
	$^{\circ}\text{C./mm.}$	g.	
a	83/0.125 - 77/0.06	6.2	1.4774
b	77/0.06 - 75/0.04	89.3	1.4773
c	75/0.035 - 75/0.04	46.1	1.4773
d	75/0.04 - 73.5/0.04	48.5	1.4774
e	73.5/0.04 - 75/0.05	12.1	1.4774

Fractions b, c, and d were combined to give a 73% yield (183.9 g.). Analysis. Calcd. for $\text{C}_{10}\text{H}_{24}\text{O}_2\text{NPS}$: C, 47.41; H, 9.55; P, 12.23; N, 5.53; S, 12.65.

Found: C, 47.1; H, 9.4; P, 12.5; N, 5.45; S, 12.73. Purity: 95%. Amine titration: 99.2%. Free thiol plus thiol acid: <0.03%. Pyro: 0.12%.

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In the same manner, a run was made using 67 g. (0.495 mole) of 2-chlorotriethylamine in 200 ml. of water and 76 g. (0.495 mole) of ethyl ethylphosphonothioate and 19.5 g. of sodium hydroxide in 40 ml. of water. After a 27-hr. extraction with benzene, the extract was evaporated under reduced pressure to give 79.0 g. of crude EA 1517. Distillation of this material gave the following fractions:

Fraction	Boiling range	Amount	n_D^{25}
	$^{\circ}\text{C./mm.}$	g.	
1	To 84/0.090	13.0	1.4776
2	84/0.090 - 76/0.030	58.0	1.4778
3	76/0.030 - 76/0.035	6.0	1.4779

Redistillation of fraction 2 gave the fractions:

Fraction	Boiling range	Amount	n_D^{25}
	$^{\circ}\text{C./mm.}$	g.	
a	To 78/0.045	3.5	1.4774
b	78/0.045 - 75/0.020	48.0	1.4778
c	75/0.020 - 75/0.025	3.5	1.4779

The yield based on fraction 2 was 38%. Analysis. Calcd. for $\text{C}_{10}\text{H}_{24}\text{O}_2\text{NPS}$: C, 47.41; H, 9.55; P, 12.23; N, 5.53; S, 12.65. Found: C, 43.7; H, 9.3; P, 12.23; N, 5.55; S, 12.58. Purity: 95% Amine titration: 99.1%. Free thiol plus thiol acid: Nil. Pyro: 0.5%.

D. (S) Preparation of EA 1664.

A mixture of 149 g. (1.1 moles) of 2-chlorotriethylamine (10% excess) and 200 ml. water adjusted to pH 13 with 7 to 8 sodium hydroxide pellets was stirred until all the amine had dissolved. This solution was filtered and mixed with a solution of 140 g. (1 mole) of ethyl methylphosphonothioate and 40 g. (1 mole) of sodium hydroxide in 80 ml. of water in

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the extractor. The mixture was then extracted continuously with benzene, under nitrogen, for 2 hr. The benzene was removed to yield 153 g. of crude product, n_D^{25} 1.4803. A second extraction for another 8 hr. yielded only an additional 7 g. of the crude product. The crude material was distilled in vacuo, to yield three fractions:

Fraction	Boiling range	Amount	n_D^{25}
	°C./mm.	g.	
1	78.5/0.13	5.5	1.4782
2	78.5/0.13 - 71/0.07	112.5	1.4790
3	71/0.07	23.0	1.4790

Fractions 2 and 3 were combined to give 135.5 g. of EA 1664 (57% yield). On redistillation the following fractions were obtained:

Fraction	Boiling range	Amount	n_D^{25}
	°C./mm.	g.	
a	73/0.09	4.2	1.4787
b	73/0.09 - 70/0.06	113.9	1.4789
c	70/0.06	15.9	1.4789

The combined fractions b and c weighed 129.8 g. (54% yield). Analysis. Calcd. for $C_9H_{22}CNP_2S$: C, 45.17; H, 9.27; P, 12.94; N, 5.85; S, 13.40. Found: C, 45.1; H, 10.4; P, 13.2; N, 5.77; S, 13.6. Purity $92 \pm 2\%$. Amine titration: 98.1%. Free thiol and thiol acid: Nil.

E. (S) Preparation of EA 1677.

A mixture of 180 g. (1.1 moles) of N-(2-chloroethyl)diisopropylamine (10% excess) and 400 ml. of water, adjusted to pH 13 with 7 to 8 sodium hydroxide pellets, was stirred at 50° for 3 hr. in order to dissolve the amine

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completely. This solution was cooled, filtered, and mixed with a solution of 154.1 g. (1 mole) of ethyl ethylphosphonothioate and 40 g. (1 mole) of sodium hydroxide in 80 ml. of water in the extractor. The mixture was extracted continuously with benzene, under nitrogen, for 4 hr. The solvent was removed under reduced pressure, leaving 219.5 g. of crude product, n_D^{25} 1.4754. A second 4-hr. extraction yielded 6.5 g. of product, n_D^{25} 1.4646. The crude product yielded the following fractions on distillation:

Fraction	Boiling range	Amount	n_D^{25}
	$^{\circ}\text{C./mm.}$	g.	
1	35/1 - 65/0.5	13.3	1.4532
2	50/0.2 - 92/0.08	2.7	1.4732
3	92/0.08 - 81/0.01	101.0	1.4740
4	81/0.01 - 86/0.01	77.9	1.4757
5	86/0.01	7.8	1.4757

The combined fractions 3, 4, and 5 weighed 186.7 g. (66.5% yield). They were redistilled, and fractions were taken as follows:

Fraction	Boiling range	Amount	n_D^{25}
	$^{\circ}\text{C./mm.}$	g.	
a	To 90/0.1	6.5	1.4733
b	90/0.1 - 82/0.035	47.5	1.4741
c	82/0.035 - 81/0.025	104.0	1.4756
d	81/0.025 - 81/0.02	23.5	1.4757

Fractions c and d were combined to give 127.5 g. of EA 1677 (45.5% yield). Analysis. Calcd. for $\text{C}_{12}\text{H}_{28}\text{O}_2\text{NPS}$: C, 51.22; H, 10.03; P, 11.01; N, 4.98; S, 11.32. Found: C, 51.1; H, 9.9; P, 11.35; N, 4.91; S, 11.45. Chlorine: <0.1%. Purity: 91.5%. Amine titration: 96.4%. Free thiol plus thiol acid: 0.8%.

F. (S) Preparation of EA 1701.

A mixture of 209 g. (1.17 moles) of N-(2-chloroethyl)diisopropylamine (38% excess) and 400 ml. of water, adjusted to pH 13 with 7 to 8 sodium hydroxide pellets, was stirred at 50° for 3 hr., during which time all the amine had dissolved in the water. This solution was cooled, filtered, and mixed with a solution of 119 g. (0.85 mole) of ethyl methylphosphonothioate and 34 g. (0.85 mole) of sodium hydroxide in 100 ml. of water in the extractor. The mixture was extracted continuously, under nitrogen, for 6 hr. with benzene. Distillation of the crude material gave four fractions:

Fraction	Boiling range	Amount	n_D^{25}
	°C./mm.	g.	
1	52/0.27 - 93/0.23	5.5	1.4756
2	93/0.23 - 77/0.09	72.0	1.4765
3	77/0.09 - 72/0.01	114.0	1.4771
4	72/0.01 - 75/0.035	22.5	1.4772

Fractions 2, 3, and 4 were combined to give a 92% yield (208.5 g.) of EA 1701. The combined fractions were redistilled to give the following cuts:

Fraction	Boiling range	Amount	n_D^{25}
	°C./mm.	g.	
a	To 84/0.065	6.5	1.4758
b	84/0.065 - 70/0.012	176.0	1.4770
c	70/0.012 - 83/0.045	11.5	1.4773
d	83/0.045 - 84/0.06	4.0	1.4773

The combined fractions b, c, and d (191.5 g.) represented an 84% yield of EA 1701. Analysis. Calcd. for $C_{11}H_{26}O_2NPS$: C, 49.41; H, 9.80; P, 11.70;

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N, 5.24; S, 11.99. Found: C, 49.8; H, 9.8; P, 11.53; N, 5.25; S, 11.88. Purity: 94 ± 2%. Amine titration: 98.9%. Free thiol plus thiol acid: <0.03%. Pyro: 1.6%.

A run was made in the same manner using 180 g. (1.1 mole) of N-(2-chloroethyl)diisopropylamine with 400 ml. of water and 140 g. (1.0 mole) of ethyl methylphosphonothioate. A 3-hr. continuous extraction gave 232 g. of crude EA 1701. An additional 16-hr. extraction increased the crude yield by only 2.0 g. These extracts were combined and distilled to give the following:

Fraction	Boiling range	Amount	n_D^{25}
	°C./mm.	g.	
1	To 90/0.20	12.5	1.4681
2	90/0.20 - 86/0.130	10.0	1.4718
3	86/0.130 - 81/0.060	14.0	1.4724
4	81/0.060 - 77/0.030	1.0	1.4774
5	77/0.030 - 72/0.015	57.5	1.4774
6	72/0.015 - 72/0.012	78.5	1.4774
7	72/0.012 - 70/0.010	23.0	1.4774

Fractions 4 to 7 were combined and redistilled, giving the following cuts:

Fraction	Boiling range	Amount	n_D^{25}
	°C./mm.	g.	
a	To 75/0.080	3.0	1.4767
b	75/0.080 - 74/0.040	95.5	1.4774
c	74/0.040 - 72/0.035	51.5	1.4774
d	72/0.035	4.5	1.4774

Fractions b to d were combined (yield is 57% of theoretical). Analysis. Calcd.

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for $C_{11}H_{26}NO_2PS$: C, 49.41; H, 9.80; N, 5.24; P, 11.70; S, 11.99. Found: C, 49.5; H, 9.9; N, 5.19; P, 11.68; S, 12.2. Purity: 97.5%. Amine titration: 99.6%. Free thiol plus thiol acid: Nil. Pyro: 0.99%.

IV. (S) DISCUSSION.

The results of this study demonstrate that the synthesis of V agents of the type I from the appropriate dialkylaziridinium ion and a suitable alkyl alkylphosphonothioate ion according to equation 5 can be extended to the preparation of V agents with $R_2 =$ isopropyl, such as EA 1677 and EA 1701. The purity of the V agents obtained in this manner was found to be far better than that obtained by any of the alternate syntheses illustrated by equation 1 to 4.

A considerable increase in the yield of product over that reported by Ford-Moore (3) could readily be attained by converting the dialkyl-N-(2-chloroethyl)amine to the dialkylaziridinium chloride prior to mixing with the aqueous solution of the sodium salt of the thiol acid, and by using a considerable excess of the aziridinium chloride. An 84% yield of twice-distilled EA 1701 was thus obtained by employing a 38% excess of N-(2-chloroethyl)diisopropylamine which was cyclized with alkali before mixing with the aqueous solution of the sodium phosphonothioate. The resulting product showed a high degree of purity and was superior to samples of EA 1701 prepared by alternate methods. While a large excess of the aziridinium ion did not have a deleterious effect on the purity of the resulting EA 1517, the purity of EA 1701 prepared with a 38% excess aziridinium chloride was somewhat less than that obtained with an excess of only 10%.

The crude material obtained by the aqueous extraction procedure had in all cases at most only a pale yellow color. In general, relatively only small foreruns resulted from the distillation of the crude product, while the distillation residues were extremely small and represented mainly the holdup of the equipment. It appears that the quality of the crude residue from the stripped benzene extracts is at least comparable with that of the distilled agents from alternate procedures.

During this study it was noted that upon mixing of the clear aqueous aziridinium chloride and sodium phosphonothioate solutions, milkiness developed within a few minutes, followed by separation of an oily layer of the desired agent. The low solubility of EA 1701 in water may allow, therefore, the isolation of the agent by simple separation of the layers and may not require an extraction procedure.

V. (C) CONCLUSIONS.

1. The V agents of the general type I can be obtained in reasonably good yield and a high degree of purity by the aqueous extraction method.

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2. If purities higher than 95% are not required, yields of 90% of the theoretical can readily be obtained by this method using a large excess of the dialkylaziridinium chloride solution.

VI. (U) RECOMMENDATIONS.

None, since work under the project is continuing.

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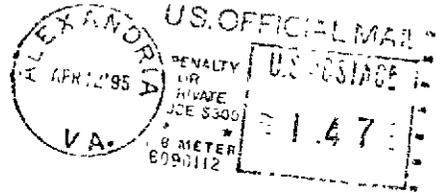
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