5.5, maximum fixation of the insecticide to the wool occurred shortly after the dyebath reached the boil. However, typically when wool is dyed, the dyebath is held at 100 °C for about 1 h to allow the dye to be evenly distributed throughout the wool. To ensure accurate color matching, the time at the boil may often be extended to allow the addition of more dye. Under these conditions the level of the insecticide on the wool was rapidly reduced by hydrolysis (Figure 2). A similar pattern of behavior was obtained when compounds **11**, **12**, and **14** were applied during the dyeing of wool at different pHs. The extent of this hydrolysis in a boiling acidic dyebath precludes the industrial development of organophosphorus esters of nitrogen heterocyclic compounds as insecticides suitable for wool.

ACKNOWLEDGMENT

I thank C. R. Nunn for technical assistance.

Registry No. **1**, 83984-16-1; **2**, 83984-17-2; **3**, 83984-18-3; **4**, 83984-19-4; **5**, 83984-20-7; **6**, 83984-21-8; **7**, 83984-22-9; **8**, 83984-23-0; **9**, 70914-48-6; **10**, 83984-24-1; **11**, 70308-06-4; **12**, 70308-11-1; **13**, 70307-97-0; **14**, 83984-25-2; 5-[(2-hydroxyethyl)-thio]-3-hydroxy-1-isopropyl-1,2,4-triazole, 83984-26-3; 1-isopropyl-3-oxo-5-thioxo-1,2,4-triazolidine, 42838-86-8; 5-[(2-hydroxyethyl)thio]-3-hydroxy-1-phenyl-1,2,4-triazole, 83984-27-4; 3-oxo-1-phenyl-5-thioxo-1,2,4-triazolidine, 53409-52-2; 1-(2-hydroxyethyl)-3-hydroxy-5-(methylthio)-1,2,4-triazole, 83984-28-5; 1-(2-hydroxyethyl)-3-oxo-5-thioxo-1,2,4-triazolidine, 83984-29-6; 5-[(cyanomethyl)thio]-1-(2-hydroxyethyl)-3-hydroxy-1,2,4-triazole, 83984-30-9; diethyl phosphorochloridothionate, 2524-04-1; *O*-ethyl *S*-*n*-propyl phosphorochloridothiolothionate, 42069-01-2.

Supplementary Material Available: A tabulation of the ^{1}H NMR spectra and microanalysis data of the organophosphorus esters (4 pages). Ordering information is given on any current masthead page.

LITERATURE CITED

American Association of Textile Chemists and Colorists *AATCC Tech. Man.* **1979**, *55*, 307–311.
Bohner, B.; Myer, W.; Dawes, D. (Ciba Geigy A.G.) German Patent 2 352 142, 1974.
Duffield, P. A. *Pestic. Sci.* **1977**, *8*, 279–283.
Eto, M. "Organophosphorus Pesticides: Organic and Biological Chemistry"; Zweig, G., Ed.; CRC Press: Cleveland, OH, 1974; p 72.
Gomaa, H. M.; Suffet, I. H.; Faust, S. D. *Residue Rev.* **1969**, *29*, 171.
Harris, F. W. "Controlled Release Technologies: Methods, Theory and Applications"; Kydonius, A. F., Ed.; CRC Press: Boca Raton, FL, 1980; Vol. II, p 73.
Hartmann, M.; Stengel, K. *Acta Polym.* **1980**, *31*, 612–613.
Hofer, W.; Maurer, F.; Hammann, I. (Bayer A.G.) U.S. Patent 3 951 975, 1976a.
Hofer, W.; Maurer, F.; Riebel, H.-J.; Rohe, L.; Hammann, I.; Stendel, K. (Bayer A.G.) U.S. Patent 1 423 954, 1976b.
Hoffman, H.; Hammann, I.; Homeyer, B. (Bayer A.G.) German Patent 2 3001 400, 1974.
Hoffman, H.; Hammann, I.; Stendel, K. (Bayer A.G.) German Patent 2 403 711, 1975.
Hoskinson, R. M.; Russell, I. M. *J. Text. Inst.* **1973**, *64*, 412–418.
Jones, F. W.; Mayfield, R. J.; O'Loughlin, G. J. *Pestic. Sci.* **1982**, in press.
Kishino, S.; Kudematu, A.; Skiokawa, K. (Bayer A.G.) U.S. Patent 3 954 919, 1976.
Riebel, H.-J.; Rohe, L.; Hammann, I.; Behrenz, W. (Bayer A.G.) U.S. Patent 3 950 334, 1976.
Schmidt, K. J. *Pestic. Chem., Proc. Int. IUPAC Congr., Pestic. Chem., 2nd, 1971* **1972**, *1*, 365.
Shafik, M. T.; Bradway, D.; Enos, H. F. *Bull. Environ. Contamin. Toxicol.* **1971**, *6*, 55–66.
St. John, L. E.; Lisk, D. J. *J. Agric. Food Chem.* **1968**, *16*, 408–410.
Williams, V. A. *Text. Res. J.* **1966**, *36*, 1–7.

Received for review March 9, 1982. Accepted October 18, 1982.

Fiber-Reactive Insecticides for Wool: Derivatives of *O*,*O*-Diethyl *O*-[4-[(2-Hydroxyethyl)thio]phenyl] Phosphorothionate

F. William Jones

O,*O*-Diethyl *O*-[4-[(2-hydroxyethyl)thio]phenyl] phosphorothionate derivatives that are capable of covalent bonding to wool were prepared and evaluated for insecticidal activity against the wool pests *Tineola bisselliella* and *Anthrenus flavipes* before and after reaction with the wool. Reaction between these compounds and the wool was brought about by application from a boiling acidic dyebath. Compounds containing reactive groups capable of cross-linking the wool possessed excellent hydrolytic stability when reacted with the wool, but the insecticidal portion of the molecule was not readily accessible to the target insects. The compounds that gave the best balance of reactivity with the wool, hydrolytic stability in the dyebath, and retention of insecticidal activity after reaction with the wool contained either a 3-[(2-chloroethyl)sulfonyl]propionate ester group or a 3-(vinylsulfonyl)propionate ester group.

Recently it has been shown that the durability on wool of certain organophosphorus esters can be improved by the incorporation of a 2-bromoacric ester group in the molecule (Jones et al., 1982; Jones, 1983). This fiber-reactive substituent is similar to the (2-bromoacryl)amido group found in the Lanasol (Ciba-Geigy) range of reactive wool dyes. Other fiber-reactive groups have been used to improve the durability of wool dyes (Lewis, 1974). In this study several different types of reactive groups have been coupled to *O*,*O*-diethyl *O*-[4-[(2-hydroxyethyl)thio]phenyl] phosphorothionate and their suitability for bonding organophosphorus esters to wool has been evaluated.

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MATERIALS AND METHODS

Preparation of Compounds. Compounds which had not been reported previously were characterized by proton nuclear magnetic resonance spectrometry and microanalysis. A tabulation of the ^{1}H NMR spectra and mi-

0021-8561/83/1431-0194$01.50/0

croanalysis data is provided as supplementary material (see paragraph at the end of paper regarding supplementary material).

Preparation of Fiber-Reactive Precursors. The following fiber-reactive precursors were prepared by known methods: *2,3-dibromopropionyl chloride*, bp 86–88 °C/20 mmHg (lit. bp 81–84 °C/18 mmHg) (Marvel et al., 1940); *2,3-dichloropropionyl chloride*, bp 61–63 °C, 20 mmHg (lit. bp 52–54 °C/16 mmHg) (Marvel et al., 1940); *4,5-dichloro-1-[2-(chloroformyl)ethyl]-6-pyridazinone* (Hensel et al., 1963); *2,4-dichloropyrimidine-5-carbonyl chloride*, bp 135–139 °C/16 mmHg (lit. bp 130 °C/12 mmHg) (Geigy, 1970); *2,3-dichloroquinoxaline-6-carbonyl chloride*, mp 111–112 °C (lit. mp 112 °C) (Geigy, 1959); *1,4-dichlorophthalazine-6-carbonyl chloride*, mp 124–125 °C (lit. mp 124–126 °C) (Siegel and Sasse, 1961); *5-chloro-2,4,6-trifluoropyrimidine*, bp 114–116 °C (lit. bp 115–116 °C) (Bayer, 1969);

Other fiber-reactive precursors were prepared as follows: *3-[(2-Chloroethyl)sulfonyl]propionyl chloride*, mp 69–70 °C, was prepared by the action of thionyl chloride on 3-[(2-chloroethyl)sulfonyl]propionic acid (Distler and Brauns, 1964).

2,4-Dichloro-6-[[2-(chloroformyl)ethyl]ethylamino]-s-triazine. An aqueous solution (30 mL) of 3-(ethylamino)propionic acid (5.8 g), prepared by alkaline hydrolysis of ethyl 3-(ethylamino)propionate (Adamson, 1949) was added to an aqueous slurry (100 mL) of freshly recrystallized cyanuric chloride (9.2 g). The temperature of the mixture was held at 0–5 °C while the pH was maintained between 6 and 8 by the addition of aqueous NaOH (6 M, 17 mL). When the reaction was complete the mixture was filtered, the filtrate was acidified to pH 1, and the mixture was chilled. The resulting acid was collected, dried over P_2O_5, and recrystallized from toluene–hexane: mp 122–123 °C (11.5 g, 87%).

The acid chloride was obtained by the action of excess of thionyl chloride on the acid, crude yield 13.4 g (97%) (bp 140–143 °C/0.01 mmHg with decomposition, mp 64–65 °C after recrystallization from hexane).

The following compounds were obtained by a similar procedure: *2,4-dichloro-6-[bis[2-(chloroformyl)ethyl]amino]-s-triazine* (mp of acid 150 °C, recrystallized from toluene–hexane, yield 64%; mp of acid chloride 116–118 °C recrystallized from toluene–hexane, yield 85%); *5-chloro-4-[[2-(chloroformyl)ethyl]amino]-2,6-difluoropyrimidine* (reaction temperature 20 °C, bp of acid chloride 126–128 °C/0.1 mmHg with decomposition).

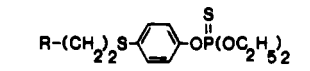
Preparation of Fiber-Reactive Esters and Ethers. These compounds were prepared by the following general method: A solution of collidine (1.2 g) in anhydrous toluene (10 mL) was added to a stirred solution of *O,O*-diethyl *O*-[4-[(2-hydroxyethyl)thio]phenyl] phosphorothionate (Jones et al., 1982) (3.1 g) and the appropriate acid chloride or heterocyclic halide (0.01 mol) in anhydrous toluene (60 mL). The mixture was stirred at 20 °C overnight and then extracted successively with dilute HCl (2 M, 3 × 20 mL), aqueous NaOH (2 M, 2 × 20 mL), and saturated NaCl (20 mL). It was then dried over $MgSO_4$ and the solvent removed to yield the desired compound as an oil.

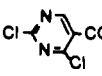
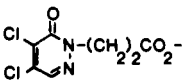
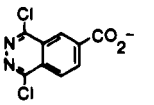
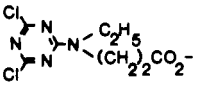
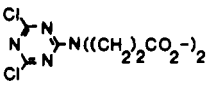
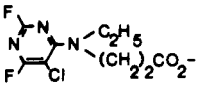
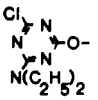
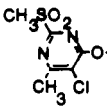
When necessary, the compounds were purified by liquid chromatography on a Waters Associates Prep LC System 500 fitted with a refractive index detector.

Silica gel was used as the adsorbent, and a mixture of ethyl acetate and hexane was used as the eluting solvent. Their yields after purification are given in Table I.

Attempts to prepare *O,O*-diethyl *O*-[4-[[[(2,3-dichloroquinoxalin-6-ylcarbonyl)oxy]ethyl]thio]phenyl] phosphorothionate by coupling 2,3-dichloroquinoxaline-6-carbonyl chloride with *O,O*-diethyl *O*-[4-[(2-hydroxyethyl)thio]phenyl] phosphorothionate were unsuccessful. The major

Table I. Fiber-Reactive Derivatives of *O,O*-Diethyl *O*-[4-(2-Hydroxyethyl)thio]phenyl] Phosphorothionate



Compound No.	R	Yield (%)
1	$ClCH_2CO_2$-	94
2	$CH_2{=}CHCO_2$-	78
3	$CH_2{=}CClCO_2$-	72[a]
4	$CH_2ClCHClCO_2$-	81
5	$CH_2{=}CBrCO_2$-	84[a]
6	$CH_2BrCHBrCO_2$-	86
7	$Cl(CH_2)_2SO_2(CH_2)_2CO_2$-	98
8	$CH_2{=}CHSO_2(CH_2)_2CO_2$-	89[a]
9		92
10		93
11		64
12		96
13		34[b]
14		72
15		78
16		98[c]
17		84
18		72
19		32

[a] These compounds were prepared from the appropriate saturated halo-substituted acid halide by dehydrohalogenation in the presence of 0.22 mol of triethylamine for 30 h at 20 °C. [b] 0.5 mol of acid halide was used. [c] Prepared by the addition of an equimolar amount of diethylamine and triethylamine to a solution of compound 15 in anhydrous toluene.

product obtained from the reaction mixture was *O,O*-diethyl *O*-[4-[(2-chloroethyl)thio]phenyl] phosphorothionate.

Application of Fiber-Reactive Insecticide to Wool from an Aqueous Emulsion. The fiber-reactive insecticide was dissolved in a solution of an ethoxylated nonylphenol containing 13 ethylene oxide units (Teric N13, ICI) (0.01 g) and calcium dodecylbenzenesulfonate (Alkanate CS, ICI) (0.01 g) in xylene (0.5 mL) and blended with water (49 mL) in a high-speed blender. This emulsion was applied to wool fabric (25 g) from an Ahiba Turbomat laboratory dyeing machine. The fabric package was wetted out and immersed in an aqueous solution (450 mL) of ammonium sulfate (1.0 g) and acetic acid (0.25 g) at 40 °C. This solution was circulated for 10 min and the emulsified insecticide added. The liquor was circulated for a further 10 min and then its temperature raised to 100 °C over 30 min and maintained at 100 °C for the required time. The treated fabric was removed, hydroextracted, and air-dried.

Analysis of Phosphorus Esters on Wool. Fiber-reactive derivatives of *O,O*-diethyl *O*-[4-[(2-hydroxyethyl)-thio]phenyl] phosphorothionate on wool were converted to *O,O*-diethyl *S*-methyl phosphorothiolate and determined by gas chromatography as described previously (Jones, 1983).

For determination of the extent of reaction between the fiber-reactive compounds and the wool, unreacted insecticide was removed from a sample of wool (4 g) by Soxhlet extraction with an azeotropic mixture of dichloromethane, methanol, and water (92:6:2) (6–10 siphon cycles of 60 mL) prior to analysis of the wool (Jones, 1983).

Insect Testing. Insecticidal activity was evaluated by assay with larvae of the common clothes moth (*Tineola bisselliella*, Hummel) and the furniture carpet beetle (*Anthrenus flavipes*, Le Conte) according to the fabric weight loss method as described in AATCC Standard Test Method 24-1977 (American Association of Textile Chemists and Colorists, 1979). Wool is considered to pass the test if the feeding damage does not exceed 8 mg, provided that the feeding damage of an untreated control is 30 mg or more.

RESULTS AND DISCUSSION

When the fiber-reactive derivatives of *O,O*-diethyl *O*-[4-[(2-hydroxyethyl)thio]phenyl] phosphorothionate were applied to the surface of the wool fibers from acetone solution, i.e., under conditions that did not promote reaction with the wool, they displayed similar levels of insecticidal activity when considered on an equimolar basis (Table II). However, when reaction between the insecticide and the wool was induced by application from a boiling dye bath, the effectiveness of the covalently bound insecticides depended on the accessibility of the active form of the insecticide to the target insect. It was necessary for the insect to digest some of the wool so that the insecticide could be cleaved from the wool in the insect's gut. This release of active insecticide is thought to occur by either simple alkaline hydrolysis or enzyme-catalyzed hydrolysis of the labile bond linking the fiber-reactive and insecticidal portions of the molecules. The ease with which this hydrolysis occurs will depend on the environment of the labile bond as well as on its strength and chemical nature. For example, in synthetic polymer–pesticide systems designed for the controlled release of pesticides by the cleavage of a carboxylic ester bond, it has been found that hydrophilic groups are required to be present for hydrolytic release to occur (Harris, 1980). There is also evidence that with enzyme-catalyzed hydrolysis the hydrophilicity of the system is more important than the bonding energy in determining the overall rate of release

Table II. Insecticidal Activity of Fiber-Reactive Compounds before and after Reaction with Wool

compd no.	min concn, μmol/g of wool, to control feeding damage due to			
	A. flavipes		*T. bisselliella*	
	unbound[a]	bound[b]	unbound[a]	bound[b]
1	0.5	0.5	0.8	1.2
2	0.8	0.9	1.6	1.7
3	0.7	0.8	1.6	1.6
4	0.7	0.8	1.5	1.6
5	0.7	0.8	1.4	1.5
6	0.6	0.7	1.4	1.4
7	0.6	0.7	1.4	1.5
8	0.6	0.7	1.4	1.5
9	0.6	15.0	1.4	5.0
10	0.7	2.8	1.6	3.6
11	0.6	1.9	1.5	3.2
12	0.7	1.2	1.4	3.0
13	0.5	1.9	1.2	2.7
14	0.6	6.2	1.3	3.7
15	0.6	4.8	1.5	9.1
16[c]	0.6		1.7	
17	0.8	10.0	1.7	10.6
18[c]	0.6		1.5	
19	>3.0		>3.0	

[a] Applied from acetone. [b] Amount present on wool after application in a dyebath and removal of unbound material by Soxhlet extraction. [c] Due to low fixation the insecticidal activity of these compounds when bound to the wool could not be determined.

Table III. Extent of Reaction of the Fiber-Reactive Compounds with Wool and Their Hydrolytic Stability on Wool

compd no.	max fixation, %	$t_{1/2}$, h, on wool in dyebath at 100 °C, pH 5.0
1	51	3.11
2	25	3.00
3	67	3.74
4	65	3.91
5	69	3.81
6	63	3.92
7	74	3.95
8	78	3.96
9	82	7.9
10	25	9.3
11	20	8.1
12	82	12.4
13	72	14.3
14	20	
15	48	6.9
16	7	
17	68	9.56
18	3	

(Wilkins, 1976). Another aspect that exerts considerably influence over the rate of release of pesticides is the cross-link density of the polymer, in that the polymer–pesticide ester bond is rendered less susceptible to hydrolysis with increasing cross-link density in the polymer (Harris, 1980).

It might be expected that different fiber-reactive groups would react at different sites on the protein chains in wool and thus exhibit differing rates of release in the insect gut (Table II). Compounds containing halogenated heterocyclic fiber-reactive groups, when bound to the wool, were required to be present at much higher levels to render the wool resistant to insect damage (Table II). These compounds, when bound to the wool, also exhibited a high degree of hydrolytic stability when wool treated with these fiber-reactive compounds was held for extended times in

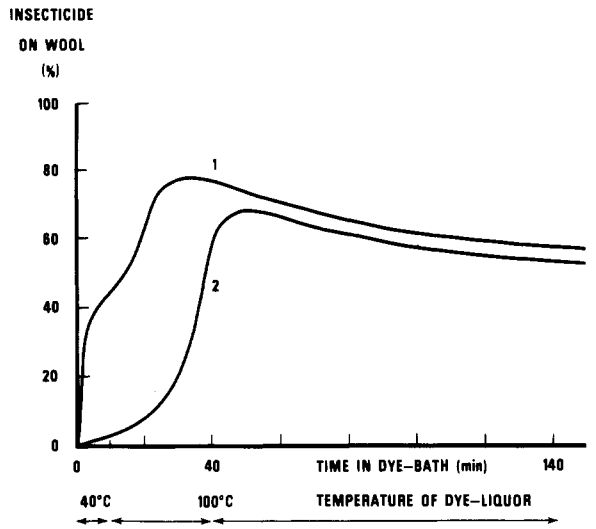
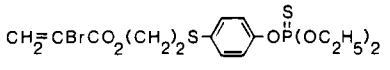


Figure 1. Application of compound **5** to wool from a dyebath. (1) Percent of applied insecticide found on wool. (2) Percent of applied insecticide found on wool after removal of unbound insecticide by Soxhlet extraction.

the boiling acidic bath (Table III). As the halogenated heterocyclic fiber-reactive groups used in this study were difunctional, and therefore potentially capable of forming cross-links in the wool, it is probable that the observed increases in hydrolytic stability of the labile bond between the fiber-reactive group and the insecticide were due to the cross-linking of the wool's polymer chains in the immediate vicinity of this bond.

Insecticides are usually applied to wool during dyeing to minimize application costs. Therefore, a fiber-reactive insecticide must possess sufficient hydrolytic stability to remain substantially intact when applied from a boiling acidic dyebath. Once these compounds have chemically combined with the wool fiber, hydrolysis of both the labile bond and the phosphorus ester group is significantly retarded. For example, emulsions of compounds **1**, **5**, **8**, **9**, and **12** have half-lives of 1.41, 1.75, 2.08, 0.26, and 0.31 h at 100 °C, pH 5, but when reacted with the wool the corresponding half-lives for the loss of the active phosphorus esters from the wool are 3.11, 3.81, 3.96, 7.90, and 12.42 h. Therefore, to avoid hydrolysis in the dyebath it is desirable that the fiber-reactive groups react rapidly with the wool. This requirement is in contrast to that of fiber-reactive dyes, where sufficient time is required for the dye to evenly penetrate the wool fiber before it is irreversibly bound to the wool. Therefore, fiber-reactive groups that are most suitable for wool dyes are not necessarily the most suitable for a fiber-reactive insecticide.

When the fiber-reactive compounds (i.e., compound **5**)



used in the present study were applied to wool under typical dyeing conditions, maximum reaction with the wool (Table III) had occurred by the time the dyebath reached the boil (Figure 1). In practice the dye bath may be held at the boil for 1–2 h to obtain an even distribution of the dye throughout the wool fibers or to facilitate the addition of any dyestuff required for color matching. Under these conditions some hydrolysis of both the phosphorus ester group and the labile bond between the fiber-reactive group and the insecticidal group occurs. The sum of this hydrolysis followed first-order kinetics, and the corresponding half-lives are given in Table III.

Compounds **12** and **13** exhibited the highest degree of reaction with the wool coupled with the greatest degree of hydrolytic stability on the wool. However, once the *O,O*-diethyl *O*-[4-[(2-hydroxyethyl)thio]phenyl] phosphorothionate had been bound to the wool by these fiber-reactive groups, the insecticidal activity was decreased, presumably because the target insects were unable to readily cleave the insecticidal portion of the molecule from the wool. Therefore, these compounds were not as effective as the less hydrolytically stable compounds **3**–**8** in which the insecticidal portion of the molecule was more accessible to the insects. Of these, the compounds containing the vinyl sulfone (compound **8**) or 2-chloroethyl sulfone (compound **7**) as the reactive group gave the highest degree of fixation to the wool.

CONCLUSIONS

Only compounds attached to the fiber by monofunctional fiber-reactive groups were readily accessible to the larvae of keratin-digesting insects. Polyfunctional fiber-reactive groups were thought to cross-link the protein chains, thus rendering the labile bond between the fiber-reactive group and the insecticide resistant to hydrolysis in the insect gut.

So that hydrolysis during application in the dye bath could be minimized, the fiber-reactive compound must exhaust readily onto the wool and react rapidly. The fiber-reactive group that best met these requirements was the 3-(vinylsulfonyl)propionate ester or its precursor, the 3-[(2-chloroethyl)sulfonyl]propionate ester.

ACKNOWLEDGMENT

I thank C. R. Nunn for technical assistance.

Registry No. **1**, 70491-79-1; **2**, 84009-59-6; **3**, 70307-86-7; **4**, 70307-87-8; **5**, 70307-82-3; **6**, 84009-60-9; **7**, 70307-88-9; **8**, 70307-89-0; **9**, 84009-61-0; **10**, 70307-27-6; **11**, 84009-62-1; **12**, 84009-63-2; **13**, 84009-64-3; **14**, 84009-65-4; **15**, 84009-66-5; **16**, 84009-67-6; **17**, 84009-68-7; **18**, 84009-69-8; **19**, 84009-70-1; 2,4-dichloro-6-[*N*-[2-(chloroformyl)ethyl]-*N*-ethylamino]-*s*-triazine, 84009-71-2; 2,4-dichloro-6-[bis[2-(chloroformyl)ethyl]amino]-*s*-triazine, 84009-72-3; *S*-chloro-4-[[2-(chloroformyl)ethyl]-amino]-2,6-difluoropyrimidine, 84009-73-4.

Supplementary Material Available: A tabulation of the ^1H NMR spectra and microanalysis data of the organophosphorus esters (5 pages). Ordering information is given on any current masthead page.

LITERATURE CITED

Adamson, D. W. *J. Chem. Soc. Suppl.* **1949**, *No. 1*, 144–155.
American Association of Textile Chemists and Colorists *AATCC Techn. Man.* **1979**, *55*, 307–311.
Bayer British Patent 1 157 948, 1969.
Distler, H.; Brauns, H. A. French Patent 1 363 046, 1964.
Geigy French Patent 1 193 734, 1959.
Geigy British Patent 1 182 086, 1970.
Harris, F. W. "Controlled Release Technologies: Method, Theory and Applications"; Kydonieus, A. F., Ed.; CRC Press: Boca Raton, FL, 1980; Vol. II, p 73.
Hensel, H. R.; Baumann, H.; Tartler, A.; Weissauer, H. U.S. Patent 3 108 103, 1963.
Jones, F. W. *J. Agric. Food Chem.* **1983**, first paper of three in this issue.
Jones, F. W.; Mayfield, R. J.; O'Loughlin, G. J. *Pestic. Sci.* **1982**, in press.
Lewis, D. M. *Wool Sci. Rev.* **1974**, *49*, 13–31.
Marvel, C. S.; Dec, J.; Cooke, H. G., Jr.; Cowan, J. C. *J. Am. Chem. Soc.* **1940**, *62*, 3495–3498.
Siegel, E.; Sasse, K. Belgium Patent 613 586, 1961.
Wilkins, R. M. *Proc.—Int. Controlled Release Pestic. Symp., 1976* **1976**, 7.

Received for review March 22, 1982. Accepted October 18, 1982.