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ARTICLES

Fiber-Reactive Insecticides for Wool: Organophosphorus Esters of Nitrogen Heterocycles

F. William Jones

O,O-Diethyl phosphorothionate esters and *O*-ethyl *S-n*-propyl phosphorothiolothionate esters of some pyridazine and 1,2,4-triazole compounds containing a 2-bromoacryloyl ester substituent have been synthesized and screened for insecticidal activity against the wool-digesting insects *Tineola bisselliella* and *Anthrenus flavipes*. These compounds were found to be hydrolytically unstable when applied to wool from a boiling acidic dye bath. The extent of this hydrolysis has been determined by the development of a method for estimating organophosphorus esters that are covalently bound to the wool.

Recently it has been demonstrated that the suitability of organophosphorus insecticides for protecting wool against insect damage can be improved if they contain a 2-bromoacryloyl ester substituent (Jones et al., 1982). This group was thought to covalently bond these insecticides to the wool so that the resistance to insect damage obtained was retained when the treated wool was washed, dry-cleaned, or exposed to light. In this earlier study the insecticidal properties of a number of different fiber-reactive organophosphorus compounds were evaluated, and the most active compounds found were *O,O*-diethyl *O*-[6-[[2-[(2-bromoacryloyl)oxy]ethyl]thio]-3-pyridazinyl] phosphorothionate and *O,O*-diethyl *O*-[1-[[(2-bromoacryloyl)oxy]methyl]-1,6-dihydro-6-oxo-3-pyridazinyl] phosphorothionate. Although these compounds displayed some promise as durable insecticides for wool, it was thought (Jones et al., 1982) that a significant degree of hydrolysis of the phosphorus ester group occurred when they were applied to wool from an acidic dyebath. Because the insecticide could not be extracted from the wool, the amount present was not determined but was inferred by the degree of feeding damage that occurred when wool treated at different levels was bioassayed against the larvae of *Tineola bisselliella* and *Anthrenus flavipes*.

In recent patent literature (Hoffman et al., 1974, 1975; Bohner et al., 1974; Riebel et al., 1976; Hofer et al., 1976a,b) it has been claimed that when the *O,O*-diethyl phosphorothionate group in a nitrogen heterocycle insecticide is replaced with a *O*-ethyl *S-n*-propyl phosphorothiolo-

thionate group, insecticidal activity against a broad spectrum of insects was increased substantially. These phosphorodithioate esters would also be expected to possess better hydrolytic stability than the corresponding diethyl phosphorothionate esters.

In the present study, *O,O*-diethyl phosphorothionate esters and *O*-ethyl *S-n*-propyl phosphorothiolothionate esters of some pyridazines and triazoles that contain a 2-bromoacryloyl substituent have been prepared and applied to wool during dyeing. The rate of hydrolysis during application to wool both in the dye–liquor and on the wool has been measured to assess the suitability of fiber-reactive organophosphorus esters based on nitrogen heterocycles for protecting wool against insect damage.
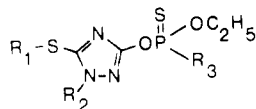
MATERIALS AND METHODS

Preparation of Phosphorus Esters. The compounds used in this study (Tables I and II) and their intermediates were prepared as described below. Where necessary they were purified by liquid chromatography on a Waters Associates Prep LC System 500 using silica gel as the adsorbent and a mixture of ethyl acetate and hexane as the eluting solvent. The compounds were obtained as oils and were characterized by proton nuclear resonance spectrometry (60 Hz) and by microanalysis. A tabulation of the ¹H NMR spectra and microanalysis data is provided as supplementary material (see paragraph at the end of paper regarding supplementary material).

O,O-Diethyl *O*-[1-[[(2-bromoacryloyl)oxy]methyl]-6-oxo-3-pyridazinyl] phosphorothionate (compound 9) and *O,O*-diethyl *O*-[6-[[2-[(2-bromoacryloyl)oxy]ethyl]thio]-3-pyridazinyl] phosphorothionate (compound 11) were prepared as described previously (Jones et al., 1982). The
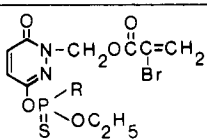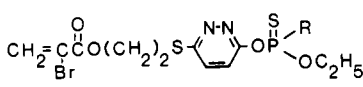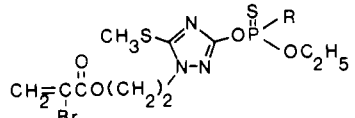
CSIRO Division of Textile Industry, Belmont, Victoria 3216, Australia.

Table I. Insecticidal Activity of Organophosphorus Esters of Some 1,2,4-Triazoles

(structure: $R_1\text{-S}$ on triazole ring, R'_2 on N, ring-O-P(=S)(OC$_2$H$_5$)R_3)

				min level, mg/g of wool, required to inhibit feeding damage due to	
compd no.	R$_1$	R$_2$	R$_3$	A. flavipes	T. bisselliella
1	HO(CH$_2$)$_2$-	(CH$_3$)$_2$CH-	C$_2$H$_5$O-	0.7	1.0
2	HO(CH$_2$)$_2$-	(CH$_3$)$_2$CH-	n-C$_3$H$_7$S-	0.4	1.5
3	HO(CH$_2$)$_2$-	C$_6$H$_5$-	C$_2$H$_5$O-	0.3	2.0
4	HO(CH$_2$)$_2$-	C$_6$H$_5$-	n-C$_3$H$_7$S-	0.1	2.5
5	CH$_3$-	HO(CH$_2$)$_2$-	C$_2$H$_5$O-	0.1	0.05
6	CH$_3$-	HO(CH$_2$)$_2$-	n-C$_3$H$_7$S-	0.2	0.08
7	NCCH$_2$-	HO(CH$_2$)$_2$-	C$_2$H$_5$O-	0.8	0.2
8	NCCH$_2$-	HO(CH$_2$)$_2$-	n-C$_3$H$_7$S-	0.1	0.4

Table II. Fibre-Reactive Esters and Their Insecticidal Activity

			min level, mg/g of wool, required to inhibit feeding damage due to	
compd	R	compd no.	A. flavipes	T. bisselliella
(pyridazinone N-CH$_2$OC(=O)C(Br)=CH$_2$, O-P(=S)(R)(OC$_2$H$_5$))	C$_2$H$_5$O-	9	0.05	0.06
	n-C$_3$H$_7$S-	10	0.07	0.1
(CH$_2$=C(Br)CO(CH$_2$)$_2$S-triazole-O-P(=S)(R)(OC$_2$H$_5$))	C$_2$H$_5$O-	11	0.02	0.07
	n-C$_3$H$_7$S-	12	0.1	0.1
(CH$_3$S-triazole-O-P(=S)(R)(OC$_2$H$_5$), N-(CH$_2$)$_2$OC(=O)C(Br)=CH$_2$)	C$_2$H$_5$O-	13	0.2	0.05
	n-C$_3$H$_7$S-	14	0.3	0.1

corresponding O-ethyl S-n-propyl phosphorothiolothionate esters (compounds 10 and 12) were prepared by an analogous method.

Preparation of Intermediates. 5-[(2-Hydroxyethyl)-thio]-3-hydroxy-1-isopropyl-1,2,4-triazole was prepared by alkylating 1-isopropyl-3-oxo-5-thioxo-1,2,4-triazolidine (Hoffman et al., 1974) with 2-chloroethanol in methanol in the presence of NaOMe (mp 118–119 °C, from ethyl acetate; 87%).

5-[(2-Hydroxyethyl)thio]-3-hydroxy-1-phenyl-1,2,4-triazole was prepared by alkylating 3-oxo-1-phenyl-5-thioxo-1,2,4-triazolidine (Hoffman et al., 1975) with 2-chloroethanol in aqueous NaOH (mp 218–219 °C, from ethanol; 92%).

1-(2-Hydroxyethyl)-3-hydroxy-5-(methylthio)-1,2,4-triazole was prepared by alkylating 1-(2-hydroxyethyl)-3-oxo-5-thioxo-1,2,4-triazolidine [prepared by the method of Hoffman et al. (1975) (mp 188–190 °C, 78%)] with methyl iodide in alcoholic NaOH (mp 196–197 °C, from ethanol; 73%).

5-[(Cyanomethyl)thio]-1-(2-hydroxyethyl)-3-hydroxy-1,2,4-triazole was prepared by alkylating 1-(2-hydroxyethyl)-3-oxo-5-thioxo-1,2,4-triazolidine with chloroacetonitrile in methanolic NaOMe (mp 120–121 °C, from ethanol–ethyl acetate; 70%).

Phosphorylation of Nitrogen Heterocycles. The following general method was used: The appropriate hydroxy nitrogen heterocycle (0.05 mol) was converted to its sodio salt by the action of NaH (1.2 g) suspended in anhydrous dimethylformamide (30 mL). The resulting so-

lution was cooled to −5 °C and either diethyl phosphorochloridothionate (9.5 g) or O-ethyl S-n-propyl phosphorochloridothiolothionate (Kishino et al., 1976) (11 g) added over 60 min. The mixture was stirred at 0 °C for 3 h and then at 20 °C overnight. The reaction mixture was then diluted with toluene (180 mL), washed successively with water (2 × 100 mL) and aqueous Na$_2$CO$_3$ (1 M, 2 × 100 mL), and dried over MgSO$_4$, and the solvent was removed in vacuo.

Preparation of 2-Bromoacryloyl Esters. These were prepared by reacting 2,3-dibromopropionyl chloride with the appropriate hydroxy organophosphorus ester in anhydrous toluene in the presence of 2 molar equiv of triethylamine.

Insect Testing. Insecticides were applied to wool fabric from an acetone solution and air-dried to produce known deposits of insecticide on the wool. These fabrics were assayed against 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). By this standard, wool is considered insect resistant if the feeding damage does not exceed 8 mg, provided that the feeding damage of an untreated control is 30 mg or more.

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 30 ethylene oxide units (Teric N30,

ICI) (0.008 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. The insecticide was applied to wool from an Ahiba Turbomat laboratory dyeing machine. The fabric package (25 g) 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 Organophosphorus Esters on Wool. The O,O-diethyl phosphorothionate esters were converted to O,O-diethyl S-methyl phosphorothiolate by either of the following two methods and determined by gas chromatography on an automated Varian 3700 series gas chromatograph fitted with a phosphorus-specific flame photometric detector and a nickel column (1.5 m, 3.17-mm i.d.) packed with Gas-Chrom Q (80–100 mesh) coated with OV-17 (3%).

Method A. Duplicate samples of wool (0.200 g) were dissolved in aqueous NaOH (2.5 M, 4 mL) at 70 °C for 20 min. The mixture was cooled, neutralized with H_2SO_4 (1 M, 5 mL), buffered with $Na_2B_4O_7 \cdot 10H_2O$ (2 g), treated with excess dimethyl sulfate (0.1 g), and shaken vigorously. After 30 min the O,O-diethyl S-methyl phosphorothiolate was extracted into toluene [2.5 mL, containing O,O-diethyl O-phenyl phosphate (0.01 g L^{-1}) as the internal standard] and determined by gas chromatography.

Method B. Duplicate samples of wool (0.200 g) were dissolved in aqueous NaOH (2.5 M, 4 mL) at 70 °C for 20 min. The mixture was cooled and acidified with HCl (10 M, 1.5 mL) and NaCl (2 g), and a mixture of diethyl ether and dichloromethane (1:1, 3 mL), containing O,O-diethyl O-phenyl phosphate (0.01 g L^{-1}) as the internal standard, was added. The mixture was agitated vigorously and centrifuged, and an aliquot (2 mL) was treated with excess ethereal diazomethane (0.25 M, 0.5 mL). The resulting O,O-diethyl S-methyl phosphorothiolate was determined by gas chromatography.

For both methods the amount of O,O-diethyl phosphorothionate present on the wool was estimated by comparison with the simultaneous analysis of samples of wool to which known amounts of the same compound had been applied dropwise from acetone.

Similarly, O-ethyl S-n-propyl phosphorothiolothionates were converted to O-ethyl S-methyl S-n-propyl phosphorodithiolate and determined by gas chromatography using O,O-di-n-propyl O-phenyl phosphate as the internal standard.

Hydrolysis of Organophosphorus Esters in Dyebath Liquors. The organophosphorus ester (0.01 g) was dissolved in a solution of an ethoxylated nonylphenol containing 30 ethylene oxide units (Teric N30, ICI) (0.008 g) and calcium dodecylbenzenesulfonate (Alkanate CS, ICI) (0.017 g) in xylene (0.5 mL). This solution was added with vigorous stirring to an aqueous solution (500 mL) of acetic acid (0.25 g) and $(NH_4)_2SO_4$ (1 g) at 98 °C in a beaker of an Ahiba Turbomat laboratory dyeing apparatus. The beaker was sealed and the temperature raised to 100 °C. Liquor samples (20 mL) were withdrawn at regular intervals, cooled to 0 °C, and saturated with NaCl. NaHCO$_3$ (0.1 g) was added and the solution extracted with a mixture of dichloromethane and heptane [1:1, 5 mL, containing N-benzoyl-2-methylaniline (0.02 g L^{-1}) as the internal standard]. The organophosphorus ester was then

determined by HPLC on a column (25 cm × 4.6 mm i.d.) packed with LiChrosorb Si60 (10 μm) using a running solvent mixture of heptane, dichloromethane, and isobutyl alcohol (500:500:1).

RESULTS AND DISCUSSION

Insecticidal Activity. A number of new phosphorus esters of 1,2,4-triazoles containing a hydroxyethyl substituent were prepared and screened for insecticidal activity against *T. bisselliella* and *A. flavipes* (Table I). The most insecticidally active compound was the diethyl phosphorothionate, 5. The corresponding O-ethyl S-n-propyl phosphorothiolothionate was slightly less active. When the hydroxyethyl group of these compounds was esterified, the slight decrease in insecticidal activity observed (Table II) could be attributed to the higher molecular weight of the respective 2-bromoacryloyl esters.

Replacing an ethoxy group in the two pyridazinyl diethyl phosphorothionate esters (compounds 11 and 13) with an n-propylmercapto group (compounds 12 and 14) also failed to improve their insecticidal activity (Table II).

Analysis of Organophosphorus Esters Covalently Bound to Wool. Because the organophosphorus esters used in this study are capable of forming covalent bonds with wool, analytical procedures relying on solvent extraction of the insecticide (Williams, 1966; Hoskinson and Russell, 1973; Duffield, 1977) were not suitable. A method involving chemical derivatization of the phosphorus ester has been described for compounds that cannot be readily determined directly by gas chromatography (St. John and Lisk, 1968; Shafik et al., 1971). This method was adapted and used in the present study.

Sodium diethyl thiophosphate or sodium O-ethyl S-n-propyl dithiophosphate, produced when the treated wool was hydrolyzed in dilute alkali, was methylated by dimethyl sulfate and the products were extracted into toluene and determined by gas chromatography. The use of diazomethane to methylate the partial phosphorus esters resulted in higher yields of the methylated products but did not increase the accuracy of the method significantly and, as this procedure was more complex, the use of dimethyl sulfate was favored.

The yield of methylated esters by these procedures depends on the original phosphorus ester (Shafik et al., 1971). Therefore, calibration standards were prepared by analyzing wool to which known amounts of the appropriate phosphorus ester had been applied from acetone solution.

Before the amount of insecticide covalently bound to the wool could be determined, it was necessary to remove any of the phosphorus ester that was only physically attached to the wool or which had been cleaved from the fiber-reactive portion of the molecule by hydrolysis during application. This was achieved by Soxhlet extraction using an azeotropic mixture of solvents such that one component was a good solvent for the insecticide and the other swelled the wool. The most satisfactory solvent system was found to be an azeotropic mixture of dichloromethane, methanol, and water (92:6:2) which completely removed O,O-diethyl O-[6-[(2-hydroxyethyl)thio]-3-pyridazinyl] phosphorothionate (compound 15), an organophosphorus ester containing no fiber-reactive group, and reduced the level of a fiber-reactive insecticide (compound 11) to a constant value in three to four siphon cycles (Table III).

Hydrolysis of Fiber-Reactive Esters. The hydrolysis of the fiber-reactive esters in the dye bath followed first-order kinetics, and the appropriate half-lives are given in Table IV. As might be expected (Harris, 1980; Hartmann and Stengel, 1980), these compounds were appreciably more susceptible to hydrolysis in the dyebath liquor than

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Table III. Soxhlet Extraction of Wool[a] Treated with Organophosphorus Esters

no. of siphon cycles of CH_2Cl_2-MeOH-H_2O azeotrope	amount of organophosphorus compd[b] on wool, mg/g	
	11	15
0	0.44	0.31
1	0.41	0.18
2	0.39	0.12
3	0.38	0.01
4	0.38	<0.01
5	0.38	
6	0.37	
10	0.38	

[a] 4 g of wool was extracted in a Soxhlet extractor with a siphon volume of 60 mL. [b] The organophosphorus esters (1 mg/g of wool) were applied from a dyebath, pH 5.5, 100 °C, for 10 min.

Table IV. Hydrolysis of Fiber-Reactive Organophosphorus Esters in the Dyebath at 100 °C, pH 5.5

compd no.	max degree of re-action with wool, %	half-life, min, of phosphorus esters in the dyebath	
		in absence of wool	after reaction with wool
9	28	17.8	48.2
10	49	48.1	61.5
11	41	26.6	72.1
12	68	38.3	98.7
13	45	22.1	65.2
14	70	41.0	82.1
15		28.2	
16		41.3	

after they had reacted with the wool. The *O*-ethyl *S-n*-propyl phosphorothiolothionate esters were more hydrolytically stable than the *O,O*-diethyl phosphorothionate esters.

The half-lives for the hydrolysis of the compounds *O,O*-diethyl *O*-[6-[(2-hydroxyethyl)thio]-3-pyridazinyl] phosphorothionate (compound 15) and *O*-ethyl *S-n*-propyl *O*-[6-[(2-hydroxyethyl)thio]-3-pyridazinyl] phosphorothiolothionate (compound 16) in the absence of wool (Table IV) were only slightly greater than those for the corresponding 2-bromoacryloyl esters (compounds 11 and 12). From these results it may be concluded that the hydrolysis of the carboxylic ester bond in the fiber-reactive compounds, 13 and 14, did not contribute greatly to the overall rate of hydrolysis of these compounds.

The much higher rate of hydrolysis of compound 9 (Table IV), both in the dyebath and on the wool, was thought to be due to the inductive effects of the neighboring pyridazone ring on the rate of hydrolysis of the carboxylic ester group (Jones et al., 1982). The rate of hydrolysis of this carboxylic ester bond in compounds 9 and 10 was shown to contribute significantly to the overall rate of hydrolysis of these compounds by the detection of either *O,O*-diethyl *O*-(1,6-dihydro-6-oxo-3-pyridazinyl) phosphorothionate or *O*-ethyl *S-n*-propyl *O*-(1,6-dihydro-6-oxo-3-pyridazinyl) phosphorothiolothionate by HPCL during the analysis of dyebath liquors. These compounds were presumably formed by hydrolysis of the carboxylic ester bond followed by loss of the hydroxymethyl group as formaldehyde.

Acid catalysis of the hydrolysis of phosphorus esters of nitrogen heterocycles having the partial structure P—
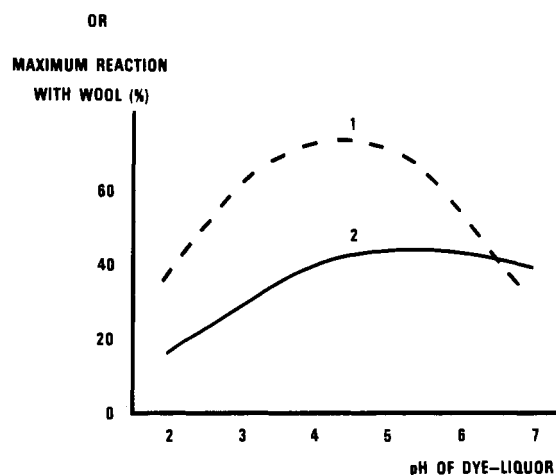

Figure 1. The effect of pH of the dyebath on the application of compound 13 to wool at 100 °C. (1) Half-life (minutes) for hydrolysis of the phosphorus ester (13) when it is bound to the wool. (2) Maximum degree of reaction of compound 13 with the wool as the percent of the compound added to the dyebath.
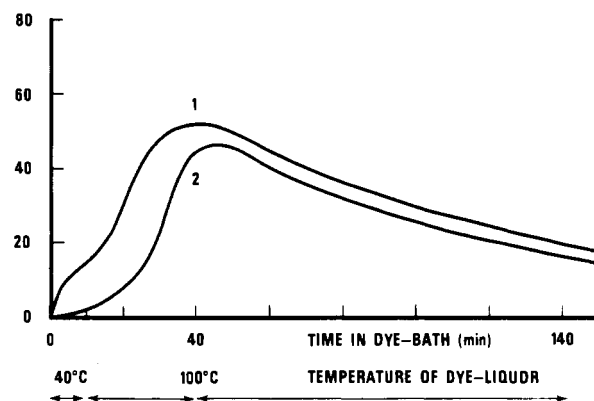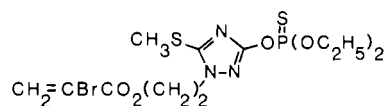

Figure 2. Application of compound 13 to wool in a dyebath at 100 °C, pH 5.5. (1) Total amount of phosphorus ester on the wool as the percent of 13 added to the dyebath. (2) Amount of phosphorus ester on the wool after Soxhlet extraction as the percent of 13 added to the dyebath.

O—C=N has been observed (Gomaa et al., 1969; Schmidt, 1972) and is thought to be due to protonation on the nitrogen atom on the heterocyclic ring (Eto, 1974). Insecticides are generally applied to wool during dyeing where the pH of the dye-liquor may range from 2.5 to 6.5, depending on the class of dye used. When the fiber-reactive triazole, 13, was applied under a range of different pHs

(Figure 1), it exhibited the greatest degree of hydrolytic stability on the wool at pH 4.5. At lower pHs there was a marked decrease in the amount of insecticide bound to the wool as well as an increase in the rate of hydrolysis of the compound on the wool. At higher pHs there was little change in the maximum degree of fixation to the wool, but there was a marked increase in the rate of hydrolysis of the compound after it had reacted with the wool. At pH

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.

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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.

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 ¹H NMR spectra and mi-

CSIRO Division of Textile Industry, Belmont, Victoria 3216, Australia.