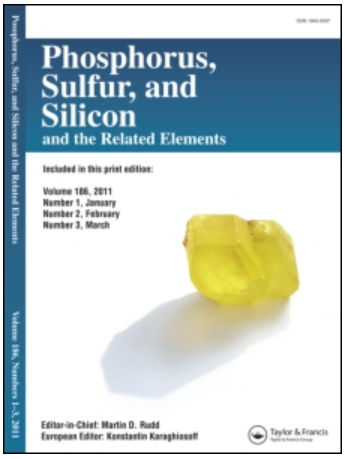


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# PRODUCTS OF THE ALKALINE HYDROLYSIS OF S-CHLOROMETHYL AND S-(*N*-ETHOXYCARBONYL-*N*-METHYLCARBAMOYLMETHYL) *O,O*-DIETHYL PHOSPHORODITHIOATE

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## *Communication*

# PRODUCTS OF THE ALKALINE HYDROLYSIS OF *S*-CHLOROMETHYL AND *S*-(*N*-ETHOXYCARBONYL-*N*-METHYLCARBAMOYLMETHYL) *O,O*-DIETHYL PHOSPHORODITHIOATE

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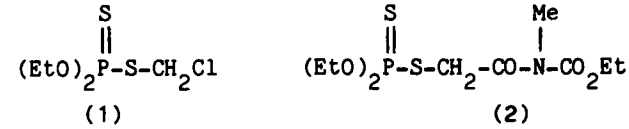
The alkaline hydrolysis of *S*-chloromethyl *O,O*-diethyl phosphorodithioate (chlormephos) and of *S*-(*N*-ethoxycarbonyl-*N*-methylcarbamoylmethyl) *O,O*-diethyl phosphorodithioate (mecarbam) may involve attack by hydroxide ion at phosphorus with phosphorus-sulfur cleavage, at the substituted *S*-methyl carbon atom with sulfur-carbon cleavage or, in the case of mecarbam, at the carbonyl carbon atom with carbonyl-nitrogen cleavage. Further reaction of the initially-formed *O,O*-diethyl hydrogen phosphorodithioate with chlormephos may lead to the formation of additional products.

*Key words:* Chlormephos; mecarbam; phosphorodithioates; alkaline hydrolysis; g.c.-m.s. data for hydrolysis products.

A knowledge of the products that may be formed from pesticidal compounds under a variety of conditions is of significance with respect to environmental safety. During studies of the alkaline hydrolysis of *S*-chloromethyl *O,O*-diethyl phosphorodithioate (chlormephos, **1**)[1] and *S*-(*N*-ethoxycarbonyl-*N*-methylcarbamoylmethyl) *O,O*-diethyl phosphorodithioate (mecarbam, **2**),[2,3] we have found that nucleophilic attack may occur initially at (a) the phosphorus atom, with phosphorus-sulfur cleavage to give *O,O*-diethyl phosphorothioate (**3**), (b) the substituted *S*-methyl carbon atom, with sulfur-carbon cleavage to give *O,O*-diethyl hydrogen phosphorodithioate (**4**)[4,5] and (c), in the case of mecarbam, at the carbamoyl carbon atom, with carbonyl-nitrogen cleavage to give *S*-carboxymethyl *O,O*-diethyl phosphorodithioate (**5**) and ethyl *N*-methylcarbamate (**6**) (Scheme I). Initial hydrolysis of the carbethoxy group of mecarbam was not observed.

In view of the low aqueous solubility of the phosphorodithioates under investigation, the hydrolyses were carried out in a two-phase system of hexane-water with vigorous shaking. Under these conditions, the *O,O*-diethyl hydrogen phos-



(1) (2)

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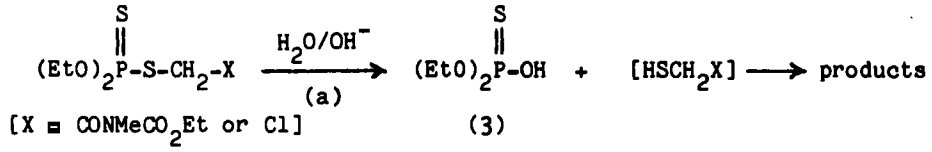
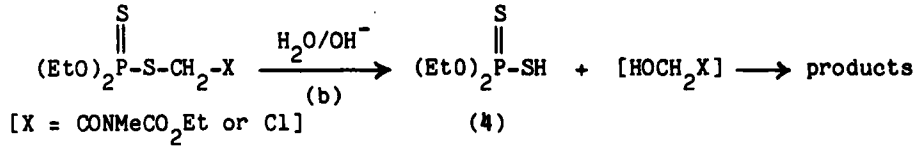
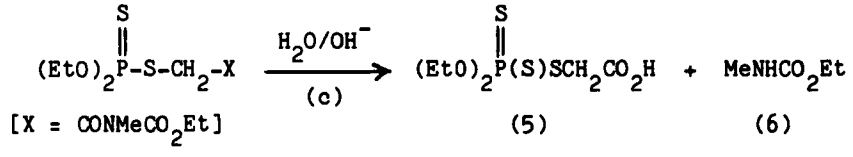
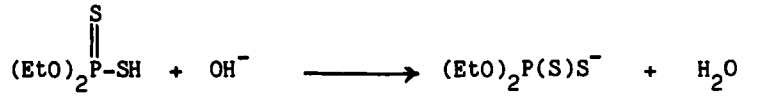
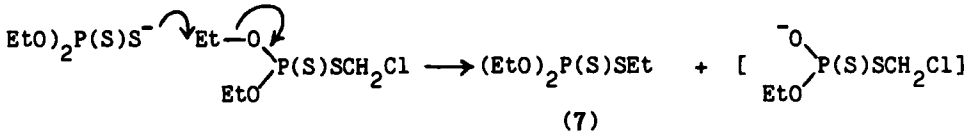


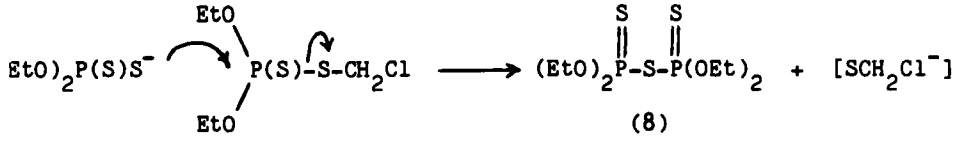



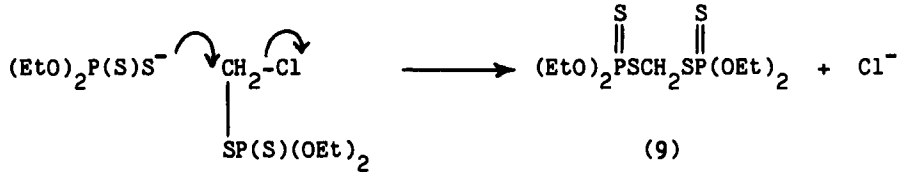




SCHEME I




SCHEME II

TABLE I

G.C.-M.S. data for hydrolysis products of chlormephos[a]

| $t_R$ (min:sec) | ion current (% intensity) | assignment | m/z (%) |
|---|---|---|---|
| 2:70 | 22 | $(EtO)_2P(S)SMe$[b]<br>$(EtO)_2P(O)SEt$[b] | 200($M^+$, 5), 172(10)<br>198($M^+$, 100), 170(15), 143(20), 121(90), 93(80), 81(40), 65(85), 41(18) |
| 5:40 | 18 | $(EtO)_2P(S)SEt$ | 214($M^+$, 20), 186(100), 158(10), 121(70), 97(70), 81(10), 65(65), 40(38) |
| 7:10 | 100 | $(EtO)_2P(S)SCH_2Cl$[c] | 236, 234($M^+$, 18, 35), 189(2), 188(2), 154(45), 121(55), 97(100), 81(10), 65(45), 47(38) |
| 12:58 | 25 | $[(EtO)_2P(S)]_2S$ | 338($M^+$, 25), 261(18), 207(1), 186(10), 153(20), 121(80), 97(100), 80(2), 65(80), 47(10) |
| 16:37 | 100 | $[(EtO)_2P(S)S]_2CH_2$ | 384($M^+$, 2), 261(1), 231(80), 199(10), 175(8), 153(70), 125(50), 109(2), 97(100), 79(2), 65(55), 45(22) |

[a]Methylated in the case of **4**.

[b]Eluting as one peak. The *S*-ethyl ester is presumably formed by transethylation of the phosphorothioate (**3**) in a similar manner to that shown for the phosphorodithioate (**4**) in Scheme II.

[c]Chlormephos (**1**) by direct insertion (20°C) gave: m/z 236, 234($M^+$20,47), 199(2), 188(5), 161(7), 154(54), 153(15), 144(6), 141(5), 129(10), 126(8), 125(26), 121(93), 115(7), 113(8), 109(11), 98(5), 97(100), 81(9), 80(6), 65(27), 63(5).



phorodithioate that was formed from chlormephos by sulfur-carbon cleavage was capable of reacting further with unchanged chlormephos to yield three additional products (Scheme II): transethylation gave *O,O,S*-triethyl phosphorodithioate (**7**), attack at phosphorus gave *O,O,O,O*-tetraethyl trithiopyrophosphate (**8**) and attack at the chloromethyl carbon atom gave bis(diethoxyphosphinothioylthio)methane (ethion, **9**).[6] The absence of *O,O*-diethyl hydrogen phosphorodithioate (**4**) and of corresponding secondary reaction products in the case of mecarbam is presumably due to faster initial reaction by hydroxide ion at the phosphorus or carbonyl centres. Under less strongly alkaline conditions, sulfur-carbon cleavage had, however, been seen to be the principal mode of decomposition.[5] Reaction products were identified by g.c.-m.s.[7-9] after treatment with diazomethane to convert acidic compounds to their methyl derivatives. The assignments shown in Tables I and II are based on the observed molecular ions and fragmentation patterns.[10-11]

## EXPERIMENTAL

Analytically pure samples of chlormephos and of mecarbam were separately subjected to vigorous shaking with aqueous potassium hydroxide (3 ml, 0.5 M) and hexane (5 ml) as follows: chlormephos (0.22 g, 1 h); mecarbam (sample A, 0.15 g, 1 h; sample B, 0.21 g, 2 h). The final solutions were acidified with an excess of hydrochloric acid and shaken to allow organic materials to dissolve in the hexane layer. The contents of the latter were methylated by reaction with diazomethane derived by the alkaline

TABLE II

G.C.-M.S. data for hydrolysis products (A) of mercarbam[a]

| $t_R$ (min:sec) | ion current (% intensity) | assignment | m/z (%) |
|---|---|---|---|
| 12:57 | 25 | $(EtO)_2P(O)SMe$ | 184($M^+$, 18), 156(18), 139(45), 128(35), 111(80), 93(60), 81(95), 65(50), 47(100) |
| 16:39 | 100 | $(EtO)_2P(S)SCH_2CO_2Me$ | 258($M^+$, 45), 226(25), 198(15), 181(28), 168(10), 153(30), 141(8), 125(48), 106(28), 97(100) |
| 16:50 | 5 | $(EtO)_2P(S)SCH_2CO_2Et$[b] | 272($M^+$, 18), 227(8), 195(15), 171(9), 153(20), 121(55), 97(100) |
| 20:15 | 45 | mecarbam (**2**)[c] | 329($M^+$, 18), 296(10), 226(8), 198(8), 159(40), 144(12), 131(85), 116(30), 97(100), 86(35), 74(28), 59(52), 42(40) |

[a]Methylated in the case of **3** and **5**. A second sample (B) showed the presence of the same compounds and, in addition, a peak at $t_R$ = 6:40, corresponding to $MeNHCO_2Et$ (**6**), m/z 103($M^+$, 28), 75($M - C_2H_4$, 45), 58($M - EtO$, 100), 40(35).

[b]The route by which this ethyl ester is formed is uncertain, but could involve an intramolecular transfer of ethyl with loss of methyl isocyanate as proposed previously in the mass spectrometric fragmentation of mercarbam.[11]

[c]cf. ref. 11.



decomposition of diazald (*N*-methyl-*N*-nitroso-*p*-toluenesulphonamide)[12] and the resulting solution was analysed by g.c.-m.s. using a Hewlett Packard model 5890 gas chromatograph with split injector system, coupled to a VG Masslab 12–253 quadrupole mass spectrometer. Products from mecarbam were analyzed on a 25 m × 0.2 mm OV1 capillary column (film thickness 0.1 μm), with a helium carrier-gas flow rate of 30 cm $sec^{-1}$ (head pressure 10 p.s.i.) and an initial temperature of 40°C (5 min), followed by a ramp rate of 15°C $min^{-1}$ up to 200°C (injector temperature, 200°C). Products from chlormephos were analyzed on a 25 m × 0.32 mm OV17 capillary column (film thickness 0.52 μm; helium flow-rate 40 cm $sec^{-1}$, head pressure 5 p.s.i.), programmed from 100°C (1 min) at 10°C $min^{-1}$ to a final temperature of 300°C (injector temperature, 250°C). Mass spectra by direct insertion were obtained on an AEI MS9 instrument at 70 eV.

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