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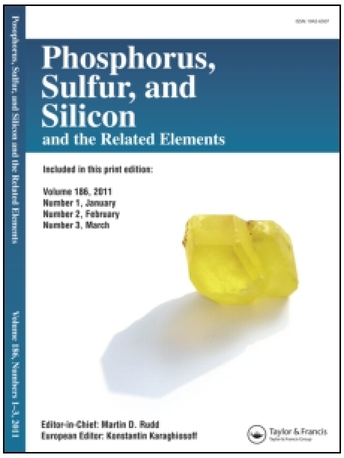

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TRANSFORMATIONS OF O,O-DIETHYL-PHOSPHOROTHIO CHLORIDATE UNDER PHASE TRANSFER CONDITIONS

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TRANSFORMATIONS OF O,O-DIETHYL-PHOSPHOROTHIOCHLORIDATE UNDER PHASE TRANSFER CONDITIONS

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O,O-Diethyl-phosphorothiochloridate reacts under phase transfer conditions to give a trithiono-triphosphate derivative. The formation and the structure of that compound have been established.

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Among the pesticides are a number of compounds which contain the diethyl-thionophosphoryl moiety. Introduction of such a group into the molecule is an important process and usually goes by acylation of the conjugate base of the weak NH, —OH, —SH acids with O,O-diethyl-phosphorothiocloridate.[1]

Using the phase transfer catalytic effect of quaternary ammonium salts, polyamines, crown-ethers and podands in solid-liquid or sometimes in liquid-liquid phase transfer conditions[2] we succeeded in acylating these types of functions in the presence of an alkali hydroxide as base (for the typical reaction and working up procedure see the Experimental Part). A small amount of pyridine or triethylamine is also added as cocatalyst[3] to the mixture if quaternary salts or crown-ethers are used in the reactions.

In the reactions which we have carried out, at least one [liquid-liquid PT conditions] or two [in solid-liquid PT conditions] by-products common for each reaction can be detected by GLC or TLC. They have been separated from the reaction mixture by preparative TLC or column chromatography. The one formed in liquid-liquid phase transfer conditions as a sole by-product (*I*) gives a lower R_f value (0.23 Kieselgel G, benzene-$CHCl_3 = 1:1$) and at GLC conditions it is more volatile than the other (*II*).

On the basis of the MS, ^1H-NMR, IR data and comparison with an authentic sample[4] product *I* is tetraethyl-dithionopyrophosphate.

By-product II (R_f: 0.52 under the conditions given above) can also be prepared in a relatively clean form simply by stirring the heterogeneous mixture of solid KOH, diethyl-phosphorothiochloridate and tetramethyl-ethylenediamine (TEMED) in dichloromethane at ambient temperature. ^1H-NMR and IR spectra of II are almost identical with those of I, but the molecular peak and the fragmentation pattern in the mass spectrum give decisive evidences that this compound has structure II.

In Scheme I we give a rational route to explain the formation of the compounds I and II.

The solid-liquid phase transfer conditions seem to be optimum for the formation of the anion intermediate III (by cleavage of I with a strong nucleophile) and for the further acylation of III by diethyl-phosphorothiochloridate. In liquid-liquid phase transfer conditions the anion III is extracted into the aqueous phase, so the formation of compound II is less probable.

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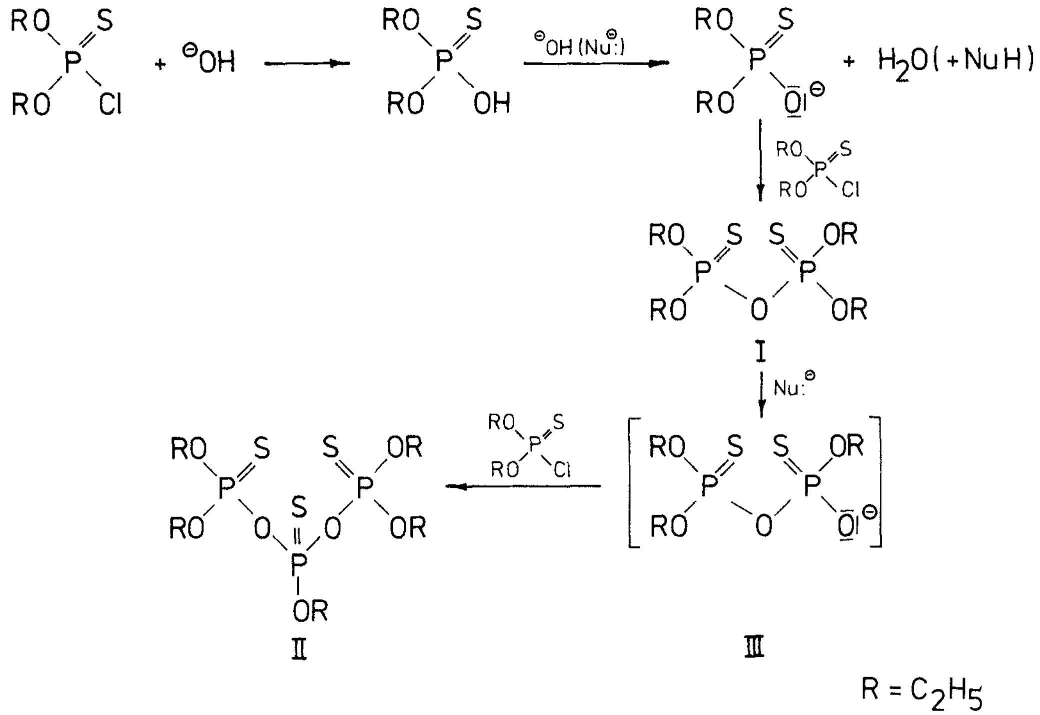

Scheme I

EXPERIMENTAL

To the solution of suspension of 0.1 mol substrate to be acylated, 0.11 mol diethyl-phosphorothiochloridate, 0.01 mol catalyst (TEMED, dibenzo-18-crown-6 or TEBAC) in dichloromethane (or acetonitrile) and 0.5 mol powdered potassium hydroxide and 0.5 mol potassium carbonate are added and the mixture is stirred at room temperature till the reaction is completed.

The suspension is filtered with suction and compounds I and II are separated from the filtrate by column chromatography (Kieselgel 40, 70–230 mesh, eluated with benzene-chloroform mixture 5:4) or by preparative TLC (Kieselgel G type 60, benzene-chloroform mixture 1:1).

Yields calculated for I, based on diethyl-phosphorothiochloridate, are 1–5%, and 10–30% for II (e.g. in case of N-acylation of phthalimide 3% I and 20% II are formed in addition to 70% diethyl-thionophosphoryl-phthalimide). If the substrate is left out from the mixture the yield of compound II can be as high as 60%.

Both I and II are liquids. Bp. for I 93–5°C at 13 Torr;

IR (KBr) (Instrument: Perkin Elmer 237) ν: 2950, 2900, 1020, 960, 795 cm^{-1}.

^{1}*H-NMR* (60 MHz, TMS CCl_4) (Instrument: Perkin Elmer R 12) δ: 1.34 (t, J = 7 Hz; 12 H) 3.77–4.46 (m, 8 H) [ppm].

MS (70 eV, Instrument: Finniger 3200) m/e: 321 (6%) M$^+$; 228 (11%); 212 (9%); 170 (55%); 125 (45%); 109 (47%); 97 (100%); 92 (99%); 81 (88%); 65 (91%).

Compound II decomposes during distillation. Anal. Found: C, 26.72; H, 10.28. Calc for $C_{10}H_{25}O_7P_3S_3$: C, 26.90; H, 5.64.

IR ν: 2960, 2910, 1020, 965, 840 cm^{-1}.

^{1}*H-NMR* δ: 1.37 (t, J = 7 Hz; 15 H) 3.95 – 4.72 (m, 10 H) [ppm].

MS m/e: 446 (24%) M$^+$; 322 (21%); 294 (19%); 277 (11%); 266 (25%); 249 (13%); 245 (100%); 238 (29%); 221 (14%); 217 (54%); 209 (27%); 202 (40%); 192 (26%); 189 (15%); 97 (25%).

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