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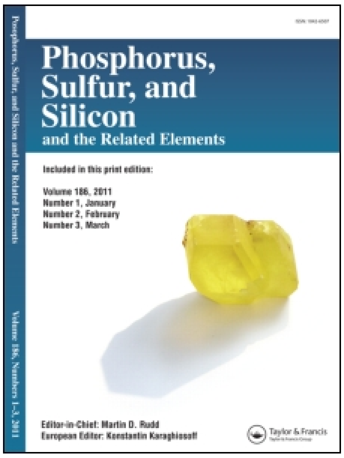

Phosphorus, Sulfur, and Silicon and the Related Elements

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SYNTHESIS OF PHOSPHORUS DERIVATIVES FROM 1,3-DIOXOLAN-2-ONE

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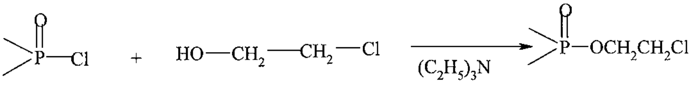
A new route for the synthesis of some mixed organic phosphorus compounds from 1,3-dioxolan-2-one is reported. By heating a mixture of phosphorus-chlorine derivatives and 1,3-dioxolan-2-one in the presence of a catalyst, mixed phosphorus derivatives having 2-chloroethyl ester groups could be obtained. A wide range of phosphorus derivatives can be obtained using this method.

Keywords: 1,3-Dioxolan-2-one; 2-chloroethyl ester; mixed phosphate; phosphinate; phosphine oxide; phosphinite; phosphite; ring opening

Phosphorus derivatives containing 2-chloroethyl groups, bonded directly to the phosphorus atom or though an oxygen atom, are important organic phosphorus compounds. They are used as flame-retardants, plant growth regulators, or lubricants.[1–6]

The literature[7–11] mentions other methods for the synthesis of mixed phosphorus derivatives having 2-chloroethyl ester groups: from 2-chloroethanol (Scheme 1) or ethylene oxide (Scheme 2). These methods have some inconveniences such as uncontrolled reactions and difficulties in product separation.



SCHEME 1

No data concerning the reaction between phosphorus-chlorine derivatives and 1,3-dioxolan-2-one were found. The investigation was

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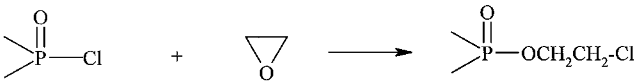
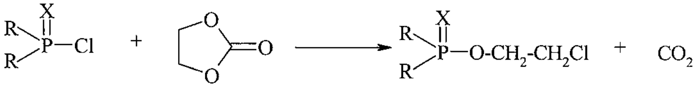


SCHEME 2

started in order to find out if 1,3-dioxolan-2-one could react with those kinds of phosphorus derivatives. Here, we report the results obtained from the study of the reaction of phosphorus derivatives and 1,3-dioxolan-2-one (ethylene carbonate) (Scheme 3).



1a-f **2** **3a-f**

SCHEME 3

RESULTS AND DISCUSSION

The reaction of diphenylchlorophosphate **1a**, 1,3-dioxolan-2-one and a catalyst (LiF or LiCl) was investigated. Heating the mixture at 120–130°C, only little carbon dioxide was released. Increasing the temperature increases the amount of carbon dioxide released. Reaction products were separated by Gas-Chromatography (column: OV-17/Gas Chrome Q; column temperature: 240°C; injector temperature: 280°C; detector temperature: 270°C; carrier gas: hydrogen) using as standards, commercial products, or synthesized compounds from 2-chloroethanol and diphenylchlorophosphate or phenyldichlorophosphate in the presence of triethylamine. During the investigation it was observed that three peaks appear in the chromatogram (Figure 1). The retention times for the studied compounds are in concordance with their molecular structure. These compounds also were separated using columns containing different stationary phases (Table I).

Thus, in all cases, the retention indices increase with increasing of molar mass and the polarity of the stationary phase. The calculated values are the same or a little bit higher than experimental ones.

They were identified as 2-chloroethyl-diphenylphosphate **3a** (^{31}P NMR: 11.4 ppm), bis(2-chloroethyl) phenylphosphate **6** (^{31}P NMR: 3.7 ppm) and triphenylphosphate **4**. Concerning these data, it was concluded that one of the reagent, diphenylchlorophosphate, gives a

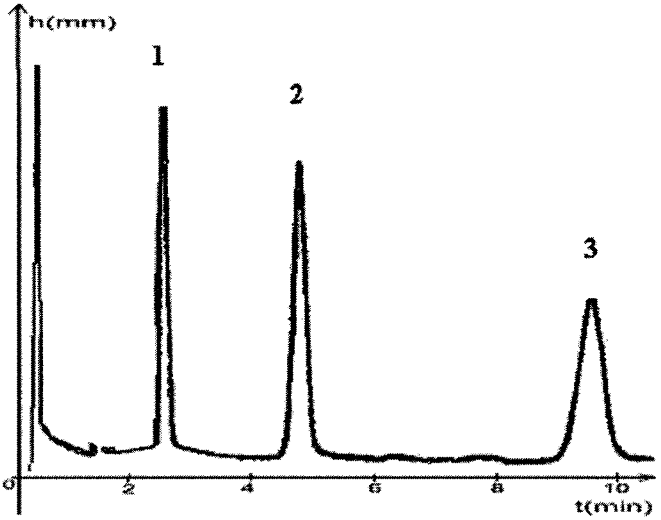
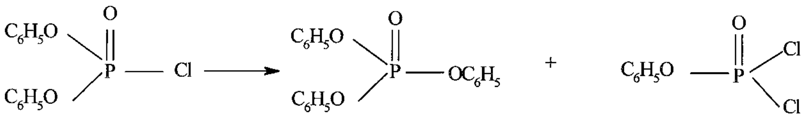


FIGURE 1 GC chromatogram for studied compounds: bis (2-chloroethyl) phenylphosphate-peak **1**, 2-chloroethyldiphenylphosphate-peak **2**, triphenylphosphate-peak **3**.

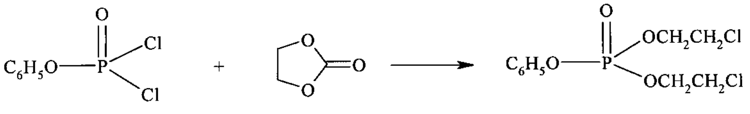


1a **4** **5**

SCHEME 4

partially disproportion reaction (Scheme 4) and the compound **5** reacts with 1,3-dioxolan-2-one giving the product **6** (Scheme 5).

In both cases, the reactions take place by ring opening of the 1,3-dioxolan-2-one and the migration of chlorine from the phosphorus atom to the carbon atom. Then we tried to find another catalyst that could decrease the reaction temperature, increase the yield of **3a**, and decrease



5 **2** **6**

SCHEME 5

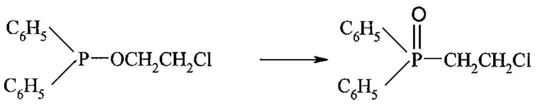
TABLE I Experimental and Calculated Retention Indices (**I**) for Compounds **1–4** from Figure 1

	I_{OV-1}		I_{OV-17}		I_{OV-225}	
Compound	Iexp.	Icalc.	Iexp.	Icalc.	Iexp.	Icalc.
1	1735	—	2104	—	2778	—
2	1929	1942	2332	2340	2943	2952
3	2140	2150	2566	2565	3132	3152
4	2358	—	2816	—	3340	—

the side reactions. The best results were obtained when guanidine sulfate (**GS**) or guanidine carbonate (**GC**) were used (Table II).

Other 2-chloro derivatives were obtained by using guanidine carbonate as catalyst. Table III presents reaction conditions and the obtained results.

For compound (**3c**) the yield was lower because 2-chloroethyldiphenylposphinite at the reaction temperature undergoes a Mikaelis-Arbuzov reaction which leads to phosphine oxide (**7**) (Scheme 6). ^{31}P NMR (standard 85% H_3PO_4) has shown two peaks at −36.3 ppm and −112.5 ppm, corresponding to compounds (**7**) and (**3c**) respectively. Compound **7** was obtained in 25% yield by recrystalization from benzene-hexane (m.p. 125–127°C).[12]



3c **7**

SCHEME 6

All compounds were obtained by a simple method which could be controlled through the reaction temperature, catalyst, and the amount of carbon dioxide released.

EXPERIMENTAL

From Ethylene Carbonate

A mixture of phosphorus-chlorine derivative **1a–f** (0.02 mmol), 1,3-dioxolan-2-one (0.03 mmol) and the catalyst (0.02 g) was heated at a selected temperature and kept until all carbon dioxide was released. The mixture was dissolved in chloroform or benzene, washed with H_2SO_4

TABLE II Synthesis of Mixed Phosphates

Reaction conditions					
Temp.,°C	Time, h	Catalyst	Yield (**3a**) %	Yield (**4**) %	Yield (**6**) %
120	2	LiCl	3	5	1
160	2	LiCl	22	12	8
170	3	LiCl	28	18	10
120	2	LiF	5	7	2
160	2	LiF	30	16	7
170	3	LiF	35	20	10
150	3	GS	50	7	5
120	3	GC	59	3	3

Yield-based on **1a** used.

0.5 N (twice with $NaHCO_3$ 5%, then twice with water) the layers separated, and the organic layer dried with anhydrous Na_2SO_4 (except **3c** which was separated without washing); the solvent was removed by distillation and the products separated using a semi-preparative HPLC-MD1510 Jasco. ^{31}P NMR spectra were performed with a Bruker Avance DRX 400.

Classical Method for 3a and 6 (Used as Standards)

3a was synthesized from diphenylchlorophosphate (0.1 mmol), 2-chloroethanol (0.12 mmol), and triethylamine (0.1 mmol) at 25°C for 5 h, chlorohydrate filtered, and then the mixture purified by distillation under reduced pressure (b.p.$_2$ 170–176°C; d_{20}1.2912, lit.[8] b.p.$_{0.5-1}$ 168–173). **6** was synthesized from phenyldichlorophosphate (0.1 mmol), 2-chloroethanol (0.22 mmol), and triethylamine (0.2 mmol) at 25°C, for 7 h, chlorohydrate filtered, then the mixture purified by distillation under reduced pressure (b.p.$_1$ 164–167°C; d_{20}1.398, lit.[8] b.p.$_{0.2-0.5}$ 160–163).

TABLE III Synthesis of 2-Chloroderivatives of Phosphorus Compounds

Comp.	R	X	Reaction temp., °C	Yield, %	b.p., °C/mm Hg	^{31}P NMR, ppm
3b	C_6H_5	O	95–110	65.3	173–177/1	−30.8
3c	C_6H_5	None	115–125	40.7	110–114/3 [13]	−110.5
3d	C_2H_5O	None	75–90	50.4	76–78/3	−137.0
3e	C_2H_5	S	90–100	39.8	112–115/5	−71.5
3f	$(CH_3)_2N$	None	90–100	36.5	76–79/8 [14]	−138.2

CONCLUSIONS

The method used is not mentioned in the literature and it allowed us to synthesize mixed 2-chloroethyl derivatives. The performed studies showed that the catalyst and the temperature are essentials for this reaction. The best catalyst was guanidine carbonate. The best results with this catalyst were obtained at 100–110°C for compound **3b**. The method could be used in the synthesis of other phosphorus derivatives.

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