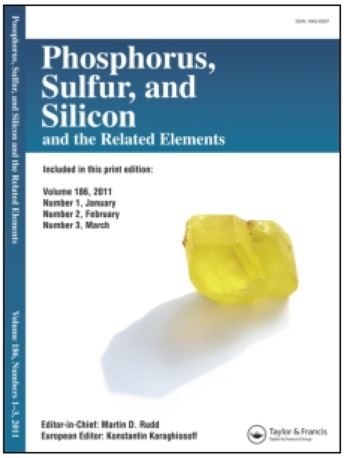


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

A STUDY ON THE TRANSESTERIFICATION REACTION OF DIMETHYL AND DIETHYL PHOSPHITE WITH 1,3-DICHLOROPROPANOL-2

K. Troev[a]; E. Tashev[a]; G. Borisov[a]
[a] Central Laboratory on Polymers, Bulgarian, Academy of Sciences, Sofia, Bulgaria

To cite this Article Troev, K. , Tashev, E. and Borisov, G.(1982) 'A STUDY ON THE TRANSESTERIFICATION REACTION OF DIMETHYL AND DIETHYL PHOSPHITE WITH 1,3-DICHLOROPROPANOL-2', Phosphorus, Sulfur, and Silicon and the Related Elements, 12: 3, 313 — 318

To link to this Article: DOI: 10.1080/03086648208078964

URL: http://dx.doi.org/10.1080/03086648208078964

Phosphorus and Sulfur, 1982, Vol. 12, pp. 313-318
0308-664X/82/1203-0313/$06.50/0

A STUDY ON THE TRANSESTERIFICATION REACTION OF DIMETHYL AND DIETHYL PHOSPHITE WITH 1,3-DICHLOROPROPANOL-2

K. TROEV, E. TASHEV and G. BORISOV

Central Laboratory on Polymers, Bulgarian, Academy of Sciences,
Sofia 1113, Bulgaria

(*Received August 15, 1981; in final form October 24, 1981*)

The transesterification process of dimethyl and diethyl phosphite with 1,3-dichloropropanol-2 is examined. It is found that the reaction proceeds in the absence of catalyst at a temperature of 155°, whereas in the presence of morpholine as a catalyst it takes place at 126°C. The transesterification of dimethyl phosphite and diethyl phosphite with 1,3-dichloropropanol-2 is accompanied by the evolution of dimethyl and diethyl ethers and alkyl halides (methyl chloride and ethyl chloride).

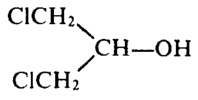
INTRODUCTION

The transesterification of dialkyl phosphites has been carried out with various hydroxyl group containing compounds.[1-3] It has been reported[1] that at high basicity transesterification proceeds as a bimolecular reaction at rates considerably higher than in the case of aliphatic diols.[2] Studies on the transesterification of dialkyl phosphites with amino alcohols[3] showed that in the presence of a base the dialkyl phosphites existed in their tercoordinated form. In this case the reaction takes place at considerably lower temperatures and the calculated initial rate constants are approximately an order of magnitude greater than the ones for the process with aliphatic diols.

The aim of the present work is to discuss the experimental data obtained on transesterifying dimethyl and diethyl phosphite with 1,3-dichloropropanol-2.

RESULTS AND DISCUSSION

The studies on the transesterification reaction between dialkyl phosphites and various hydroxyl-group containing compounds have shown that the rate of the process depends on the basicity[2] of the oxygen atom of the hydroxyl group. In this connection, it was considered interesting to examine the transesterification of dialkyl phosphites with alcohols of considerably lower basicity than the aliphatic diols and amino alcohols. 1,3-dichloropropanol-2 was employed as a suitable alcohol in this respect:



The basicity of the oxygen atoms is considerably reduced, because of the inductive effect of the chlorine atoms, in respect to the aliphatic diols and amino alcohols.

The transesterification studies revealed that dimethyl phosphite reacted with 1,3-dichloropropanol-2 at a considerably higher temperature (155°) than that with aliphatic diols (130°), amino alcohols (88°) and the guaiacol series (100°). The calculated initial rates at different mole ratios at 160° indicated that the reaction proceeded at a reduced rate in comparison with the alcohols of lower basicity

$$W_{o\mathrm{DMP/DCP\text{-}2}=1:1} = 0.44\ \mathrm{mole.L^{-1}min^{-1}}.$$
$$W_{o\mathrm{DMP/DCP\text{-}2}=1:2} = 0.19\ \mathrm{mole.L^{-1}min^{-1}}.$$

where W_o is the initial rate, DMP—dimethyl phosphite and DCP-2—1,3-dichloropropanol-2.

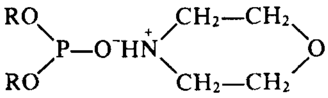
The higher temperature at which the reaction takes place can only be explained by the basicity of 1,3-dichloropropanol-2. The decreased basicity of the oxygen atom, on the other hand, will bring about a lower rate of P—O bond formation and in this manner a lower rate of the transesterification process. Transesterification of dimethyl phosphite with 1,3-dichloropropanol-2 in the presence of morpholine proceeds at 126°, at which temperature no reaction takes place in the absence of catalyst. The calculated initial rate at 145° is

$$W_{o\mathrm{DMP/DCP\text{-}2}=1:2} = 0.57\ \mathrm{mole.L^{-1}min^{-1}}.$$

which is three times higher than that at 160° at the same mole ratio but in the absence of catalyst.

The results obtained indicate that the transesterification rate depends on the basicity of the hydroxyl group, the rates being higher the higher the basicity.

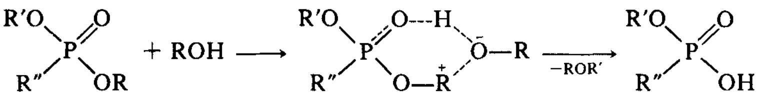
Most probably the role played by the morpholine catalyst is to form a salt in which the dialkyl phosphite is in the tercoordinated state:



Experimental data give evidence that this interaction proceeds and facilitates transesterification. Subsequently, the transesterification reaction follows the scheme depicted in a previous communication.[3]

The results from the transesterification of dialkyl phosphites with 1,3-dichloropropanol-2 also showed that low boiling products were concurrently eliminated. The gas evolved in the interaction between dimethyl phosphite and 1,3-dichloropropanol-2 was shown by infrared spectroscopy to consist of methyl chloride (b.p. −24°) and dimethyl ether (b.p. −23.6°). To confirm this the infrared spectra of pure methyl chloride and of the gaseous mixture were taken. The two spectra overlapped completely with the sole exception of the band at 1460 cm^{-1} which is the characteristic absorption band of the CH_3O group in dimethyl ether.[7] Ethyl chloride and diethyl ether were determined by gas chromatography in the interaction of diethyl phosphite with 1,3-dichloropropanol-2.

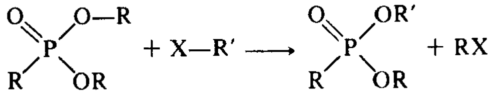
Formation of ethers in the transesterification of dialkyl phosphites is known.[8-10] According to the authors, the ethers arise as suggested by Runavot and co-workers.[11]



(1)

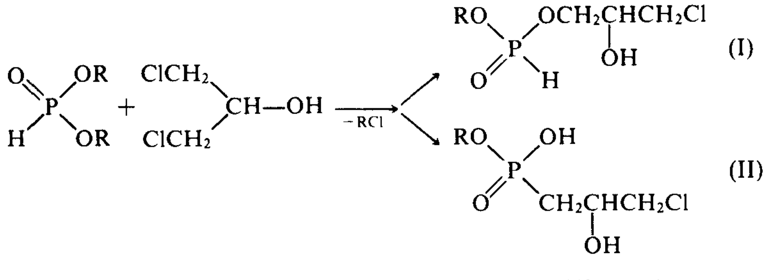
A survey of the literature[6,9] revealed that the percentage of evolved ethers (dimethyl or diethyl ether) is higher in the cases of lower basicity.

In addition to ethers, alkyl chlorides were also evolved in the transesterification reaction of dialkyl phosphites. It is known[12] that phosphonic esters interact with halides giving alkyl halides according to the following scheme:



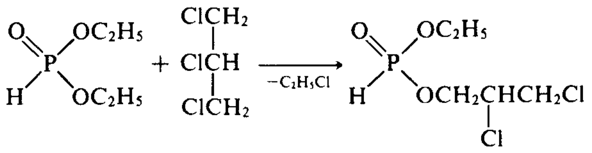
(2)

With dialkyl phosphites, because of the presence of an acidic (labile) hydrogen atom, this interaction can proceed in two ways; i.e. the hydrogen migrating to the negatively charged alkoxy oxygen atom, whose alkyl group interacts with the halogen thus leading to the formation of the P—OH group:



(3)

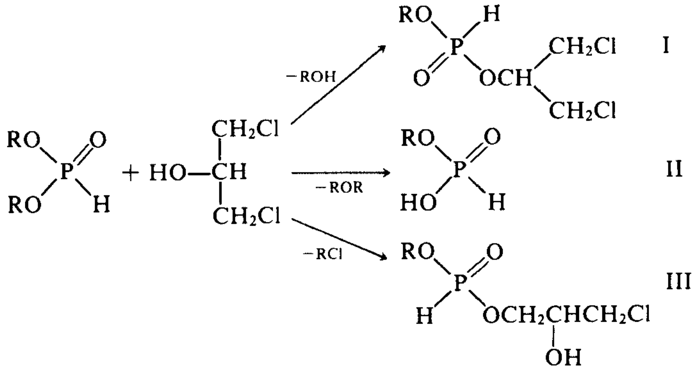
The NMR spectra of the two end products should be different because of the P—OH group. However, the NMR spectrum of the reaction mixture would not be informative in this respect since P—OH groups are formed with the evolution of ether compounds (Eq. 1). For this reason diethyl phosphite was treated with 1,2,3-trichloropropane:



(4)

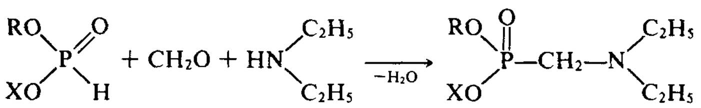
The ethyl chloride evolved in the reaction was determined by gas chromatography. The NMR spectrum supported structure (I).

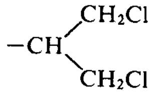
It was established in this manner that the interaction between dimethyl or diethyl phosphite and 1,3-dichloropropanol-2 proceeds in the following three directions:



(5)

Products I and III possess an active hydrogen at P—H, which permits phosphorus, chlorine and nitrogen-containing monomers and oligomers to be prepared by the Mannich reaction by the following scheme:[13]



Where X is  $-CH(CH_2Cl)_2$ or $-CH_2CH(OH)CH_2Cl$

The reaction is strongly exothermic. The structures of the phosphonic acid esters obtained were confirmed by elemental analysis and IR spectra which show the absence of absorption in the characteristic P—H group region of 2330–2440 cm^{-1}.

The products obtained are of interest as flame retardants. Their application in improving the resistance to combustion of elastic foamed polyurethanes[14] indicated that the flame retardant with the OH group is more effective.

EXPERIMENTAL

Initial compounds: dimethyl phosphite (Fluka) purified by vacuum distillation, $n_D^{20} = 1.4018$; diethyl phosphite (Fluka) purified by vacuum distillation, $n_D^{20} = 1.4081$; 1,3-dichloropropanol-2 was prepared according to Ref. 4 and 5, $n_D^{20} = 1.4800$; 1,2,3-trichloropropane (Fluka) purified by vacuum distillation.

A. Transesterification of dimethyl phosphite with 1,3-dichloropropanol-2 in the absence of a catalyst

Dimethyl phosphite (49.35 g, 0.45 mole) and 1,3-dichloropropanol-2 (57.2 g, 0.44 mole) are placed in a three-necked round-bottom flask provided with a condenser, an argon inlet and thermometer. The reaction is conducted at a temperature of 160 ± 0.5°, the evolved methanol being collected in a graduated collector and the gases in a cold trap (liquid nitrogen). After 5 hrs the reaction mixture is brought to 90° and subjected to vacuum distillation at 1 mm Hg. Under these conditions 27 g (30%) distills and 57.2 does not distill at 160° and 1 mm Hg.

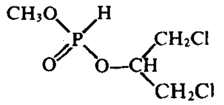
The distillate was subjected to fractionation, affording the following fractions:

1st fraction: b.p. to 35°/2 mm, about 2 g, $n_D^{20} = 1.4378$;
2nd fraction: b.p. 41–42°/2 mm, about 6.8 g, $n_D^{20} = 1.4260$;
3rd fraction: b.p. 63–64°/2 mm, about 5 g, $n_D^{20} = 1.4250$;
4th fraction: b.p. 74–75°/2 mm, about 2 g, $n_D^{20} = 1.4530$;
5th fraction: at 160° and pressure of 1 mm Hg about 1 g does not distill, $n_D^{20} = 1.4685$.

Fractions 2 and 3 were analyzed.

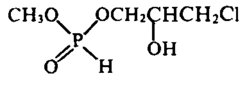
Fraction 2: calc.: mol. mass 207; P% 14.98; Cl% 34.30; CH_3O% 14.98
found: mol. mass 206; P% 14.40; Cl% 33.85; CH_3O% 15.60

This fraction consists of 1,3-dichloroisopropyl methyl phosphite



Fraction 3: calc.: mol. mass 188.5; P% 16.44; Cl% 18.83; CH_3O% 16.44
found: mol. mass 181.3; P% 16.76; Cl% 19.30; CH_3O% 17.07

The fraction consists of 1-chloro-2-hydroxypropyl methyl phosphite:



The molecular mass was established by the vapor-phase procedure using benzene as solvent.

The structures of the products were determined by infrared spectroscopy: the IR spectrum of 1-chloro-2-hydroxypropyl methyl phosphite exhibited a band at 3380 cm^{-1}, characteristic for an OH group.

The transesterification of dimethyl phosphite with 1,3-dichloropropanol-2 at a 1:2 mole ratio was conducted under the same conditions.

B. Transesterification of diethyl phosphite with 1,3-dichloropropanol-2

The process was carried out as in the case of dimethyl phosphite at a 1:1 mole ratio. The evolution of ethyl chloride and diethyl ether was determined by gas chromatography.

C. Transesterification of dimethyl phosphite with 1,3-dichloropropanol-2 in the presence of morpholine as a catalyst

Dimethyl phosphite (23.8 g, 0.216 mole) and morpholine (2 g, 0.023 mole) are mixed (an exothermic effect is observed) in a three-necked, round-bottom flask provided with a condensor, argon inlet and thermometer. The reaction mixture is cooled to 22° and 1,3-dichloropropanol-2 (58.2 g, 0.451 mole) added. The reaction begins at 126° and is conducted at 145°. The methanol evolved is collected in a receiver. The reaction is stopped after 1 hr after which interval were obtained 6.2 g of methanol and 3.8 g of a volatile product.

D. Interaction between diethyl phosphite and 1,2,3-trichloropropane

Diethyl phosphite (32.8 g, 0.24 mole) and 1,2,3-trichloropropane (67.35 g, 0.46 mole) are placed in a three-necked flask provided with a condenser, an argon inlet and thermometer. The reaction is carried out at 160° for 7 hrs. The difference in the weight of the flask before and after the heating was 2.89 g.

The evolution of ethyl chloride was determined by gas chromatography. The reaction mixture was subjected to vacuum distillation after which in the flask remain 3.4 g of product that does not distill at 160° and 1 mm Hg.

E. Interaction between 1,3-dichloroisopropyl methyl phosphite, formaldehyde and diethylamine

1,3-dichloroisopropyl methyl phosphite (20.7 g, 0.1 mole) and diethylamine (7.3 g, 0.1 mole) are placed in a three-necked flask provided with thermometer and mixer. To this reaction mixture is added an equimolar quantity of formaldehyde. The temperature is kept below 85°. 15 minutes after the addition is ended, the mixture is dried and distilled in vacuo, b.p. 143°/1 mm. Yield 78%.

		C%	H%	Cl%	N%	P%
$C_{10}H_{22}Cl_2NO_3P$	calc.:	39.21	7.18	23.20	4.58	10.13
	found:	39.00	7.02	22.78	5.02	10.77

F. Interaction between 1-chloro-2-hydroxypropyl methyl phosphite, formaldehyde and diethylamine

1-chloro-2-hydroxypropyl methyl phosphite (18.8 g, 0.1 mole) and diethylamine (7.3 g, 0.1 mole) are placed in a three-necked flask provided with thermometer and mixer. To this reaction mixture is added an equimolar quantities of formaldehyde. The temperature is kept below 85°. 15 minutes after the addition is ended, the mixture is dried and distilled in vacuo, b.p. 162°/1 mm. Yield 85%.

		C%	H%	Cl%	N%	P%
$C_{10}H_{23}ClNO_4P$	calc.:	41.74	8.00	12.35	4.86	10.78
	found:	42.34	8.11	11.20	5.56	10.80

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