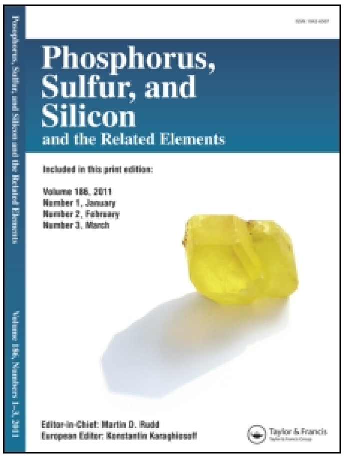


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

INTERACTION BETWEEN 2,4,6-TRIAMINO-1,3,5-TRIAZINE AND ALKYL ESTERS OF PHOSPHONIC AND PHOSPHORUS ACIDS

K. Troev[a]; R. Tsevi[a]
[a] Institute of Polymers, Bulgarian Academy of Sciences, Sofia, BULGARIA

To cite this Article Troev, K. and Tsevi, R.(1998) 'INTERACTION BETWEEN 2,4,6-TRIAMINO-1,3,5-TRIAZINE AND ALKYL ESTERS OF PHOSPHONIC AND PHOSPHORUS ACIDS', Phosphorus, Sulfur, and Silicon and the Related Elements, 133: 1, 61 — 68

To link to this Article: DOI: 10.1080/10426509808032453

URL: http://dx.doi.org/10.1080/10426509808032453

Phosphorus, Sulfur and Silicon, 1998, Vol. 133. pp. 61-68
Reprints available directly from the publisher
Photocopying permitted by license only

Amsterdam N.V. Published under license by
the Gordon & Breach Science Publishers imprint.
Printed in Malaysia

INTERACTION BETWEEN 2,4,6-TRIAMINO-1,3,5-TRIAZINE AND ALKYL ESTERS OF PHOSPHONIC AND PHOSPHORUS ACIDS

K. TROEV and R. TSEVI

Institute of Polymers, Bulgarian Academy of Sciences 1113 Sofia, BULGARIA

(Received 11 August, 1996; In final form 23 January, 1998)

2,4,6-triamino-1,3,5-triazinealkylammonium alkyl- phosphonates -$\{C_3H_6N_6R\}^{+-}OP(O)(X)(OR)$ (X=H, CH_3; R=CH_3; C_2H_5) and 2,4,6-triamino-1,3,5-triazineammonium dimethyl phosphate were synthesized (X=OCH_3; R=CH_3). When R=CH_3 these salts decompose evolving carbene "CH_2" and convert into the corresponding ammonium salts $\{C_3H_7N_6\}^{+-}OP(O)(X)(OR)$. It has been established that when X=OCH_3 and R=CH_3 alkylammonium salts quantitatively convert into the corresponding ammonium salts. It has been assumed that the low basicity of the amino groups of the monoalkylated melamine is the reason to obtain only monoalkylated products.

Keywords: dialkyl phosphonates; alkyldialkyl phosphonates; trialkyl phosphates; triazine; alkylation

INTRODUCTION

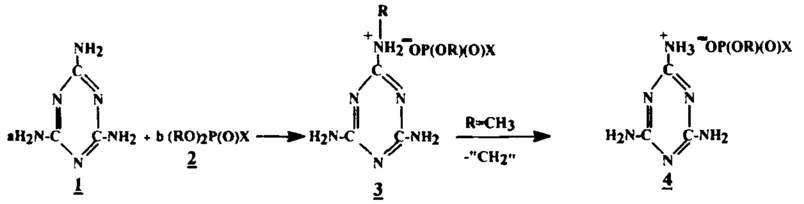
The present paper represents a continuation of our investigation on the interaction between amines with esters of phosphonic (1–4) and phosphorus (5) acids. Our interest in melamine in based on the fact that melamine and its derivatives are important compounds having various biological activity (6,7). It has been shown that when melamine reacts with dialkyl phosphonates taken in manifold excess the result is a monoalkylated product(8).

This paper reports on the synthesis of alkylammonium salts of melamine and alkyl esters of phosphonic and dialkyl esters of phosphorus acids as well as their decomposition to the corresonding ammonium salts.

EXPERIMENTAL PART

Starting materials: dimethyl phosphonate, diethyl phosphonate, dimethylmethyl phosphonate, trimethyl phosphate (Fluka) were distilled under vacuum; 2,4,6-triamino-1,3,5-triazine (melamine) used as obtained from Fluka.

The numerical assignments of the reaction products are shown in scheme 1.



2a X = H; R=CH3
2b X = H; R =C2H5
2c X = CH3; R = CH3
2d X = OCH3; R =CH3

3a X =H; R = CH3
3b X =H; R =C2H5
3c X = CH3; R=CH3
3d X = OCH3 ; R= CH3

4a X =H; R = CH3;
4c X = CH3 ; R=CH3
4d X= OCH3 ; R=CH3

SCHEME 1

Mono-2,4,6-triamino-1,3,5-triazinemethylammonium monomethyl phosphonate – 3a and mono-2,4,6-triamino-1,3,5-triazineammonium monomethyl phosphonate – 4a

1. 9 g (0.015 mol) 2,4,6-triamino-1,3,5-triazine and 24.8 g (0.225 mol) dimethyl phosphonate were mixed in a two neck flask equipped with a stirrer and reflux condensor. The reaction proceeded at 100°C for 100 hrs. Then the mixture was filtered. The solid phase was washed several times with diethyl ether and dried at 30°C. The product is a mixture of **3a** (42.4%)*and **3d** (57.6%)*. Yield 3.4 g, 96%. ^{1}H NMR (250 MHz) (DMSO) δ=3.33 ppm, d, 3J(POCH)=11.7 Hz, $POC\underline{H}_3$, 3H; 3.31 ppm, s, $N\text{-}C\underline{H}_3$, 3H; 6.56 ppm, d, 1J(PH)=614.5 Hz, $P\underline{H}$, 1H ; 7.41 pmm, s, $N\underline{H}_2$, 2H; 8.18 ppm, s, $N\underline{H}_2$, 4H. ^{31}p NMR (DMSO) δ=4.79 ppm, dq, 1J(PH)=588.9 Hz, 3J(POCH)= 11.9 Hz; ^{13}C NMR (DMSO) δ=32.3 ppm, $N\text{-}\underline{C}H_3$; 50.1 ppm, $PO\underline{C}H_3$; 157.4 and 163.4 ppm; C_2, C_4 and C_6carbon atoms of 2,4,6-triamino-1,3,5-triazine.

Mono-2,4,6-triamino-1,3,5-triazineethylammonium monoethyl phosphonate – 3b

1.9 g (0.015 mol) 2,4,6-triamino-1,3,5-triazine and 31.07g (0.225 mol) diethyl phosphonate were mixed in a two neck flask equipped with a stirrer and reflux condensor. The reaction proceeded at 100°C for 80 hrs. Then the mixture was filtered. The solid phase was washed several times with diethyl ether and dried at 30°C. Yield 2.9 g, 73%. ^{1}H NMR (250 MHz) (DMSO) δ=1.11 ppm, t, 3J(HH)=4.9 Hz, $POCH_2C\underline{H}_3$ and $NCH_2C\underline{H}_3$, 6H; 3.71–3.80 ppm, m, $POC\underline{H}_2CH_3$ and $NC\underline{H}_2CH_3$, 4H; 3.81–4.02 ppm (b.s), $N\underline{H}_2$, 6H; 6.58 ppm, d, 1J(PH)=589.0 Hz, P$\underline{H}$, 1H; ^{31}p NMR (DMSO) δ=4.78 ppm, dt, 1J(PH)=597.7 Hz; ^{13}C NMR (DMSO) δ=16.0 ppm, $NCH_2\underline{C}H_3$. 18.4 ppm, $POCH_2\underline{C}H_3$; 63.2 ppm, $PO\underline{C}H_2CH_3$; 45.2 ppm $N\underline{C}H_2CH_3$; 155.4 and 161.4 ppm C_2, C_4 and C_6 carbon atoms of 2,4,6-triamino-1,3,5-triazine.

Mono-2,4,6-triamino-1,3,5-triazinemethylammonium methyl-monomethylphosphonate-3c and mono-2,4,6-triamino-1,3,5-triazineammonium monomethylphosphonate – 4a

1.9 g (0.015 mol) 2,4,6-triamino-1,3,5-triazine and 27.9 g (0.225 mol) dimethylmethyl phosphonate were mixed in a two neck flask equipped with a stirrer and reflux condensor. The reaction proceeded at 100°C for 80 hrs. Then the mixture was filtered. The solid phase was washed several times with diethyl ether and dried at 30°C. The product is a mixture of **3c** (39%)* and **4c** (61%)*. Yield 3.5 g, 91%. ^{1}H NMR (250 MHz) (DMSO) δ=0.96 ppm, d, 2J(POCH)=15.9 Hz, P-C$\underline{H}$3, 3H; 3.31 ppm, d 3J(POCH)=10.4 Hz, 3H, P-O$C\underline{H}_3$; 3.35 ppm, s, N-$C\underline{H}_3$, 3H; 7.38 ppm, s, $N\underline{H}_2$, 2H; 8.24 ppm, s, NH_2, 4H. ^{31}P{^{1}H} NMR (DMSO) δ=28.9 ppm, ^{13}C NMR (DMSO) δ=13.9 ppm, P-$\underline{C}H_3$; 35,4 ppm, N-$\underline{C}H_3$; 51.5 P-O$\underline{C}H_3$; 153.4 and 160.4 ppm; C_2, C_4 and C_6 carbon atoms of 2,4,6-triamino-1, 3,5-triazine.

Mono-2,4,6-triamino-1,3,5-triazinemethylammonium dimethylphosphate – 4d

1. 9 g (0.015 mol) 2,4,6-triamino-1,3,5-triazine and 31.5 g (0.225 mol) trimethyl phosphate were mixed in a two neck flask equipped with a stirrer

and reflux condensor. The reaction proceeded at 100°C for 100 hrs. The mixture homogenizes after 54 hrs of heating. After being treated with diethyl ether the mixture forms two phases soluble and insolble in diethyl ether. Then the products were dried at 30°C. The insoluble product in diethyl ether is mono-2,4,6-triamino-1,3,5-triazinemethylammonium dimethyl phosphate-**4d**. ^{1}H NMR (250 MHz) (DMSO) δ=3.49 ppm, d, 3J(POCH)=10.9 Hz, P-OC$\underline{H}$3, 6H; 4.20–4.45 pmm, m (b.s), N$\underline{H}_2$, 7H; ^{31}P{^{1}H} NMR (DMSO) δ=2.89 ppm, ^{13}C NMR (DMSO) δ=55.7 P-O$\underline{C}$H$_3$; 153.4 and 165.4 ppm; C_2, C_4 and C_6 carbon atoms of 2,4,6-triamino-1,3,5-triazine.

RESULTS AND DISCUSSION

The existence of a partial positive charge of α-carbon atoms from alkyloxy groups of alkyl esters of phosphonic and phosphorous acids and the experimentally found fact that the nucleophilic nitrogen atom from amino compounds prefers to attack this electrophilic center (1) determine the possibility an interaction between 2,4,6-triamino-1,3,5-triazine **1** and dialkyl esters of phosphonic and phosphorous acids **2** (Scheme 1). Two phases – solid insoluble in diethyl ether and liquid soluble in diethyl ether were isolated after treating with diethyl ether the reaction mixture obtained by the interaction between dimethyl phosphonate **2a** and 2,4,6-triamino-1,3,5-triazine **1**, in excess of dimethyl phosphonate. A signal at δ=3.31 ppm, singlet, appears in ^{1}H-NMR spectrum of the solid phase. It can be assigned to N^+-CH_3 group formed as a result from the alkylation of melamine by dimethyl phosphonate. The salt structure of **3a** has been proved by ^{31}p NMR spectrum (Fig. 1). The chemical shift for the phosphorous atom is doublet of quartets at δ=4.79 ppm with a spin-spin interaction constant 3J(POC)=11.91 Hz characteristic for P-OC$\underline{H}$3 protons. That doubtlessly means that phosphorous atom is bound only to single OCH_3 group and with 1J(PH)=585.4 Hz typical of a phosphorus atom bound to a negatively charged oxygen atom (2). The negative charge of the oxygen atom determines the shift: (i) of the signal for P-OC$\underline{H}_3$ protons in ^{1}H NMR spectrum to a stronger field from 3.41ppm for dimethyl phosphonate to 3.33 ppm for product **3a**; (ii) of the signal for P-O$\underline{C}$H$_3$ for the carbon atoms in ^{13}C NMR spectrum from 51.07 ppm for dimethyl phosphonate to 50.1 ppm for **3a**. This salt represents 2,4,6-triamino-1,3,5-triazine methylammonium monomethyl phosphonate **3a**. The ratio between the integral intensities for P-OCH_3 and N^+CH_3 protons in alkylated melamine should be 1:1. ^1H NMR spectral data show that the ratio is 1:0.57, *i.e.* the integral intensity for N^+CH_3 is rather lower than the theoretical. That means salt **3a** is unstable and decomposes under the reaction conditions to salt **4a**. This result confirms our finding that methylammonium salts of phosphonic(4) and phosphorus (5) acids are unstable and decompose to the corresponding salts by a carbene "CH_2" cleavage reaction.

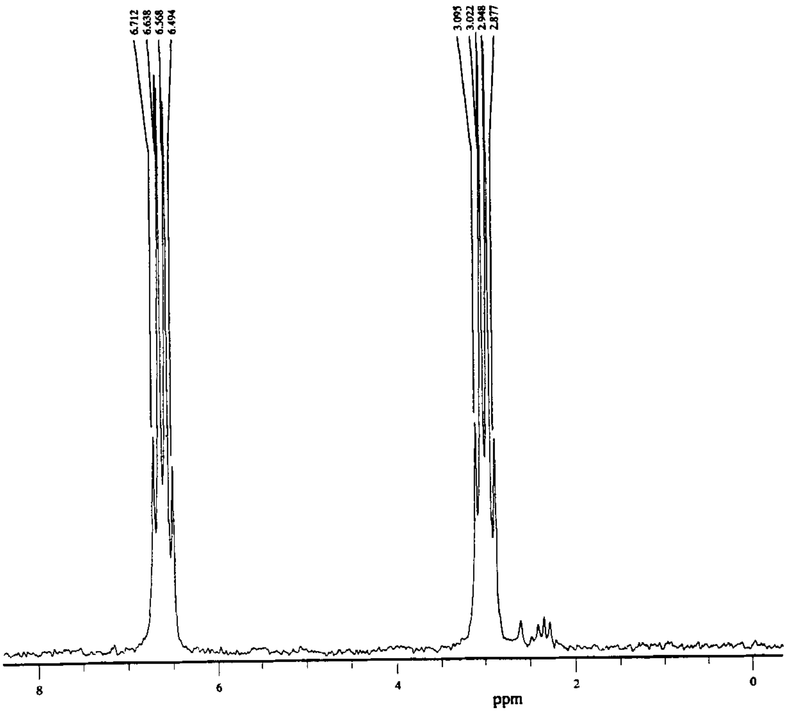


FIGURE 1 ^{31}P NMR spectrum of 2,4,6-triamino-1,3,5-thazinemethyl ammonium monomethyl phosphonate

When 2,4,6-triamino-1,3,5-triazine was reacted with diethyl phosphonate the isolated product was mono-2,4,6-triamino-1,3,5-triazineethylammonium monoethylphosphonate **3b**. The chemical shift for the phosphorous atom is doublet of triplets at δ=4.25 ppm. The results obtained demonstrate that the salt **3b** is stable under the reaction conditions and does not change. It has been established that these salts evolve ethylene undergoing Hofmann elimination at temperatures higher than 140°C (3).

It has been established that the reaction of melamine with methyl dimethylphosphonate or with trimethyl phosphate also result in monoalkylated products **3c** and **4d**. The structure of the products has been proved by ^1H ^{13}C and ^{31}P NMR spectroscopy. In both cases the signal for P-OCH_3 protons in product **3c** (3.31 ppm) and **4d** (3.49 ppm) is shifted to a stronger field if compared to dimethyl methylphosphonate (3.76 ppm) and trimethyl phosphate (3.69 ppm). This fact proves the salt structure of both products. It should be pointed out that only in the case of trimethyl phosphate the product at the first stage of the reaction **3d** quantitatively converts into the **4d**. The explanation might be in the fact that only at reactions between 2,4,6-triamino-1,3,5-triazine and trimethyl phosphate the reaction mixture homogenizes after heating for 54 hours. This favours the transformation of alkylammonium salts into ammonium salts since in solution the positive charge of nitrogen atom has greater influence upon the mobility of hydrogen atoms of the methyl group, bound to the nitrogen atom, than in the case when the alkylammonium salts are solid. In solid state alkylammonium salts exist as ion pairs and the influence of the positive charge upon the mobility of hydrogen atoms of the methyl group, bound to the nitrogen atom, will be smaller as the positive charge will be balanceed by the negative one. In solution they can exist as free ions. Then a proton can be cleaved from monoalkyphosphonate or dialkylphosphonate anion, leading to the formation of an unstable alkylammonium salt which decomposes to carbene and amine (4).

To obtain only monoalkylated products is an unexpected result from the reaction between 2,4,6-triamino-1,3,5-triazine and dialkyl esters of phosphonic acid and trialkyl esters of phosphorus acid in manifold excess of the esters since there are three primary amino groups in 2,4,6-triamino-1,3,5-triazine. This could be explained by the influence of the alkylated amino group upon the basicity of remaining amino groups of the melamine. W. Feldmann (9) has found that when melamine reacts with phosphorous acid in molar ratio 1:2 only one molecule of phosphorus acid is strongly bound to melamine. The second molecule is easily eliminated under the influence of water, ethanol or melamine even at room temperature. The results are well illustrated by K_{b1}=1.26.10–9 and K_{b2}=1.58.10–14 (10) values for melamine. Obviously, the second amino group is a much weaker base in comparison with the first one. Therefore melamine forms a weak bond with the second molecule of the acid. The higher acidity of monoalkylated esters (R=CH_3; C_2H_5) of phosphonic acid than that of phosphorus acid (Table I) is obviously not sufficient enough for the formation of stable dialkylated products.

TABLE I pK_1 values for the phosphorus-containing compounds discussed in this paper

Compound	*pK_1*	*Compound*	*pK_1*
$HP(O)(OH)_2$	1.42[a] ; 1.5[b]	$OP(OH)_3$	1.97 [a,d]; 2.12 [e]
$HP(O)(OCH_3)OH$	0.81[a]	$OP(OCH_3)_2OH$	1.29 [d] ; 0.76[e]
$HP(O)(OC_2H_5)OH$	0.9[c]		

[a] Reference 11.
[b] Reference 12.
[c] Reference 13.
[d] Reference 14.
[e] Reference 15.

The achieved results show that the reaction between melamine and dialkyl esters of phosphonic acid and trialkyl esters of phosphorus acid is realized only by one amino group from melamine. The existence of a positive charge of nitrogen atom from the monoalkylated product determines the lowered basicity of the remaining melamine amino groups which does not allow the formation of stable di- and trialkylated products.

Acknowledgements

We thank the National Foundation "Scentific Investigations" (X-531) for financial support.

References

[1] K. Troev and G. Borisov, Phosphorus and Sulfur, **29**, 129 (1987).
[2] K. Troev and D. M. Roundhill, Phosphorus and Sulfur, **36**, 189 (1988).
[3] K. Troev and D. M. Roundhill, Phosphorus and Sulfur, **37**, 243 (1988).
[4] E. Georgiev, R. Tsevi, V. Vassileva, K. Troev and D. M. Roundhill, Phosphorus, Sulfur, and Silicon, **88**, 139 (1994).
[5] V. Vassileva, E. Georgiev, K. Troev and D. M. Roundhill, Phosphorus, Sulfur, and Silicon, **92**, 101 (1994).
[6] U.S.Pat. 4,275,204 (1981); C. A. **95**, 62268p (1981).
[7] N. N. Mel'nikov, Pestitzidi, Izd. Khimiya, Moscow, 1987, p.641.
[8] V. Orlovski and B.A. Vovsi, Zh. Obshch. Khim., **39**, 926 (1969).

[9] W. Feldmann, Z. anorg. allg. Chem., **600**, 169 (1991).
[10] E. N. Boitsov, A. I. Finkelshtein, Opt. Spektoskopiya, **9**, 26 (1969).
[11] A. Razumov and Sim Do-Hen, Zh. Obshch. Khim. **26**, 2233 (1956).
[12] R. M. Smith and A. E. Martell, Critical Stability Constants, **4**, Plenum Press, New York, NY. 1976.
[13] J. P. Guthrie, Can. J. Chem., **57**, 236 (1979).
[14] W. D. Kumler and J. J. Eiler. J. Am. Chem. Soc., **65**, 2355 (1943).
[15] J. P. Guthrie, J. Am. Chem. Soc., **99**, 3991 (1977).