

Syntheses of 2,4,6-tris(di-tetrahydrofurfuroxy)phosphinyl-*s*-triazine and its derivatives as fire-retardants for cellulose

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MS received 6 September 1979 ; revised 15 April 1980

Abstract. The synthesis of 2,4,6-tris(di-tetrahydrofurfuroxy)phosphinyl-*s*-triazine (2) was achieved by the reaction of cyanuric chloride with tris(tetrahydrofurfuryl)phosphite (1) or with sodium bis(tetrahydrofurfuryl)phosphite (3). 2 on treatment with anhydrous ammonia yielded ammonium salt of 2,4-diamino-6-tetrahydrofurfuroxy-phosphinyl-*s*-triazine (3), which on methylation yielded (4). The reaction of 2 and 4 with cellulose powder under different experimental conditions was carried out and they were found to exhibit promising fire-retardant properties.

Keywords. Triazine ; fire-retardants.

1. Introduction

Considerable research is currently being carried out to impart flame retardance to cotton textiles through chemical treatment. The best permanent flame retardants developed for cotton in recent years have been those based on organo-phosphorus compounds. One of the more recent laboratory finishes of this type is based on phosphinyltriazines (Chance and Moreau 1971). 2,4,6-Tris (dialkoxyphosphinyl)-*s*-triazines are commonly prepared by the Arbuzov or Michaelis reactions of chloro-*s*-triazines with tris- and bis-alkyl phosphites respectively (Hewertson *et al* 1963; Morrison 1957; Schröder 1959). This prompted us to synthesise 2,4,6-tris(dialkoxyphosphinyl)-*s*-triazine and its amino derivatives containing a heterocyclic ring and to evaluate their fire-retardant properties.

2. Discussion

Tris(tetrahydrofurfuryl)phosphite (1), prepared by the transesterification (Arbuzov and Zoroastrova 1961) of triethyl phosphite with tetrahydrofurfuryl alcohol in presence of phosphoric acid, when reacted with cyanuric chloride in 3 : 1 molar ratio at 80-90° for 2 hr under atmosphere of nitrogen yielded 2,4,6-tris (ditetrahydrofurfuroxy) phosphinyl-*s*-triazine (2) in 60% yield as an undistillable dark yellow syrupy liquid (decomposed above 180°/2 mm). Phosphinyl-*s*-

triazine (2) was stored under nitrogen atmosphere since it underwent decomposition on standing as indicated by the deposition of white amorphous product. Decomposition of liquid esters of cyanuric chloride has also been reported in literature (Hewertson *et al* 1963). A sample of compound (2) was purified by passing through a small column of florisil and eluting with a mixture of anhydrous acetone and diethylether (1 : 1). Elemental analyses, IR spectrum and NMR spectrum were consistent with the proposed structure 2. IR spectrum showed bands at 2960, 2860 ($-\text{CH}_2-$), 1510 (triazine ring), 1460, 1420 ($-\text{CH}_2-$), 1270 ($\text{P}=\text{O}$), 1075 ($-\text{C}-\text{O}-\text{C}$), 1040 ($\text{P}-\text{O}-\text{C}$) and 828 cm^{-1} (triazine ring). NMR spectrum showed signals at δ 1.40–1.98 (m, 18 H, β -hydrogens of tetrahydrofuran ring), 2.30–2.60 (m, 6H β' -hydrogens of tetrahydrofuran ring) and 2.97–4.00 (m, 30H, 18 protons of α -hydrogens of tetrahydrofuran ring and 12 protons of $\text{CH}_2-\text{O}-\text{P}$).

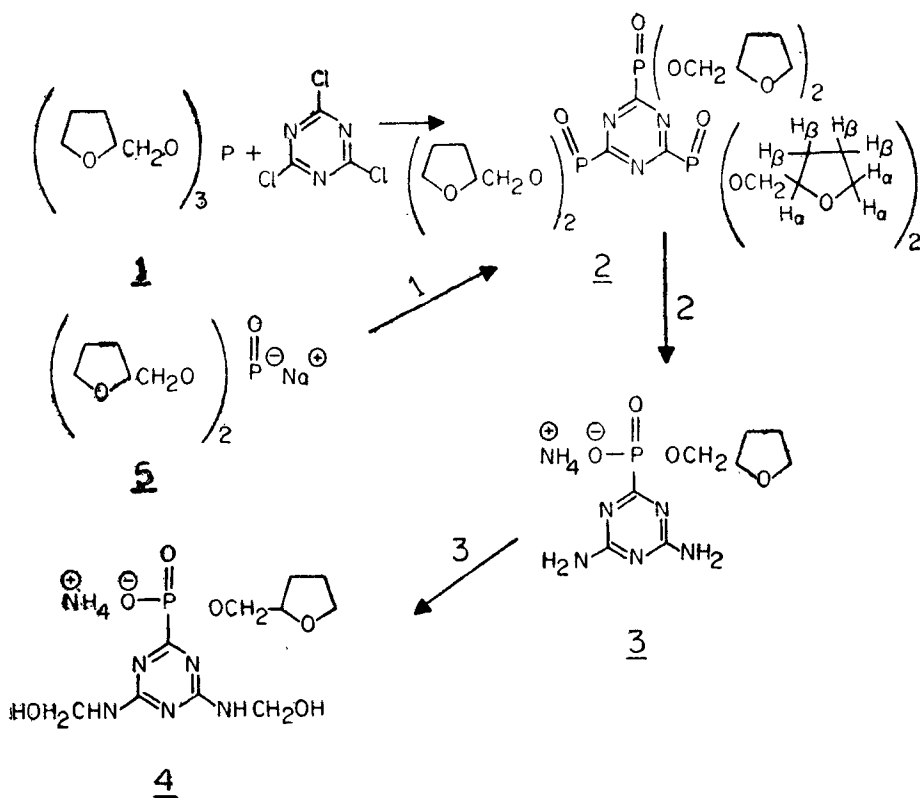


Chart I. 1. Cyanuric chloride, ether; 2. Anhydrous NH_3 and $\text{O}_2\text{H}_4\text{OH}$ or Benzene; 3. Formation.

2,4,6-Tris (di-tetrahydrofurfuroxy)phosphinyl-s-triazine (2) was also prepared by Michaelis reaction i.e. by refluxing an ethereal solution of cyanuric chloride and sodium bis (tetrahydrofurfuryl) phosphite (5) for 24 hr. The syrupy oil was identified by superimposable IR spectrum and elemental analyses. The yield in the latter method is, however, lower than the former one.

The amination product 3 of 2,4,6-tris (di-tetrahydrofurfuroxy)phosphinyl-s-triazine (2) was obtained by saturating an ethanolic solution of 2 with dry ammonia

following the method of Moreau (Moreau and Chance 1974). IR spectrum and elemental analyses showed that instead of the desired 2,4-diamino-6-bis(tetrahydrofurfuroxy)phosphinyl-*s*-triazine, a monoammonium salt (**3**) of the diamino compound was obtained. IR spectrum showed bands at 3380, 3200 ($-\text{NH}_2$ and $-\text{NH}_4^+$), 1640 (NH_2), 1530 (triazine ring), 1400 (NH_4^+), 1250 ($\text{P}=\text{O}$), 1080 ($\text{C}-\text{O}-\text{C}$), 1040 ($\text{P}-\text{O}-\text{C}$) and 800 cm^{-1} (triazine ring). **3** on boiling with dilute alkali gave ammonia which further supported the structure **3**. Ammonium salt (**3**) was also obtained when the amination of **2** was carried in anhydrous benzene. Formation of ammonium salts during the amination of 2,4,6-tris(diethoxy)phosphinyl-*s*-triazine has also been reported in literature (Moreau and Chance 1974).

Attempts to prepare the diamino derivative by reaction of 2,4-diamino-6-chloro-*s*-triazine with tris(tetrahydrofurfuryl)phosphite (**1**) resulted in failure. **3** when treated with formalin at pH 8.0 at 50° gave methylol derivative **4** which is characterised by the sec. NH str. at 1550 cm^{-1} .

Reaction of **2** and **4** with cellulose powder was studied under different conditions (*vide* tables 1 and 2 respectively). *p*-Toluene sulphonic acid as catalyst and trimethylether of hexamethylol melamine (TMM) as fixer were used in the present investigation to give the better add-on of P and N, the fire-retardant elements. The percentage of phosphorus in the compounds synthesised is 2.5–3.8% whereas the minimum requirement for P to render the cellulose self-extinguishing is 1.5% (Little 1947). The reaction results further show that percentage add-on of P and N in the reaction products both with and without solvent are more or less the same. Increase of refluxing period did not give better results. On the contrary, presence of TMM showed good results probably because of its capacity to form polymeric skeleton with the phosphinyl triazines (**2** and **4**) and the cellulosic hydroxyls. From the IR spectra of the reaction products obtained from cellulose and phosphinyl triazines (**2** and **4**), no conclusive evidence regarding the type of bonding could be obtained.

3. Experimental

Cyanuric chloride was recrystallised from carbon tetrachloride, dried in vacuum and stored under nitrogen and tetrahydrofurfuryl phosphites were distilled immediately before use. A pure sample of cellulose, supplied by Dassel, West Germany, was used. Infrared spectra were recorded on a Beckman IR 20 spectrophotometer. NMR spectrum was recorded on a Perkin Elmer 90 MHz spectrometer in $\text{DMSO}-d_6$ using TMS as the internal reference. TLC was performed on silica gel plate and column chromatography was run through florisil. All b.p. and m.p. are uncorrected.

3.1 Tris (tetrahydrofurfuryl) phosphite (**1**)

This was prepared by the transesterification of triethylphosphite with tetrahydrofurfuryl alcohol (Arbuzov and Zoraostrova 1961) in 60% yield b.p. $185-90^\circ/2.5\text{ mm}$ (Lit. (Arbuzov and Zoraostrova 1961) b.p. $170-71^\circ/1\text{ mm}$). IR $\nu_{\text{max}}^{\text{neat}}$ 2970, 2930 (CH_2), 1630, 1450, 1255 ($\text{P}=\text{O}$), 1075 ($\text{C}-\text{O}-\text{C}$), 1030 ($\text{P}-\text{O}-\text{C}$), 830 and 800 cm^{-1} .

3.2. 2,4,6-Tris(ditetrahydrofurfuroxy)phosphinyl-*s*-triazine (2)

(a) By Arbuzov reaction

Cyanuric chloride (18.4 g, 0.1 mole) was added in small portions to tris(tetrahydrofurfuryl)phosphite (1, 100 g, 0.3 mole) taken in a three-necked flask equipped with a stirrer, nitrogen inlet tube and a reflux condenser carrying a calcium chloride guard tube. The flask was gradually heated to 80–90° in an atmosphere of nitrogen and maintained at this temperature for 2 hr. Tetrahydrofurfuryl chloride and unreacted cyanuric chloride were removed under vacuum (100°/2 mm). The undistillable dark yellow oily syrup (2) (40 g, 60%) was stored under nitrogen. The analytical sample was prepared by passing a solution of compound 2 in dry acetone through a small column of florisil and eluting with a mixture of dry acetone and diethyl ether (1 : 1). The chromatographed product gave a single spot when run on a silica gel TLC plate using acetone, pet. ether (40–60°) and methanol (7 : 5 : 1), R_f value 0.51. (Found : C, 47.87; H, 7.17; N, 4.8; P, 10.74. $C_8H_{17}N_6O_4$ requires C, 48.0; H, 6.54; N, 5.1; P, 11.30%).

(b) By Michaelis reaction

A mixture of cyanuric chloride (4.6 g, 0.025 mole) and sodium bis(tetrahydrofurfuryl)phosphite (5, 20.4 g, 0.075 mole, prepared by reacting 1.725 g of sodium with 18.75 g of bis(tetrahydrofurfuryl)phosphite) in anhydrous ether (150 ml) was refluxed for 24 hr under nitrogen atmosphere. Sodium chloride was removed and evaporation of solvent furnished 8 g (40%) of the desired product as a dark yellow liquid. Its identity was established by superimposable IR spectrum and R_f value 0.51.

3.3 Ammonium salt of 2,4-diamino-6-tetrahydrofurfuroxy-phosphinyl-*s*-triazine (3)

2,4,6-Tris(di-tetrahydrofurfuroxy)phosphinyl-*s*-triazine (2), 20 g in absolute ethanol (100 ml) was saturated with dry ammonia. Ammonia was passed at such a rate that the temperature did not rise above 10°. The reaction mixture was then kept at room temperature for 3 days. The white solid thus separated was filtered and washed with acetone. On crystallisation from water, it furnished white needles, m.p. 275° (decomposition), yield 4 g (56%). (Found C, 32.03; H, 5.36; N, 28.40; P, 10.91. $C_8H_{17}N_6PO_4$ requires C, 32.53; H, 5.82; N, 28.76; P, 10.61%).

3.4 Methylation of (3) formation of 4

To 3 (1.92 g, 0.01 mole) was added 36% formalin (1.66 ml, 0.02 mole) and the pH of the mixture was adjusted to 8 by the addition of NaOH. The reaction mixture was heated under stirring at 50° for 2 hr. The mixture was concentrated in vacuum and the syrupy liquid, obtained in almost quantitative yield, could not be distilled as it polymerised on heating above 150° even under reduced pressure (2 mm). (Found C, 33.86; H, 5.81; N, 23.52; P, 8.65. $C_{10}H_{21}N_6PO_6$ requires C, 34.09; H, 5.96; N, 23.76; P, 8.80%).

3.5 Reaction of cellulose with 2 and with 4

A stirred mixture of cellulose powder and compound 2 and 4 (*vide* tables 1 and 2) in presence of 0.5 g of *p*-toluenesulphonic acid and 60 ml of dry *p*-xylene was refluxed for 3 hr using a Dean and Stark water separator. After 0.3 ml of water was separated, the solvent decanted off and the product was washed with water and finally with acetone till the filtrate is free from P and N. Dried in vacuum and analysed for P and N (*vide* tables 1 and 2). In a separate lot, the period of refluxing was increased to 6 hr. The same reaction was also studied in presence of trimethylether of hexamethylmelamine. Similar reaction was also carried out using no solvent and no fixer (TMM). The results obtained with or without solvent or TMM are recorded in tables 1 and 2.

Table 1. Reaction of cellulose with 4.

| Reaction mixture composition | | | Molar ratio of reactants | Solvent | Temp. °C | Time (hr) | Analysis | |
|------------------------------|----------|------|--------------------------|------------------|----------|-----------|----------|-------|
| Cellulose | Compound | TMM | | | | | P | N |
| (4) | | | | | | | | |
| 1.62* | 3.52 | .. | 1 : 1 : 0 | <i>p</i> -xylene | 138 | 6.0 | 2.56 | 6.92 |
| 1.62 | 3.52 | 3.48 | 1 : 1 : 1 | <i>p</i> -xylene | 138 | 6.0 | 2.91 | 10.90 |
| 1.62 | 3.52 | .. | 1 : 1 : 0 | .. | 160 | 1.5 | 2.58 | 6.79 |
| 1.62 | 3.52 | 3.48 | 1 : 1 : 1 | .. | 160 | 1.5 | 2.99 | 12.24 |
| 1.62 | 7.04 | .. | 1 : 2 : 0 | <i>p</i> -xylene | 138 | 6.0 | 2.69 | 7.50 |
| 1.62 | 7.04 | 3.48 | 1 : 2 : 1 | <i>p</i> -xylene | 138 | 6.0 | 2.87 | 12.01 |
| 1.62 | 7.04 | .. | 1 : 2 : 0 | .. | 160 | 1.5 | 2.46 | 6.48 |
| 1.62 | 7.04 | 3.48 | 1 : 2 : 1 | .. | 160 | 1.5 | 2.93 | 12.06 |

* Based on the molecular weight of one anhydrous glucose unit i.e. 162.

Table 2. Reaction of cellulose with 2.

| Reaction mixture composition | | | Molar ratio of reactant | Solvent | Temp. °C | Time (hr) | Analysis % | |
|------------------------------|----------|------|-------------------------|------------------|----------|-----------|------------|-------|
| Cellulose | Compound | TMM | | | | | P | N |
| (2) | | | | | | | | |
| 1.62 | 8.25 | 3.48 | 1 : 1 : 1 | <i>p</i> -xylene | 138 | 6.0 | 3.65 | 12.01 |
| 1.62 | 8.25 | 3.48 | 1 : 1 : 1 | .. | 160 | 1.5 | 3.81 | 14.58 |
| 1.62 | 16.50 | 3.48 | 1 : 2 : 1 | <i>p</i> -xylene | 138 | 6.0 | 3.76 | 14.04 |
| 1.62 | 16.50 | 3.48 | 1 : 2 : 1 | .. | 160 | 1.5 | 3.86 | 15.10 |

Acknowledgements

The authors wish to express their sincere thanks to Professor H K Pujari for keen interest and useful discussions and to the US Department of Agriculture, Far Eastern Agriculture Research Service, for the grant of research fellowship to BSS and IH.

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