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Syntheses of *bis* (tetrahydrofurfuryl) phosphonopropyl nitrile, 1-methyl-2-*bis* (tetrahydrofurfuryl) phosphonopropyl nitrile and 0,0-*bis* (tetrahydrofurfuryl)-2,2,2-trichloro-1-hydroxyethyl-phosphonate as possible flame retardants to cellulose

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Abstract. The reaction of *bis* (tetrahydrofurfuryl)-phosphite (1) with acrylonitrile (2), methyl acrylonitirle (4) and chloral (6) gave *bis* (tetrahydrofurfuryl)phosphonopropyl nitrile (3), 1-methyl-2-*bis* (tetrahydrofurfuryl)-phosphonopropyl nitrile (5) and 0-0-*bis* (tetrahydrofurfuryl)-2,2,2-trichloro-1-hydroxyethyl-phosphonate (7) respectively. The reaction of cellulose powder with compounds 3, 5 and 7 were studied under different conditions and their fire retardancy properties explained based on the elemental analysis.

Keywords. Synergistic effects; flame retardants; alkylphosphonates.

1. Introduction

The synergistic effects of phosphorus and nitrogen (Tesoro *et al* 1969) and phosphorus and halogens (Weill and Smith 1965) have been studied in various phosphorus compounds and found useful in giving durable and better flame retardant finishes to cotton textiles. The present communication deals with the syntheses of three alkylphosphonates containing a heterocyclic ring, i.e., a tetrahydrofuran ring and their possible fire retardant properties.

2. Discussion

Bis (tetrahydrofurfuryl) phosphite (1) when treated with acrylonitrile (2) in presence of small amount of a saturated solution of sodium tetrahydrofurfuroxide in tetrahydrofurfuryl alcohol gave *bis* (tetrahydrofurfuryl) phosphonopropyl nitrile (3) as a viscous liquid b.p. 220°/1·5 mm. In an another reaction, *bis* (tetrahydrofurfuryl) posphite (1) was treated with methylacrylonitrile (4) in the presence of a saturated solution of sodium tetrahydrofurfuroxide in tetrahydrofurfuryl alcohol to give 1-methyl-2-*bis* (tetrahydrofurfuryl) phosphonopropyl nitrile (5)

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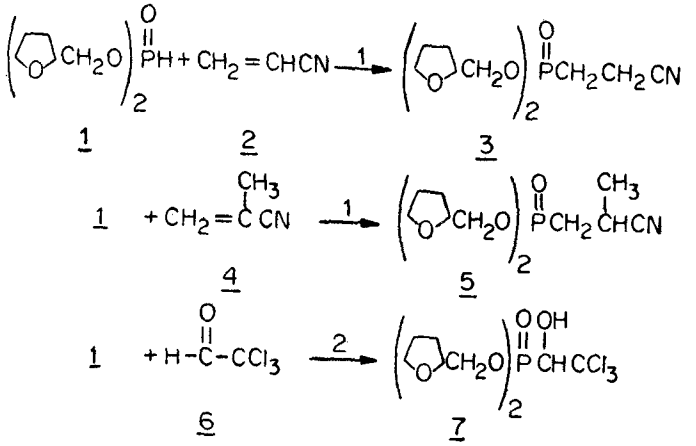
as a viscous liquid. 5 could not be distilled as it decomposed above 220°/1·5 mm. Reaction of *bis* (tetrahydrofurfuryl) phosphite (1) was also studied with chloral (6) with a view to synthesizing a compound containing phosphorus and halogen which are found to augment the fire-retardant properties (Weil and Smith 1965) in addition to a free CH_2OH group available for reaction with the cellulose molecule. 0, 0-*bis* (tetrahydrofurfuryl)-2, 2, 2-trichloro-1-hydroxyethylphosphonate (7) was formed through an exothermic reaction between 1 and chloral.



1. Sodium tetrahydrofurfuroxide in tetrahydrofurfuryl alcohol,80–90°.
2. 25° (Room temp.)

Chart 1

Analytical samples of 3, 5 and 7 were prepared by passing them through columns of florisil. Their structures have been characterized by elemental analyses, IR and NMR spectral data. IR spectrum of 3 showed bands at 2940, 2880 (CH_2), 2240 (C≡N), 1455 (CH_2–CN), 1250 (P=O), 1040 (C–O–C) and 850 (P–O–C) cm^{-1}. NMR spectrum showed signals at δ 1·2–2·0 (m, 8H, β-hydrogens of tetrahydrofuran), 3·7–4·0 (M, 10H, 6 protons for α-hydrogens of tetrahydrofuran, 4 protons for two-CH_2–O–P), 2·27–2·70 (*m*, 4H, 2 for CH_2–P) and 2 for CH_2CN). IR spectrum of 5 showed bands at 2880 (CH_2), 2240 (C≡N), 1455 (CH_2–CN), 1250 (P=O), 1040 (C–O–C), 850 (P–O–C) cm^{-1}. NMR spectrum showed signals at δ 1·4 (*m*, 3H, $-\overset{CH_3}{\overset{|}{C}}-CN$), 1·75–2·05 (*m*, 8H, β-hydrogens of tetrahydrofuran), 2·4–3·2 (*m*, 3H, 2 for CH_2–P and one for $-CH-CN$), 3·7–4·1 (*m*, 10H, 6 protons for α-hydrogens of tetrahydrofuran and 4 protons for two CH_2–O–P). IR spectrum of 7 showed band at 2950, 2880 (CH_2), 1260 (P=O), 1025, 920 (–C–O–C), 870 (P–O–C), 730 ($-CCl_3$), 620 (CCl_3) cm^{-1}. NMR spectrum showed signals at 1·2 (*s*, 1H, $O-P-\overset{H}{\overset{|}{C}}(OH)\,CCl_3$), 1·4–2·2 (*m*, 8H, β-hydrogens of tetrahydrofuran), 3·6–4·6 (*m*, 10H, 6 protons for α-hydrogens of tetrahydrofuran and 4 protons for two CH_2–O–P). The hydroxyl proton was not observed in the normal range of the spectrum.

3. Experimental

IR spectra were taken neatly on a Beckman IR–20 spectrophotometer and NMR spectra were recorded on a Perkin–Elmer 90 MHz spectrometer in $CDCl_3$ and CCl_4 using TMS as the internal reference. TLC was performed on silica gel and column chromatography was run through florisil. A pure sample of cellulose, supplied by Dassel, West Germany, was used. Boiling points and melting points are uncorrected.

3·1 *Preparation of* bis (*tetrahydrofurfuryl*) *phosphonopropyl nitrile* (3)

To a stirred mixture of *bis* (tetrahydrofurfuryl) phosphite (1, 12·5 g, 0·05 mole) and acrylonitrile (2, 2·65 g, 0·05 mole) was added dropwise and a saturated solution of sodium tetrahydrofurfuroxide in tetrahydrofurfuryl alcohol (8 ml). On addition of approximately 5 ml of the catalyst, a vigorous exothermic reaction took place and temperature rose to 90°. Further addition of the catalyst was regulated so as to control the reaction temperature between 80° and 90°. The reaction mixture was further heated at 80–90° under stirring for another 1 hr. Tetrahydrofurfuryl alcohol and unreacted acrylonitrile were removed under vacuum The residual product was distilled at 220°/1·5 mm to give 10 g of compound 3, yield 66%. 2·0 g of 3 was further purified by passing through a column of florisil (30 g) using ether : acetone in different ratio as eluent. The fraction corresponding to the solvent system of ratio 1 : 1 on evaporation gave colourless moderately viscous liquid. It gave a single spot on a silica gel plate using acetone benzene (1 : 1) solvent system, R_f value 0·54 found C, 51·39 ; H, 7·21 ; P 10·16 ; N, 4·84 ; $C_{13}H_{22}NO_5P$ require C, 51·48 ; H, 7·26 ; P, 10·23 ; N, 4·64%

3·2. 1-*Methyl*-2-*bis* (*tetrahydrofurfuryl*) *phosphonopropyl nitrile* (5)

This was obtained from 1 and methyl acrylonitrile (4) following the above procedure. Attempts to distil the residue failed as the product decomposed above 220°/1·5 mm. However, the crude product (2·59 g) was purified by passing through a column of florisil (30 g) using pet. ether (60–80°) : ethyl acetate (1 : 3) as eluent. It gave a single spot on silica gel TLC plate using ethyl acetate : pet. ether (60–80°) (9 : 1) as solvent, R_f value of 0·44, yield 1·5 g (60%) found C, 53·58 ; H, 7·15 ; N, 4·53 ; P, 10·01 ; $C_{14}H_{24}NO_5P$ requires C, 53·00 ; H, 7·57 ; N, 4·41 ; P, 9·78%.

3.3 0, 0-Bis (*tetrahydrofurfuryl*)-2, 2, 2-*trichloro*-1-*hydroxyethyl-phosphonate* (7)

Chloral (6, 7·5 g, 0·05 mole), purified by distilling chloral hydrate over concentrated H_2SO_4, was added dropwise to *bis* (tetrahydrofurfuryl) phosphite (1, 12·5 g, 0·05 mole) with constant stirring. An exothermic reaction ensued and temperature shot up to 100°. Further additions were made at such a rate that temperature did not rise above 90°. After complete addition of chloral, the reaction mixture was kept at 90° for 1 hr. The viscous colorless product, thus obtained, could not be distilled as it decomposed on heating above 220°/1·5 mm. The crude product (2·5 g) was, however, purified by passing through a column of florisil (30 g) using ethyl acetate : Pet. ether (60–80°) (1 : 1), gave a single spot on silica

gel TLC plate using ethyl acetate : pet. ether (60–80°) (3 : 1), R_f value 0·4, yield 80% found C, 35·69 ; H, 4·81 ; P, 7·92 ; Cl, 26·12 ; $C_{12}H_{20}O_6PCl_3$ requires : C, 36·23 ; H, 5·03 ; P, 7·79 ; Cl, 26·79%.

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