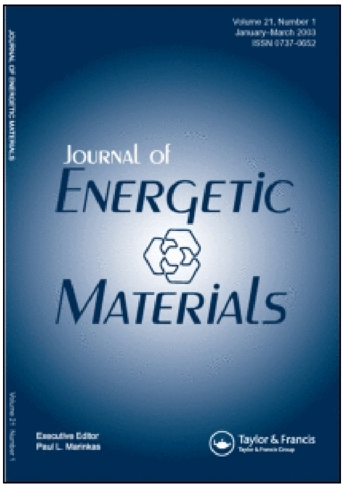

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Synthesis of 1-Oxo-4-Hydroxymethyl-2,6,7-Trioxa-1-Phosphabicyclo[2,2,2] Octane Derivatives*

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ABSTRACT

Three 1-oxo-4-hydroxymethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2] octane energetic derivatives were synthesized. The molecular structure of the products has been confirmed by MS, IR,^{1} H NMR and elemental analysis.Some physical properties of these products including density and thermal decomposition are reported.

INTRODUCTION

1-Oxo-4-hydroxymethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2] octane (PEPA) (1)was first synthesized by Verkade[1] in 1960. Its derivatives have many special properties[2] due to highly symmetric caged molecular structure. Some derivatives have been used as pesticide[3], weedicide[4], fungicide, insecticide, fire retardant and other kinds of additives[5,6,7], so its derivatives have attracted considerable interests of researchers[8]. Phosphate group has plasticizing function and the bonding property; The energetic additives with nitrate or azido group are preferred to non-energetic ones in the rocket propellants due to contribution of the energy to system (azido group can provide with high heat of formation ΔH_f=365kJ/mol).In view of the above considerations we synthesised three title compounds which are expected to be used as additives of energetic material.

RESULTS AND DISCUSSION

We work out the reaction routes as follows:

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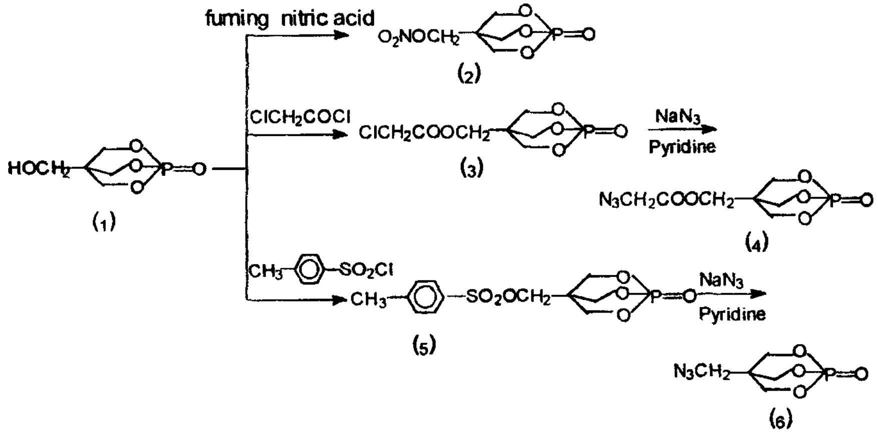

The compound (2) has easily been obtained by direct treatment of 1-oxo-4-hydroxymethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2] octane (1) with fuming nitric acid, with yields higher than 90% even under conditions of long reaction time and high temperature. The preparation of 1-oxo-4-(chloro-acetoxy)methylene-2,6,7-trioxa-1-phosphabicyclo[2.2.2] octane (3) by the reaction of (1) with chloroacetyl chloride is so easy that no catalyst is needed.The reaction of (3) with sodium azide takes 48 hours at 40 ℃ and the yield of 1-Oxo-4-(azido-acetoxy) methylene-2,6,7-trioxa-1-phosphabicyclo[2.2.2] octane(4) obtained is low. Its molecular structure has been confirmed by elemental analysis IR and ^1H NMR. In the synthesis of 1-oxo-4-(azido)-methylene-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (6), the preparation of raw material 1-oxo-4-(p-tosyl)-methylene-2,6,7-trioxa-1-phosphabicyclo[2.2.2] octane (5) was convient, but the introduction of azido group was so difficult that high temperature and long time are required.

Table 1 Comparison of Physical Properties (2),(4) and (6)

Properties	(2)	(4)	(6)
Decomposition temperature (DSC, 10 ℃/min)	215 ℃	240 ℃	260 ℃
Density(g/cm^3)	1.663	1.600	1.595

The physical properties of the three compounds are illustrated in table 1.The data of DSC shows that the decomposition temperature of compound (4) is lower than (6) probably due to the presence of electron-withdrawing carboxilic group near the azido group in the molecule of compound (4). It can also be seen in table 1 that compound (6) is more stable to heat than compound (2), this means that in this case the azido group is more stable than the nitrate.

EXPERIMENTAL

Melting point were measured on WC-1 hot-stage apparatus and elemental analyses on Carlo Erba 1102 instrument. IR spectra were recorded on a Shimadzu IR-408 spectrophotometer, MS spectra were recorded on a Varian-MAT-731 spectrophotometer and ^{1}H NMR spectra on Bruker DMX-300 spectrophotometer (TMS as internal standard).

1-Oxo-4- (nitrate group)methylene-2,6,7-trioxa-1-phosphabicyclo[2.2.2] octane (2)

1-oxo-4-hydroxymethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2] octane (1) (1.0g) was slowly added to fuming nitric acid (10ml) in an open beaker below 5 ℃ and continued the stirring for 30 min. After the addition, large amount of ice was added with rapid stirring. The precipitate was filtered off and washed with water and then dried. The product was recrystallised from ethanol and give 1.2 g of product. The yield is 96.0%. mp 188 – 190 ℃. IR(KBr): 1630, 1320 (ONO_2), 1270 (P=O) cm^{-1}. ^{1}H NMR(Me_2CO-d_6):δ4.78-4.80(d,6H), 4.63(s,2H) .MS(m/z): 226(M^+). Anal Calcd for $C_5H_6O_7P$: C, 26.67; H,3.55; N,6.22. Found: C, 26.46; H, 3.44; N, 6.10%.

1-Oxo-4-(chloro-acetoxy)methylene-2,6,7-trioxa-1-phosphabicyclo[2.2.2] octane (3)

1-oxo-4-hydroxymethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2] octane (3.0g) was slowly added to chloroacetyl chloride (7ml) at ice-water bath and the reaction mixture was maintained at 60 ℃ for 8h, then the precipitate was obtained by filtration and washing with water. The product was crystallised from acetone and give 3.0g(70.2%) of product. mp 151 – 153 ℃.IR(KBr): 1760 (C=O), 1280 (P=O) cm^{-1}.Anal calcd for $C_7H_{10}O_6P$: C, 32.76; H, 3.9; H. Found: C, 32.76; H,4.01%.

1-Oxo-4-(azido-acetoxy) methylene-2,6,7-trioxa-1-phosphabicyclo[2.2.2] octane (4)

1-oxo-4-(chloro-acetoxy)methylene-2,6,7-trioxa-1-phosphabicyclo[2.2.2] octane (3) (1.0g) dissolved in pyridine (10ml) was added to sodium azide (1.0g) in pyridine (25ml) at ambient temperature. After the addition, the reaction mixture was heated at 40 ℃ for 48h. The solids were removed by filtration. The solvent was removed from the filtrate under reduced pressure to give a crude product which was distillated (28 ℃, 5 torr) to yield 0.7g (68.2%) of light yellow crystal. The product was crystallised from acetone. mp 141 – 143 ℃.IR(KBr): 2100 (N_3), 1750 (C=O), 1295 (P=O) cm^{-1}. ^{1}H NMR(Me_2CO-d_6): δ4.75-4.77(d,6H), 4.20(s,2H),4.13(s,2H). MS(m/z):264(M^+).Anal calcd for $C_7H_{10}O_6N_3P$: C, 31.94; H, 3.80; N, 15.97. Found: C,32.69; H, 3.73; N, 15.64%.

1-Oxo-4-(p-tosyl)-methylene-2,6,7-trioxa-1-phosphabicyclo[2.2.2] octane (5)

p-toluenesulfochloride (1.1g) dissolved in pyridine (6.2ml) was added to 1-oxo-4-hydroxymethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2] octane (1.0g) in pyridine (12.0ml) below 3 ℃. The reaction mixture was stirred for 12h at ambient temperature, then poured onto ice-water (200ml). The crude product was obtained by filtration, washed with water, and recrystallised from Cloroform-ethnol(1:1). The yield is 0.93g (50.3%). mp 250 – 251 ℃.

IR(KBr): 1350 (SO_2), 1300 (P=O), 1600 (C=C)cm^{-1}.Anal calcd for $C_{12}H_{15}O_7PS$: C, 43.11; H,4.49. Found: C, 42.85; H,4.39%.

1-Oxo-4-(azido)-methylene-2,6,7-trioxa-1-phosphabicyclo[2.2.2] octane (6)

1-oxo-4-(p-tosyl)-methylene-2,6,7-trioxa-1-phosphabicyclo[2.2.2] octane (5) (1.0g) dissolved in pyridine (7ml) was added to sodium azide (1.0g) in pyridine (20ml). The reaction mixture was heated at 105 ℃ for 30h. After cooling, the solids were removed by filtration. The solvent was removed from the filtrate under reduced pressure and the semi-solid product was obtained. When petroleum ether was added , the solid product was entirely precipitated. The crude product was recrystallised from acetone.The yield is 48.9%. mp 179 - 182 ℃.IR(KBr): 2200 (N_3), 1300 (P=O)cm^{-1} . ^{1}H NMR(Me_2CO-d_6):δ4.66-4.68(d,6H), 3.61(s,2H) .MS(m/z):206(M^+).Anal calcd for $C_5H_8O_5N_3P$: C, 29.27; H, 3.90; N, 20.49. Found: C, 29.03; H, 3.74; N, 20.46%.

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