p-NITROPHENYL AND p-NITROBENZOYL DERIVATIVES OF O,O' – ALKYLENE DITHIOPHOSPHATE

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(Received: May 28, 2007 - Accepted: March 4, 2008)

ABSTRACT

p-Nitrophenyl and p-nitrobenzoyl derivatives of O,O'-alkylene dithiophosphate, OGOP(S)SC₆H₄NO₂ and OGOP(S)SCOC₆H₄NO₂ (Where G = -CMe₂CMe₂-, -CH₂CMe₂CH₂-, -CMe₂CH₂CHMe-, -CH₂CH₂CHMe-) have been synthesized by the reactions of p-bromo nitrobenzene / p-nitrobenzoyl chloride with ammonium salt of alkylene dithiophosphoric acids. These derivatives are yellow and red coloured solids, respectively and are soluble in common organic solvents. These are characterized by elemental analysis, IR and NMR (¹H and ³¹P) spectral studies. In contrast to the bi-dentate chelating behaviour of the ligand in the metal and organometal derivatives of alkylene dithiophosphates, the behaviour of dithiophosphato moiety in these derivatives is found to be mono-dentate in nature.

Keywords :- p-Bromo nitrobenzene, p-nitrobenzoyl chloride, ammonium salt of alkylene dithiophosphoric acids.

INTRODUCTION

Alkylene dithiophosphoric acids are known as cyclic analogous of dialkyl dithiophosphoric acid (open chain)¹. Large number of organic derivatives of dialkyl dithiophosphate have been described in the early literature²⁻⁴ but the corresponding organic derivatives of alkylene dithiophosphate are still less known⁵⁻⁸.

The chemistry of metal alkylene dithiophosphates has been extensively reported in the literature⁹⁻¹². Alkylene dithiophosphate and their metal derivatives are used as agro chemical¹³, oil additive¹⁴, antioxidant¹⁵ and as floating agents¹⁶.

The present paper deals with the corresponding reaction of p-bromo nitrobenzene and p-nitrobenzoyl chloride with ammonium salt of alkylene dithiophosphates.

EXPERIMENTAL

Ammonium salts of O,O'-alkylene dithiophosphoric acids, p-bromo nitrobenzene and p-nitrobenzoyl chloride have been synthesized by the methods reported in the literature¹⁴. All the solvents used during present investigation, were of reagent grade and even made anhydrous by standard methods. Sulphur was estimated gravimetrically as barium sulphate (Messenger's method)¹⁷. Molecular weights were determined by Knauer vapour pressure osmometer in chloroform. FTIR spectra were recorded on Shimadzu 8201 PC spectrophotometer in the range of 4000-400 cm⁻¹ using CsI cells. ¹H NMR spectra were recorded in CDCl₃ and ³¹P NMR spectra were recorded in benzene on Bruker DRX 300 spectrophotometer using TMS (for ¹H) and H₃PO₄ (for ³¹P) as external references.

Reaction of p-nitrobenzoyl chloride with ammonium tetramethyl ethylene dithiophosphate

Ammonium tetramethyl ethylene dithiophosphate (1.12g; 4.89 mmole) was refluxed with p-nitrobenzoyl chloride (0.92g; 4.96 mmole) in anhydrous benzene for 6 hrs. Ammonium chloride was removed by filtration. Yellow coloured product was separated out by removing the solvent from the filtrate. The product was washed 3-4 times with n-hexane and recrystallized (Calcd. for -OCMe₂CMe₂OP(S)SC(O)PhNO₂ H=4.43%, C=43.21%, S=17.73%) Found - H=4.36%, C=42.98%, S=17.60%).

RESULTS AND DISCUSSION

Synthesis of p-nitrophenyl derivatives of alkylene dithiophosphate have been successfully carried out by the reactions of p-bromo nitrobenzene with ammonium salts of alkylene dithiophosphoric acid in anhydrous benzene for 10hrs. Ammonium bromide is precipitate out as side product and is being removed by filtration. Then the product is obtained by stripping off the solvent from the filtrate.

p-nitro benzoyl derivatives of alkylene dithiophosphate have been prepared by similar method.

(Where G = -CMe₂CMe₂-, -CH₂CMe₂CH₂-, -CMe₂CH₂CHMe-, -CH₂CH₂CHMe-)

During the reaction period, it has been observed that the colour of reaction mixture (I) changes from colourless to yellow and as the reaction progressed, it becomes dirty yellow while colour of reaction mixture (II) changes from colourless to reddish yellow and as the reaction progressed, it becomes red. Reaction (II) seem to be fast in comparison to reaction (I). It appears that due to the presence of deactivating carbonyl group, nucleophilic displacement of chloride ion by dithiophosphato moiety becomes easy. So these reactions require short duration in comparison to reaction of p-bromo nitrobenzene with ammonium salt of alkylene dithiophosphates, for completion. The products, thus obtained are yellow and red coloured solids, soluble in common organic solvents but are insoluble in n-hexane and are purified by washing 3-4 times with n-hexane and then re-crystallized.

SPECTRAL ANALYSIS

IR Spectra

IR spectra of these derivatives are summarized in Table-2 and show the following characteristic changes:

- (1) An absorption band at 3080-3060 cm⁻¹ in all the compounds may be ascribed to aromatic C-H stretching vibrations.
- (2) Nitro group in these derivatives show strong absorption band at 1550-1520 cm⁻¹ which show slight shift towards lower wave number (15 cm⁻¹) in comparison to p-bromo nitrobenzene. It may be due to lesser nucleophilicity of dithiophosphato moiety in comparison to bromine atom present in p-bromo nitrobenzene.
- (3) The absorption band present in the region 1145-1130 cm⁻¹ and 885-870 cm⁻¹ may be assigned to (P)-O-C and P-O-(C) stretching vibrations, respectively.
- (4) A strong absorption band due to dioxaphospholone and dioxaphosphorinane ring vibrations is present in the region 955-800 cm⁻¹.
- (5) A sharp band assigned to ν_{P=S} absorptions in the region 860-810 cm⁻¹ show shifting towards higher frequency with respect to its position in the free ligand. This shifting is due to presence of deactivating nitro group in the aromatic ring.
- (6) A new band has been observed in the region 710-625 cm⁻¹ due to the carbon-sulphur bond. Appearance of this band supports the formation of

- (7) The absorption bands of medium intensity in the region 565-540 cm⁻¹ have been attributed to ν_{P-S} asymmetric and symmetric vibrations.

Syntheses of similar derivatives are summarized in Table-1.

Table.1. Synthetic and analytical data of p-nitrophenyl and p-nitrobenzoyl derivatives of O,O' –alkylene dithiophosphates.

S.No.	Reactants (g)		Product -----g; -----%	Analyses Found -----(Calcd.-----)			Mol.Wt. Found----- (Calcd.-----)
	OGOP(S)SNH ₄ G = ----- -----g(-----mmole)	XC ₆ H ₄ NO ₂ X = ----- -----g(-----mmole)		C %	H %	S %	
1	-CMe ₂ CMe ₂ - 1.09(4.76)	Br 0.96(4.78)	OCMe ₂ CMe ₂ OP(S)SPhNO ₂ 1.24 78.48	42.98 (43.24)	4.58 (4.80)	18.83 (19.21)	-
2	-CH ₂ CMe ₂ CH ₂ - 1.14(5.30)	Br 1.07(5.32)	OCH ₂ CMe ₂ CH ₂ OP(S)SPhNO ₂ 1.34 79.29	40.99 (41.38)	4.24 (4.39)	19.60 (20.06)	300 (319)
3	-CMe ₂ CH ₂ CHMe- 1.19 (5.20)	Br 1.06(5.27)	OCMe ₂ CH ₂ CHMeOP(S)SPhNO ₂ 1.42 82.08	43.00 (43.24)	4.62 (4.80)	18.72 (19.21)	-
4	-CH ₂ CH ₂ CHMe 1.01 (5.02)	Br 1.01 (5.02)	OCH ₂ CH ₂ CHMeOP(S)SPhNO ₂ 1.32 86.22	39.01 (39.34)	3.84 (3.93)	20.45 (20.98)	-
5	-CMe ₂ CMe ₂ - 1.12(4.89)	Cl(O)C 0.92 (4.96)	OCMe ₂ CMe ₂ OP(S)SC(O)PhNO ₂ 1.41 80.11	42.98 (43.21)	4.36 (4.43)	17.60 (17.73)	351 (361)
6	-CH ₂ CMe ₂ CH ₂ - 1.25(5.81)	Cl(O)C 1.08(5.82)	OCH ₂ CMe ₂ CH ₂ OP(S)SC(O)PhNO ₂ 1.65 82.08	41.01 (41.50)	3.92 (4.03)	18.36 (18.41)	-
7	-CMe ₂ CH ₂ CHMe- 1.14(4.98)	Cl(O)C 0.93 (5.01)	OCMe ₂ CH ₂ CHMeOP(S)SC(O)PhNO ₂ 1.61 89.44	42.95 (43.21)	4.36 (4.43)	17.65 (17.73)	-
8	-CH ₂ CH ₂ CHMe- 0.92(4.58)	Cl(O)C 0.85(4.58)	OCH ₂ CH ₂ CHMeOP(S)SC(O)PhNO ₂ 1.22 80.26	38.94 (39.64)	3.50 (3.60)	19.13 (19.21)	308 (333)

Table 2. IR spectral data of p-nitrophenyl and p-nitrobenzoyl derivatives of O,O' – alkylene dithiophosphates

S.No.	Compound	v(P)-O-C	vP-O-(C)	Ring vibrations	vP=S	vC-S	vP-S	vC=O	vC-NO ₂
1	OCMe ₂ CMe ₂ OP(S)SPhNO ₂	1145	885	955	810	670	550	-	1550
2	OCH ₂ CMe ₂ CH ₂ OP(S)SPhNO ₂	1130	870	800	825	690	565	-	1520
3	OCMe ₂ CH ₂ CHMeOP(S)SPhNO ₂	1150	880	910	820	625	540	-	1545
4	OCH ₂ CH ₂ CHMeOP(S)SPhNO ₂	1140	880	920	815	645	555	-	1525
5	OCMe ₂ CMe ₂ OP(S)SC(O)PhNO ₂	1143	890	920	860	700	570	1730	1525
6	OCH ₂ CMe ₂ CH ₂ OP(S)SC(O)PhNO ₂	1145	870	900	850	695	565	1720	1560
7	OCMe ₂ CH ₂ CHMeOP(S)SC(O)PhNO ₂	1155	875	870	840	710	565	1735	1520
8	OCH ₂ CH ₂ CHMeOP(S)SC(O)PhNO ₂	1150	880	890	850	700	575	1740	1530

Table 3. ¹H and ³¹P NMR spectral data of p-nitrophenyl and p-nitrobenzoyl derivatives of O,O' – alkylene dithiophosphates

S.No.	Compound	¹ H Chemical Shift (δ ppm)	³¹ P
1	OCMe ₂ CMe ₂ OP(S)SPhNO ₂	1.6, s, 12H(CH ₃); 7.5, m, 4H(C ₆ H ₄)	94.09
2	OCH ₂ CMe ₂ CH ₂ OP(S)SPhNO ₂	1.1, s, 6H(CH ₃); 5.1, d, 4H(CH ₂ O); 7.6, m, 4H(C ₆ H ₄)	82.92
3	OCMe ₂ CH ₂ CHMeOP(S)SPhNO ₂	1.5, m, 11H(CH ₃ , CH ₂); 5.1, m, 1H(OCH); 7.6, m, 4H(C ₆ H ₄)	81.17
4	OCH ₂ CH ₂ CHMeOP(S)SPhNO ₂	1.5, s, 3H(CH ₃); 4.4, m, 2H(CH ₂ O); 5.0, m, 1H(POCH); 7.7, m, 4H(C ₆ H ₄)	91.00
5	OCMe ₂ CMe ₂ OP(S)SC(O)PhNO ₂	1.6, s, 12H(CH ₃); 7.8, m, 4H(C ₆ H ₄)	77.89
6	OCH ₂ CMe ₂ CH ₂ OP(S)SC(O)PhNO ₂	1.1, s, 6H(CH ₃); 5.1, d, 4H(CH ₂ O); 7.7, m, 4H(C ₆ H ₄)	71.32
7	OCMe ₂ CH ₂ CHMeOP(S)SC(O)PhNO ₂	1.6, m, 11H(CH ₃ , CH ₂); 5.1, m, 1H(OCH); 7.8, m, 4H(C ₆ H ₄)	74.27
8	OCH ₂ CH ₂ CHMeOP(S)SC(O)PhNO ₂	1.5, s, 3H(CH ₃); 4.6, m, 2H(OCH ₂); 5.1, m, 1H(OCH); 7.9, m, 4H(C ₆ H ₄)	70.28

¹H NMR spectra

¹H NMR spectral data of these derivatives are tabulated in Table-3 and show characteristic resonance signal due to glycoxy and aromatic protons. A multiplet for –OCH₂ and –OCH protons have been observed at 5.1-4.4 and 5.1-5.0 ppm, respectively.

A multiplet has been observed for the P-O-CH₂ and P-O-CH protons which is due to 3-bond coupling of the protons with phosphorus atom. A multiplet at 7.7-7.5 ppm has been observed which is ascribed to aromatic protons.

³¹P NMR Spectra

³¹P NMR spectra of these derivatives are given in Table-3 and show only one resonance signal in the region 94.09-70.28 ppm. On comparison with parent dithiophosphoric acid, it has been observed that derivatives of the type

 $\text{OGOP(S)SC}_6\text{H}_4\text{NO}_2$ (I) and $\text{OGOP(S)S-C(=O)-C}_6\text{H}_4\text{NO}_2$ (II) shows down-field (5-12 ppm) and up-field (4-10 ppm) shifting, respectively. The up-field shifting of these derivatives appears due to the presence of deactivating carbonyl group.

CONCLUSION

On the basis of elemental analysis, molecular weight measurements and spectral analysis (IR, ¹H and ³¹P NMR), monodentate nature of alkylene dithiophosphate moiety has been established. Following tentative structure may be proposed for the newly synthesized complexes.

ACKNOWLEDGEMENT

One of the authors (Leena Chordia) is grateful to C.S.I.R., New Delhi for Financial Assistance as J.R.F. and S.A.I.F. (C.D.R.I.), Lucknow for spectral analysis.

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