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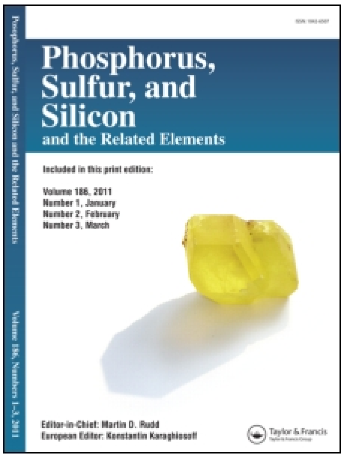

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Organic Derivatives of Alkylene Dithiophosphates Part III: Synthesis and Properties of 2-(p -nitrophenyl) and 2-(p -nitrobenzoyl) Derivatives of Alkylene Dithiophosphates

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ORGANIC DERIVATIVES OF ALKYLENE DITHIOPHOSPHATES PART III: SYNTHESIS AND PROPERTIES OF 2-(*p*-NITROPHENYL) AND 2-(*p*-NITROBENZOYL) DERIVATIVES OF ALKYLENE DITHIOPHOSPHATES

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Reactions of p-*bromonitrobenzene and* p-*nitrobenzoyl chloride with ammonium salt of alkylene dithiophosphates* ($\overline{OGOP}S_2\overset{+}{N}H_4$: $G = —CMe_2CMe_2—$, $—CH_2CMe_2CH_2—$, $—CMe_2CH_2CHMe—$, $—CH_2CH_2CHMe—$) *in 1:1 molar ratio in refluxing benzene solution yields: non-volatile yellow colored solids and red colored viscous liquids respectively of the type* $\overline{OGOP}(S)SR$ ($R = —C_6H_4NO_2$, $(O)CC_6H_4NO_2$) *which are monomeric in nature. The newly synthesized complexes have been characterized by physico-chemical and spectroscopic techniques (M.W., IR, NMR [*^1H *and* ^{31}P*]). On the basis of above studies, the formation of P—S—C and P—S—C(O) chemical bonds has been established.*

Keywords: IR; NMR spectra; O,O′-alkylene dithiophosphates; *p*-bromonitrobenzene, *p*-O,O′-alkylene dithiophosphato-(S)-nitrobenzene; *p*-nitrobenzoyl chloride

INTRODUCTION

In continuation to our earlier investigations on metal, organometal and organic derivatives of phosphonate and phosphate esters[1–11] it was considered of interest to the synthesize and characterize the complexes of the type $\overline{OGOP}(S)SC_6H_4NO_2$ and $\overline{OGOP}(S)SC(O)C_6H_4NO_2$.

RESULTS AND DISCUSSION

Reactions of *p*-bromonitrobenzene and *p*-nitrobenzoyl chloride with ammonium salt of alkylene dithiophosphates in 1:1 molar ratio have

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been carried out in refluxing benzene for ~10 h and ~6 h which yield yellow colored solids (A) and red colored viscous liquids (B) respectively.

$$\text{A. } \overline{\text{OGOP}}\text{S}_2\text{NH}_4 + \text{BrC}_6\text{H}_4\text{NO}_2 \xrightarrow[\sim 10\,\text{hrs.}]{\text{C}_6\text{H}_6} \overline{\text{OGOP}}\text{S}_2\text{C}_6\text{H}_4\text{NO}_2 + \text{NH}_4\text{Br}\downarrow$$

$$\text{B. } \overline{\text{OGOP}}\text{S}_2\text{NH}_4 + \text{CI(O)C}_6\text{H}_4\text{NO}_2 \xrightarrow[\sim 6\,\text{hrs.}]{\text{C}_6\text{H}_6} \overline{\text{OGOP}}\text{S}_2\text{C(O)C}_6\text{H}_4\text{NO}_2 + \text{NH}_4\text{CI}\downarrow$$

(where G = $-\text{CMe}_2\text{CMe}_2-$, $-\text{CH}_2\text{CMe}_2\text{CH}_2-$, $-\text{CMe}_2\text{CH}_2\text{CHMe}-$, $-\text{CH}_2\text{CH}_2\text{CHMe}-$)

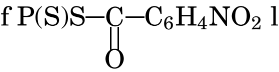
Desired products have been isolated by stripping off the solvent from the filtrate under reduced pressure. These derivatives are nonvolatile, monomeric, soluble in common organic solvents and get decomposed on heating at ~140°C. It has been observed that the reactivity of the alkylene dithiophosphate group toward substituted aromatic halide ion is increased by taking deactivating nitro group at para position in aromatic ring. It seems that the nucleophillic displacement of the bromide ion by alkylene dithiophosphato group is faster by taking deactivating groups at para position. In our earlier publication it was reported that the synthesis of 2-acetanilide (benzanilide) alkylene dithiophosphates requires longer refluxing ~28 h.[10]

IR SPECTRA

IR spectra of these derivatives shows the following characteristic changes:

1. A stretching vibration at 3080–3060 cm^{-1} in all the complexes may be ascribed to aromatic νC—H stretching vibrations.
2. Nitro group in these derivatives shows absorption band at 1150–1530 cm^{-1} which shows slight shift toward lower wave numbers (15 cm^{-1}) in comparison to *p*-bromonitrobenzene. It may be due to lesser nucleophillicity of dithio moiety in comparision to the bromide ion present in the *p*-bromonitrobenzene.
3. The absorption band in the region 1145–1130 cm^{-1} and 885–870 cm^{-1} may be assign to ν(P)—O—C and νP—O—(C) stretching vibrations respectively.
4. A strong absorption band due to dioxaphospholane and dioxaphosphorinane ring vibrations is present in the region 955–910 cm^{-1}.
5. A sharp band assigned to νP=S absorptions in the region 780–765 cm^{-1} indicates shifting toward 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. New bands have been observed in the region 680–625 cm^{-1} which may be due to the C—S bond. Appearance of this bond supports the formation of  $P(S)S{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}C_6H_4NO_2$ linkage in these derivatives.
7. The absorption bands of medium intensities in the region 565–540 cm^{-1} have been attributed to νP—S asymmetric and symmetric vibrations.

NMR SPECTRA

^{1}H NMR spectral data of these derivatives are tabulated in Table I and show characteristic resonance signal due to glycoxy and aromatic protons. A multiplet for —OCH$_2$ and O—CH protons has been observed due to long range coupling with phosphorus atom. A multiplet has been observed in the region δ 7.7–7.9 ppm, which was assigned to aromatic protons while aromatic protons of *p*-bromonitrobenzene appeared as distorted doublet.

^{31}P NMR spectra of these derivatives show single resonance signal in the region δ 70.28–94.09 ppm which indicates purity of these complexes. A comparison of the chemical shift values indicates that phosphorous atom is more deshielded (δ 77.99–70.28 ppm) in the complexes $\overline{\mathrm{OGOP}}(S)SC(O)C_6H_4NO_2$, thus shifting the NMR signal to upfield. It may be due to deactivating effects of both carbonyl and nitro groups. In the complexes $\overline{\mathrm{OGOP}}(S)SC_6H_4NO_2$ the ^{31}P signal have been shifted upfield (Table I).

EXPERIMENTAL

Stringent precautions were taken to exclude moisture during the experimental manipulations. Solvents were dried by standard methods. *p*-bromonitrobenzene and *p*-nitrobenzoyl chloride, alkylene dithiophosphates were prepared by the methods reported in literature.[12] Sulfur was estimated gravimetrically as barrium sulphate (messenger's method).[12] Molecular weiglets were determined by the "Knauer vapour pressure osmometer" using chloroform solutions at 45°C. Infrared spectra recorded in nujol mull (4000–200 cm^{-1}) on Perkin-Elmer spectrophotometer. Carbon and hydrogen analyses were performed on a Perkin-Elmer CHNS/O analyser. ^{1}H NMR spectra were recorded in CDCl$_3$ solution on a 90MHz JEOL FX 90Q spectrometer using TMS as

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TABLE I ^{1}H and ^{31}P NMR Spectra of 2-(p-nitrophenyl and 2-p-nitrobenzoyl) of Alkylene Dithiophosphates

S. no.	Compounds	^{1}H (δ ppm)	^{31}P (δ ppm)
1	$\overline{\mathrm{OCMe_2CMe_2OP}}\mathrm{(S)SC_6H_4No_2}$	1.6, S, 12H (CH_3); 7.5, m, 4H (C_6H_4)	94.09
2	$\overline{\mathrm{OCH_2CMe_2CH_2OP}}\mathrm{(S)SC_6H_4NO_2}$	1.1, S, 6H (CH_3); 5.1, d, 4H (CH_2O); 7.65, m, 4H (C_6H_4)	82.92
3	$\overline{\mathrm{OCMe_2CH_2CHMeOP}}\mathrm{(S)SC_6H_4NO_2}$	1.55, m, 11H (CH_3, CH_2); 5.1, m, 1H (O—CH); 7.6, m, 4H (C_6H_4)	81.17
4	$\overline{\mathrm{OCH_2CH_2CHMeOP}}\mathrm{(S)SC_6H_4NO_2}$	1.5, S, 3H (CH_3); 4.4, m, 2H ($POCH_2$); 5.0, m, 1H (POCH) 7.7, m, 4H (C_6H_4)	91.00
5	$\overline{\mathrm{OCMe_2CMe_2OP}}\mathrm{(S)SC(O)C_6H_4NO_2}$	1.62, S, 12H (CH_3); 7.8, m, 4H (C_6H_4)	77.99
6	$\overline{\mathrm{OCH_2CMe_2CH_2OP}}\mathrm{(S)SC(O)C_6H_4NO_2}$	1.15, S, 6H (CH_3); 5.15, d, 4H (H_2O); 7.82, m, 4H (C_6H_4)	71.32
7	$\overline{\mathrm{OCMe_2CH_2CHMeOP}}\mathrm{(S)SC(O)C_6H_4NO_2}$	1.6, m, 11H (CH_3, CH_2); 5.15, m, 1H (O—CH); 7.8, m, 4H (C_6H_4)	74.27
8	$\overline{\mathrm{OCH_2CH_2CHMeOP}}\mathrm{(S)SC(O)C_6H_4NO_2}$	1.5, S, 3H (CH_3); 4.6, m, 2H ($POCH_2$); 5.1, m, 1H (POCH) 7.82, m, 4H (C_6H_4)	70.28

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TABLE II Synthetic and Analytical Data of *p*-nitrobenzene 2-(p-nitrophenyl), 2-(p-nitrobenzoyl) and Benzoyl Derivatives of Alkylene Dithiophosphates

	Reactants (g)				Analyses			
S. no.	$\overline{OGOP}(S)NH_4$ G = …,	$XC_6H_4NO_2$ X = …	Products …g…	% Yields	C	H	S	M. wt. found (cal.)
1	—CMe_2CMe_2— 1.09 g	Br— .96 g	$\overline{OCMe_2CMe_2OP}(S)SC_6H_4NO_2$ 1.24 g	78	42.98 (43.24)	4.58 (4.80)	18.83 (19.21)	—
2	—$CH_2CMe_2CH_2$— 1.14 g	Br— 1.07 g	$\overline{OCH_2CMe_2CH_2OP}(S)SC_6H_4NO_2$ 1.34 g	79	44.99 (45.14)	4.24 (4.38)	19.60 (20.06)	300 319
3	—CMe_2CH_2CHMe— 1.19 g	Br— 1.04 g	$\overline{OCMe_2CH_2CHMeOP}(S)SC_6H_4NO_2$ 1.42 g	82	43.00 (43.24)	4.62 (4.80)	18.72 (19.21)	— —
4	—CH_2CH_2CHMe— 1.01 g	Br— 1.01 g	$\overline{OCH_2CH_2CHMeOP}(S)SC_6H_4NO_2$ 1.32 g	86	39.01 (39.34)	3.84 (3.93)	19.99 (20.98)	— —
5	—CMe_2CMe_2— 1.12 g	Cl(O)C .90 g	$\overline{OCMe_2CMe_2OP}(S)SC(O)C_6H_4NO_2$ 1.41 g	80	42.98 (43.21)	4.36 (4.43)	17.60 (17.73)	371 361
6	—$CH_2CMe_2CH_2$— 1.25 g	Cl(O)C 1.08 g	$\overline{OCH_2CMe_2CH_2OP}(S)SC(O)C_6H_4NO_2$ 1.65 g	82	41.01 (41.50)	4.52 (4.61)	18.36 (18.45)	—
7	—CMe_2CH_2CHMe— 1.22 g	Cl(O)C .99 g	$\overline{OCMe_2CH_2CHMeOP}(S)SC(O)C_6H_4NO_2$ 1.50 g	78	42.95 (43.21)	4.36 (4.43)	17.65 (17.73)	— —
8	—CH_2CH_2CHMe— .92 g	Cl(O)C .85 g	$\overline{OCH_2CH_2CHMeOP}(S)SC(O)C_6H_4NO_2$ 1.22 g	80	38.94 (39.64)	3.50 (3.60)	19.13 (19.21)	308 333

an internal reference. ^{31}P NMR spectra were recorded in $CHCl_3$ using H_3PO_4 as an external reference. The other complexes were synthesized by similar route. The experimental details of a representative complex is being described below. Analytical results are summarized in Table II.

Preparation of $\overline{OCMe_2CMe_2OP}(S)SC_6H_4NO_2$

p-bromonitrobenzene (0.96 gm) was dissolved in 30 ml benzene. To this, a solution of ammonium tetramethylene dithiophosphate (1.09 gm) was added slowly and refluxed for ~10 h. The precipitated ammonium bromide was filtered off. The solvent was removed from the filtrate under reduced pressure to obtain the desired product, yellow sticky solid. The compound on analyses show: C, 42.98; H, 4.58; N, 18.83% calculated for $\overline{OCMe_2CMe_2OP}(S)SC_6H_4NO_2$. The above procedure was adopted for all the other reactions. Relevant data are given in Table II.

Preparation of $\overline{OCMe_2CMe_2OP}(S)SC(O)C_6H_4NO_2$

Ammonium tetramethylene dithiophosphate (1.12 g) was refluxed with *p*-nitrobenzoyl chloride (0.90 g) in benzene for ~6 h. Ammonium chloride was removed by filtration. A red colored product was separated out by removing the solvent from the filtrate. The compound on analysis show C, 43.21%; H, 4.43%; S, 17.73; calculated for the $\overline{OCMe_2CMe_2OP}(S)SC(O)C_6H_4\ NO_2$. The above procedure was adopted for all other reactions. Relevant data are given in Table II.

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