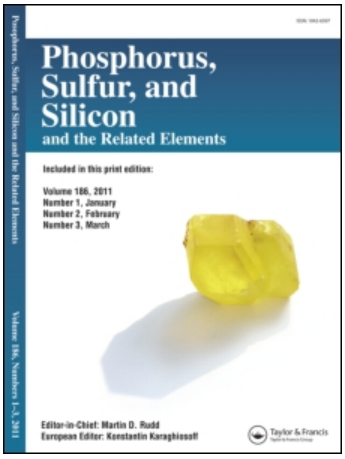

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Chandra S. Sharma[a]; Padam N. Nagar[a]
[a] Department of Chemistry, University of Rajasthan, Jaipur, India

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Organic Derivatives of Alkylene Dithiophosphates, Part IV: Synthesis and Properties of Phenyl Acetyl and *p*-Methyl Benzoyl Derivatives of Alkylene Dithiophosphates

Chandra S. Sharma
Padam N. Nagar
Department of Chemistry, University of Rajasthan, Jaipur, India

Reactions of phenyl acetyl chloride and p*-methylbenzoyl chloride with ammonium salt of alkylene dithiophosphates in a 1:1 molar ratio in refluxing benzene solution yields nonvolatile dark yellow- or brown-colored viscous liquids of the type* $\overline{OGOPS_2}R$ *(*$R = -OCCH_2C_6H_5$, $-OCC_6H_4CH_3$, $G = -CMe_2CMe_2-$, $-CH_2CH_2CHMe-$, $-CH_2(CH_2)_2\ CH_2-$, *and* $-CMe_2CH_2CHMe-$*). The compounds thus obtained are hygroscopic and monomeric in nature. The newly synthesized compounds have been characterized by physicochemical and spectroscopic techniques (MW, IR, NMR [*^1H *&* ^{31}P*]).*

Keywords 2-Phenyl acetyl *O*,*O*′-alkylene dithiophosphates; 2-(*p*-methyl benzoyl) *O*, *O*′-alkylene dithiophosphates; ammonium alkylene dithiophosphates

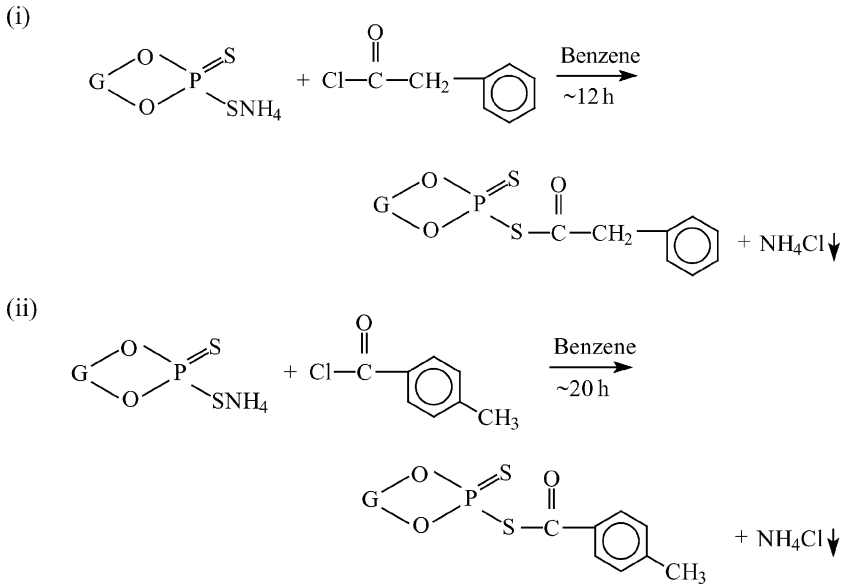
INTRODUCTION

A lot of work had been reported on metal and organometal derivatives of *O*,*O*′-alkylene dithiophosphates from our laboratories;[1–9] amongst them the organic derivatives have a wide range of utility as contact insecticides,[10] acaricides[11] and ovicides.[12,13] In continuation of our earlier investigations on a variety of organic derivatives of alkylene dithiophosphates,[14–17] it is interesting to extend the present course of investigation on the synthesis of phenyl acetyl and *p*-methyl benzoyl derivatives of *O*,*O*′-alkylene dithiophosphates.

RESULTS AND DISCUSSION

Nucleophilic substitution reactions of phenyl acetyl chloride (Scheme 1) and *p*-methylbenzoyl chloride (Scheme 2) with ammonium salt of

Received March 18, 2004; accepted March 1, 2005.
Address correspondence to Padam N. Nagar, University of Rajasthan, Department of Chemistry, Jaipur, 302004 India. E-mail: rkbohra@satyam-net.in



[Where G = -CMe_2CMe_2-, -CH_2CH_2CHMe-, -$CH_2(CH_2)_2CH_2$- and -CMe_2CH_2CHMe-]

SCHEME 1

alkylene dithiophosphates in a 1:1 molar ratio have been carried out in refluxing benzene (~ 12–20 h). The reaction mixture was initially colorless but on gradual refluxing (~ 6 h). It turns to a dark radish color.

The Compounds formed get decomposed on attempted distillation under reduced pressure and are hygroscopic and monomeric in nature. The phenyl acetyl derivatives obtained as dark yellow-colored viscous liquids, while the *p*-methyl benzoyl derivatives dark brown-colored semisolids. The compound's complexes formed are soluble in common organic solvents *viz.* benzene, chloroform, and dichloromethane.

The previously mentioned derivatives have also been synthesized by the following alternate route. It has been observed that the nucleophilic displacement of the chloride ion is faster in comparison to the previous method (Eq. 1).

$$[\overline{OGOP}S_2H] + Et_3N + R - Cl \xrightarrow{\text{Benzene}} [(\overline{OGOP}S_2)R] + Et_3N \cdot HCl \downarrow \quad (1)$$

$R = C_6H_5CH_2C(O)$, p-$CH_3C_6H_4C(O)$

Although the alkylene dithiophosphoric acid can be obtained in a purer form, even then it was conjectured that their ammonium salts might be more pure and the reactions of these salts with organic halides

may be more facile. In view of this, the synthetic route first was preferred over the latter one.

IR SPECTRA

IR Spectra of these compounds derivatives show the following characteristic changes:

1. The IR spectra show the absence of peaks due to νC—Cl (present at $\sim 740 \pm 10$ cm^{-1} in *p*-methylbenzoyl chloride) and the appearance of a new peak of weak intensity at $\sim 650 \pm 20$ cm^{-1}, which may be assigned to the νC—S absorption band.
2. An absorption band of sharp intensity is present at 1750–1710 cm^{-1}, which is due to νC═O vibrations. A shift towards lower wave numbers (~ 20 cm^{-1}) have been observed in comparison to its position in the IR spectra of phenyl acetyl and *p*-methyl benzoyl chlorides.
3. The νP═S and νP—S absorption bands are present in the regions of $\sim 650 \pm 30$ cm^{-1} and $\sim 560 \pm 25$ cm^{-1} respectively.
4. The strong absorption band present in the regions of 1160–1010 cm^{-1} and 880–760 cm^{-1} have been assigned to ν(P)—O—C and νP—O—(C) stretching vibrations, which do not show any notable change as compared to the parent dithio ligand. The broad absorption bands around $\sim 960 \pm 40$ cm^{-1} are due to ring vibrations of a dithiophosphate moiety, which is also coupled with aromatic C—H ring vibrations (Table 1).

NMR SPECTRA (^{1}H & ^{31}P)

The ^{1}H NMR spectral data for the previously mentioned compounds are tabulated in Table II. There is an overlapping of NMR signals of the glyloxy protons and *p*-methyl group in the region of δ 1.10–1.49 ppm. The protons on the α-carbon atom of the alkylene chain show three-bond coupling with a magnetically active phosphorus atom [^3J(^{1}H-^{31}P)]=$\sim$16 Hz, and the signal appeared in the region of 3.79–4.30 ppm for these protons. The benzenoid protons appears as a multiplet at δ 6.85–7.95 ppm (Table II).

In the proton-decoupled ^{31}P NMR spectra, only one ^{31}P resonance signal has been observed for each compound. The ^{31}P chemical shift values observed in the parent dithiophosphate (δ = 78–96 ppm) are shifted towards upfield (5–8 ppm) in the corresponding phenyl acetyl and 4-methyl benzoyl derivatives (88.7–93.0 ppm), indicating a covalent character of sulfur carbon linkage as an well as an absence of any coordinating tendencies in the previously mentioned compounds.

TABLE I IR Spectral Data for Phenyl Acetyl and p-Methyl Benzoyl Derivatives of Alkylene Dithiophosphates

S. no.	Compounds	ν(P) —O—C	νP—O—(C)	Ring vibrations	νP═S	νP—S	νC═O	νC—S
1.	$OC(Me)_2C(Me)_2OPS_2C(O)CH_2C_6H_5$	1140s	820s	985w	670	545s	1730s	665m
2.	$OCH_2CH_2CH(Me)OPS_2C(O)CH_2C_6H_5$	1020s	785m	920s,br	625	550s	1725s	650m
3.	$OCH_2CH_2CH_2CH_2OPS_2$ $C(O)CH_2C_6H_5$	1160s	760m	—	685	580s	1750s	630m
4.	$OC(Me)_2CH_2CH(Me)OPS_2$ $C(O)CH_2C_6H_5$	1010s	880m	920s,br	620	555s	1740s	680m
5.	$OC(Me)_2C(Me)_2OPS_2C(O)C_6H_4CH_3$	1150s	785s	960s,br	695m	560s	1719s	645m
6.	$OCH_2CH_2CH(Me)OPS_2C(O)C_6H_4CH_3$	1090s	790m	—	675m	545s	1725s	655m
7.	$OCH_2CH_2CH_2CH_2OPS_2C(O)C_6H_4CH_3$	1125m	760m	—	680m	550s	1730s	635m
8.	$OC(Me)_2CH_2CH(Me)OPS_2C(O)C_6H_4CH_3$	1120m	850m	920m,br	668m	575m	1710s	665w

TABLE II NMR (^{1}H and ^{31}P) Spectral Data of Phenyl Acetyl and p-Methyl Benzoyl Derivatives of Alkylene Dithiophosphates

S. no.	Compounds	^{1}H (δppm)[a]	^{31}P (δppm)
1.	$\overline{OC(Me)_2C(Me)_2O}PS_2C(O)CH_2C_6H_5$	1.41, s, 12H (Me); 3.8, s, 2H (CH_2); 6.75, m, 5H (C_6H_5)	90.85
2.	$\overline{OCH_2CH_2CH(Me)O}PS_2C(O)CH_2C_6H_5$	1.35, d, 3H (Me); 3.79–4.15, m, 3H (OCH_2, OCH); 3.8, s, 2H (CH_2; 7.39, m, 5H (C_6H_5)	79.55
3.	$\overline{OCH_2CH_2CH_2CH_2O}PS_2C(O)CH_2C_6H_5$	1.49, m, 4H (CH_2); 3.83–4.56, m, 4H (OCH_2); 3.95, s, 2H (CH_2); 7.95, s, 5H (C_6H_5)	89.80
4.	$\overline{OC(Me)_2CH_2CH(Me)O}PS_2C(O)CH_2C_6H_5$	1.35–2.20, s, 6H (Me); 4.85, m, 1H (OCH); 3.79, s, 2H (CH_2); 7.85, s, 5H (C_6H_5)	85.00
5.	$\overline{OC(Me)_2C(Me)_2O}PS_2C(O)C_6H_4CH_3$	1.39, s, 12H (Me); 2.35, s, 3H (CH_3); 7.29, m, 4H (C_6H_4)	93.05
6.	$\overline{OCH_2CH_2CH(Me)O}PS_2C(O)C_6H_4CH_3$	1.35, d, 3H (Me); 3.79–4.20, m, 3H (OCH_2); 2.35, s, 3H (CH_3); 7.49, m, 4H (C_6H_4)	80.55
7.	$\overline{OCH_2CH_2CH_2CH_2O}PS_2C(O)C_6H_4CH_3$	1.45, m, 4H (CH_2); 3.80–4.30, m, 4H (OCH_2); 2.35, s, 3H (CH_3); 7.15, m, 4H, (C_6H_4)	91.00
8.	$\overline{OC(Me)_2CH_2CH(Me)O}PS_2C(O)C_6H_4CH_3$	1.35–2.29, m, 11H (Me); 4.85, s, 1H (OCH); 2.79, s, 3H (CH_3); 7.15-785, m, 4H (C_6H_4)	84.65

[a] s = singlet; d = doublet; m = mulplet.

TABLE III Synthetic and Analytical Data of Phenyl Acetyl and p-Methyl Benzoyl Derivatives of Alkylene Dithiophosphates

S. No.	Reactants g/mmole: R = R—Cl, R = ...	Reactants g/mmole: $OGOPS_2NH_4$, G=.....	Products: gms	Products: %yield	Analysis: S% found (calcd.)
1.	$C_6H_5CH_2C(O)$— 0.78 (5.04)	—CMe_2CMe_2— 1.15 (5.04)	$[OC(Me)_2C(Me)_2OPS_2]C(O)CH_2C_6H_5$ 1.57	95.00	19.05 (19.39)
2.	$C_6H_5CH_2C(O)$— 0.75 (4.83)	—CH_2CH_2CHMe— .98 (4.86)	$[OCH_2CH_2CH(Me)OPS_2]C(O)CH_2C_6H_5$ 1.33	91.23	20.82 (21.19)
3.	$C_6H_50CH_2C(O)$— 0.80 (5.17)	—$CH_2CH_2CH_2CH_2$— 1.03 (5.15)	$[OCH_2CH_2CH_2CH_2OPS_2]C(O)CH_2C_6H_5$ 1.37	88.25	20.46 (21.19)
4.	$C_6H_5CH_2C(O)$— 0.90 (3.82)	—CMe_2CH_2CHMe— 1.33 (5.83)	$[OC(Me)_2CH_2CH(Me)OPS_2]C(O)CH_2C_6H_5$ 1.77	92.2	19.16 (19.36)
5.	$CH_3C_6H_4C(O)$— 0.81 (5.24)	—CMe_2CMe_2— 1.19 (5.24)	$[OC(Me)_2C(Me)_2OPS_2]C(O)C_6H_4CH_3$ 1.57	91.53	18.76 (19.39)
6.	$CH_3C_6H_4C(O)$— 0.83 (5.37)	—CH_2CH_2CHMe— 1.07 (5.37)	$[OCH_2CH_2CH(Me)OPS_2]C(O)C_6H_4CH_3$ 1.42	87.88	20.85 (21.19)
7.	$CH_3C_6H_4C(O)$— 0.92 (5.95)	—$CH_2CH_2CH_2CH_2$— 1.19 (5.95)	$[OCH_2CH_2CH_2CH_2OPS_2]C(O)C_6H_4CH_3$ 1.60	89.3	19.76 (21.19)
8.	$CH_3C_6H_4C(O)$— 0.95 (6.15)	—CMe_2CH_2CHMe— 1.40 (6.15)	$[OC(Me)_2CH_2CH(Me)OPS_2]C(O)C_6H_4CH_3$ 1.74	86.53	(19.13) (19.39)

However, the pronounced ring size effect is observed in the ^{31}P NMR spectra of these derivatives as a downfield shift for the five-membered heterocyclic ring (δ93.05 ppm) as compared to ^{31}P chemical shift of the six-membered ring (87–90 ppm).

EXPERIMENTAL

Stringent precautions were taken to exclude moisture during the experimental manipulations. Alkylene dithiophosphates and its ammonium salts were prepared by the methods reported in the literature.[1] Sulfur was estimated by the messenger's method. Molecular weights were determined by the Knauer vapour pressure osmometer using chloroform solutions at 45°C. IR spectra were recorded as neat liquids or nujol mules using CsI cells on a Perkin-Elmer spectrophotometer. Carbon and hydrogen analyses were performed on a Perkin-Elmer CHNS/O analyzer. ^1H NMR spectra were recorded in a $CDCl_3$ solution on a 90MHz JEOL FX90Q spectrometer using TMS as an internal reference. ^{31}P NMR spectra were recorded in benzene using H_3PO_4 as an external reference.

Synthesis of $[\overline{OCMe_2CH_2CHMeOPS_2}]C(O)CH_2C_6H_5$

Phenyl acetyl chloride (0.90 g) and ammonium hexylene dithiophosphates (1.33 g) were mixed in anhydrous benzene ($\sim$ 50 mL). This reaction mixture was refluxed for $\sim$ 12 h. The reaction mixture was initially colorless but it turned to dark red on refluxing. The precipitated ammonium chloride (0.11 g) was filtered off and the desired products were obtained as dark yellow-colored viscous liquid after removing the solvent from the filtrate. The other compounds were also synthesized by similar route (Table III).

Synthesis of $[\overline{OCMe_2CMe_2OPS_2}]C(O)C_6H_4CH_3$

A mixture of *p*-methylbenzoyl chloride (0.81 g) and ammonium tetramethylethylene dithiophosphate (1.19 g) was taken in benzene ($\sim$40 mL). The reaction mixture was refluxed for ($\sim$20–22 h). After complete precipitation of ammonium chloride, the desired product was obtained by filtering it and removing the solvent (Table III).

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