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ORGANIC DERIVATIVES OF ALKYLENE DITHIOPHOSPHATES. PART II: SYNTHESIS AND PROPERTIES OF 2- ACETANILIDE (BENZANILIDE) DERIVATIVES OF ALKYLENE DITHIOPHOSPHATES

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ORGANIC DERIVATIVES OF ALKYLENE DITHIOPHOSPHATES. PART II: SYNTHESIS AND PROPERTIES OF 2- ACETANILIDE (BENZANILIDE) DERIVATIVES OF ALKYLENE DITHIOPHOSPHATES

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Reactions of p- bromoacetanilide (benzanilide) with ammonium salt of alkylene dithiophosphates $\text{OGOP(S)S}^-\text{NH}_4^+$; $\text{G} = -\text{CMe}_2\text{CMe}_2-$, $-\text{CH}_2\text{CMe}_2\text{CH}_2-$, $-\text{CMe}_2\text{CH}_2\text{CHMe}-$, $\text{CH}_2\text{CH}_2\text{CHMe}-$) in 1:1 molar ratio in refluxing benzene solution yields; acetanilide (benzanilide) derivatives of alkylene dithiophosphates, $\text{OGOP(S)S}-\text{C}_6\text{H}_4\text{NH COR}$ ($\text{R} = \text{Me}$ or Ph). The newly synthesized derivatives have been characterized by elemental analysis, molecular weight determination, IR, NMR (^1H & ^{31}P) spectral studies. In contrast to bidentate behavior in metal and organometal derivatives of alkylene dithiophosphate (adttp), the behavior of the dithiophosphato moiety in these derivatives is found to be monodentate. On the basis of above studies the formation of P(S)S-C linkage have been established.

Keywords: O, O'- Alkylene dithiophosphate (adttp); p - Bromoacetanilide; P(S)S-C ; (Benzanilide); IR and NMR spectra

INTRODUCTION

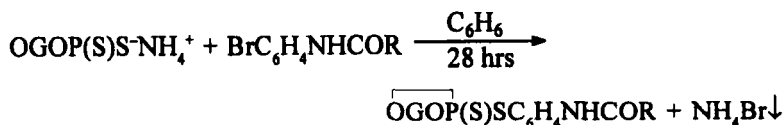
O,O' – alkylene dithiophosphoric acids^[1] contribute an important series of ligands and behave either as unidentate^[2] or bidentate^[3,4]. The use of organophosphorus specially as pesticides^[5-8] in general and specially as organic derivatives of O,O'-dialkyldithiophosphate and their derivatives,

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well known as contact insecticides^[9], acaricide^[10] and ovicide^[11]. A lot of work had been reported from our laboratories on the metal and organo-metal derivatives of phosphonate and phosphate esters^[12-16]. In continuation to our earlier investigations on organic derivatives of alkylene dithiophosphates^[17], the work has been extended to the synthesis and characterization of some acetanilide (benzanilide) derivatives of alkylene dithiophosphates.

RESULTS AND DISCUSSION

The reactions of p-bromo acetanilide (benzanilide) with ammonium salt of alkylene dithiophosphates in 1:1 molar ratio in refluxing benzene solution yield the formation of monomeric 2-acetanilide (benzanilide) derivatives of alkylene dithiophosphates.



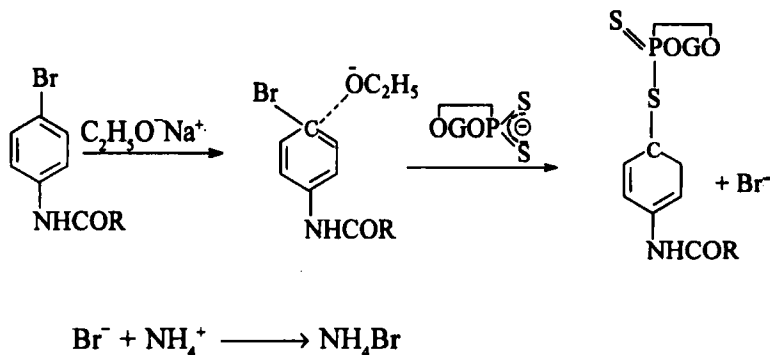
Where $G = -\text{CMe}_2\text{CMe}_2-, -\text{CH}_2\text{CMe}_2\text{CH}_2-, -\text{CMe}_2\text{CH}_2\text{CH}_2\text{CHMe}-, -\text{CH}_2\text{CH}_2\text{CHMe}-$ and $R = \text{Me or Ph}$

These compounds are obtained by filtering the ammonium bromide and the solvent have been evaporated under reduced pressure. These compounds are soluble in common organic solvents, (benzene, chloroform and carbontetrachloride etc.).

There is a very slow precipitation of NH_4Br in these reactions. It appears that due to the presence of activating group in the aromatic ring on one hand, and on the other, weak nucleophilic character of the dithiophosphato

$\left(-\text{P} \begin{smallmatrix} \nearrow \text{S} \\ \searrow \text{S} \end{smallmatrix} \right)$ moiety in the ligand, the nucleophilic displacement of the bromide ion from the aromatic ring by dithiophosphato moiety becomes very slow. During the course of reaction, it has been observed that the reaction with benzoyl substitution on nitrogen atom seems to be rather faster than acetyl group. These reactions have also been carried out in the

presence of strong base (EtONa) and thus, reaction has been completed within ~10 hrs of refluxing in benzene. It seems that, nucleophilic displacement of bromide ion is fast in the presence of sodium ethoxide. A tentative reaction mechanism has been suggested for the above reactions:



IR SPECTRA

A strong absorption band appear in the range $3260 - 3230 \text{ cm}^{-1}$ which are attributed to asymmetrical and symmetrical νNH stretching vibrations. The absorption band in the region $3070 - 3060 \text{ cm}^{-1}$ which are assigned to aromatic $\nu\text{C-H}$ stretching, while aliphatic $\nu\text{C-H}$ stretching vibrations are observed in the region $2950 - 2930 \text{ cm}^{-1}$. The absorption band due to carbonyl group in these compounds have been observed in the range $1730 - 1710 \text{ cm}^{-1}$. A comparison of the position of $\nu\text{C}=\text{O}$ absorption in acetanilide and benzanilide with those of the newly synthesized derivatives, shows slight shifting of carbonyl absorption band towards lower wave numbers. The absorption bands observed in the region $1020 - 1010$ and $865 - 850 \text{ cm}^{-1}$ have been assigned to $\nu(\text{P})-\text{O}-\text{C}$ and $\nu\text{P}-\text{O}-(\text{C})$ stretching vibrations, respectively. The stretching vibrations observed in the range $950-910 \text{ cm}^{-1}$ may be assigned to dioxaphospholane and dioxaphosphorinane ring system. A sharp absorption band in the region $670 - 650 \text{ cm}^{-1}$ has been assigned to $\nu\text{P}=\text{S}$ vibration in acetanilide (benzanilide) derivatives of alkylene dithiophosphates. The band present in the region $580 - 550 \text{ cm}^{-1}$ are due to $\nu(\text{P}-\text{S})$ symmetric and asymmetric vibrations. The occurrence of this absorption band supports the formation of $\text{P}(\text{S})$ S-C linkage in these derivatives (Table I).

TABLE I IR spectra of acetanilide and benzanalide derivatives of alkylene dithiophosphates

S. No.	Compound	$\nu(P)-O-C$	$\nu P-O-(C)$	Ring Vibration	$\nu P=S$	$\nu P-S$	$\nu C=O$	νNH
1.	$\boxed{OCMe_2CM_e_2OP(S)SC_6H_4NHCOMe}$	1015	840	950	660	550	1710	3230
2.	$\boxed{OCH_2CM_e_2CH_2OP(S)SC_6H_4NHCOMe}$	1010	860	955	655	565	1710	3245
3.	$\boxed{OCMe_2CH_2CHMeOP(S)SC_6H_4NHCOMe}$	1020	850	960	670	570	1720	3235
4.	$\boxed{OCH_2CH_2CHMeOP(S)SC_6H_4NHCOMe}$	1020	865	950	650	580	1725	3240
5.	$\boxed{OCMe_2CM_e_2OP(S)SC_6H_4NHCOPh}$	1020	860	950	655	570	1725	3240
6.	$\boxed{OCH_2CM_e_2CH_2OP(S)SC_6H_4NHCOPh}$	1030	845	940	670	560	1730	3250
7.	$\boxed{OCMe_2CH_2CHMeOP(S)SC_6H_4NHCOPh}$	1025	870	960	640	550	1720	3260
8.	$\boxed{OCH_2CH_2CHMeOP(S)SC_6H_4NHCOPh}$	1015	850	965	680	565	1730	3255

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TABLE II NMR ^1H & ^{31}P spectral data of acetanilide and benzanilide derivatives of alkylene dithiophosphates

S. No.	Compounds	^1H (δ ppm)	^{31}P (δ ppm)
1.	$\text{OCMe}_2\text{CMe}_2\text{OP}(\text{S})\text{SC}_6\text{H}_4\text{NHCOMe}$	1.5s,s,12H(Me); 7.33,m,4H(Ph); 2.9,s,3H(COMe); 5.5,bs,1H(NH)	99.88
2.	$\text{OCH}_2\text{CMe}_2\text{CH}_2\text{OP}(\text{S})\text{SC}_6\text{H}_4\text{NHCOMe}$	1.0s,s,6H(Me); 5.0,d,4H(OCH_2); 7.4,m,4H(Ph); 5.8,bs,1H(NH); 3.1,s,3H(Me)	88.35
3.	$\text{OCMe}_2\text{CH}_2\text{CHMeOP}(\text{S})\text{SC}_6\text{H}_4\text{NHCOMe}$	1.5m,11H(Me_2CH_2); 5.0,m,1H(OCH); 7.42,m,4H(Ph); 5.9,bs,1H(NH); 2.8,s,3H(Me)	89.20
4.	$\text{OCH}_2\text{CH}_2\text{CHMeOP}(\text{S})\text{SC}_6\text{H}_4\text{NHCOMe}$	1.45,s,3H(Me); 4.9,m,1H(OCH); 4.0,m,2H(OCH_2); 7.4,m,4H(Ph); 5.4,bs,1H(NH); 3.0,s,3H(Me)	87.19
5.	$\text{OCMe}_2\text{CMe}_2\text{OP}(\text{S})\text{SC}_6\text{H}_4\text{NHCOPh}$	1.6,s,12H(Me); 7.5,m,4H(S-Ph); 7.1,m,5H(Ph); 5.6,bs,1H(NH)	91.40
6.	$\text{OCH}_2\text{CMe}_2\text{CH}_2\text{OP}(\text{S})\text{SC}_6\text{H}_4\text{NHCOPh}$	1.5,s,6H(Me); 5.0,d,4H(OCH_2); 7.5,m,4H(S-Ph); 5.8,bs,1H(NH); 6.9,m,5H(Ph)	82.92
7.	$\text{OCMe}_2\text{CH}_2\text{CHMeOP}(\text{S})\text{SC}_6\text{H}_4\text{NHCOPh}$	7.6m,11H(CH_2CH_2); 5.2,m,1H(OCH); 7.5,m,4H(S-Ph); 6.8,m,5H(Ph); 5.8,bs,1H(NH)	90.12
8.	$\text{OCH}_2\text{CH}_2\text{CHMeOP}(\text{S})\text{SC}_6\text{H}_4\text{NHCOPh}$	1.5,s,3H(Me); 4.7,m,1H(OCH); 4.0,m,2H(OCH_2); 7.6,m,4H(S-Ph); 7.2,m,5H(Ph); 6.2,bs,1H(NH)	89.16

TABLE III Synthetic & Analytical data of acetanilide and benzanilide derivatives of alkylene dithiophosphates

S. No.	Reactants(g)		Product -----g:-----	Analyses Found(Calcd.)			M. Wt. Found(Calcd.)
	$\overline{\text{OGOP}}(\text{S})\text{SNH}_4$	$\text{BrC}_6\text{H}_4\text{NHCOR}$		C	H	S %	
	G = -----	R = -----					
1.	$-\text{CMe}_2\text{CMe}_2-$ 1.21	Me 1.13	$\overline{\text{OCMe}_2\text{CMe}_2\text{OP}}(\text{S})\text{SC}_6\text{H}_4\text{NHC(O)Me}$ 1.31 72	48.00 (48.69)	5.72 (5.80)	18.01 (18.55)	-
2.	$-\text{CH}_2\text{CMe}_2\text{CH}_2-$ 1.19	Me 1.18	$\overline{\text{OCH}_2\text{CMe}_2\text{CH}_2\text{OP}}(\text{S})\text{SC}_6\text{H}_4\text{NHC(O)Me}$ 1.43 78	46.80 (47.13)	5.39 (5.44)	18.94 (19.34)	341 (331)
3.	$-\text{CMe}_2\text{CH}_2\text{CHMe}-$ 1.32	Me 1.23	$\overline{\text{OCMe}_2\text{CH}_2\text{CHMeOP}}(\text{S})\text{SC}_6\text{H}_4\text{NHC(O)Me}$ 1.39 70	48.00 (48.69)	5.72 (5.80)	17.96 (18.55)	355 (345)
4.	$-\text{CH}_2\text{CH}_2\text{CHMe}-$ 1.26	Me 1.34	$\overline{\text{OCH}_2\text{CH}_2\text{CHMeOP}}(\text{S})\text{SC}_6\text{H}_4\text{NHC(O)Me}$ 1.47 72	44.80 (45.43)	4.96 (5.05)	18.84 (20.19)	-
5.	$-\text{CMe}_2\text{CMe}_2-$ 1.34	Ph 1.61	$\overline{\text{OCMe}_2\text{CMe}_2\text{OP}}(\text{S})\text{SC}_6\text{H}_4\text{NHC(O)Ph}$ 1.90 80	55.78 (56.02)	5.32 (5.41)	14.90 (15.72)	-
6.	$-\text{CH}_2\text{CMe}_2\text{CH}_2-$ 1.13	Ph 1.45	$\overline{\text{OCH}_2\text{CMe}_2\text{CH}_2\text{OP}}(\text{S})\text{SC}_6\text{H}_4\text{NHC(O)Ph}$ 1.53 74	57.70 (58.02)	4.98 (5.09)	15.98 (16.28)	370 (393)

S. No.	Reactants(g)		Product -----g;-----	Analyses Found(Calcd.)			M. Wt. Found(Calcd.)
	$\overline{\text{OGOP}}(\text{S})\text{SNH}_4$	$\text{BrC}_6\text{H}_4\text{NHCOR}$					
	G = -----	R = -----		C	H	S %	
7.	$-\text{CMe}_2\text{CH}_2\text{CHMe}-$ 1.22	Ph 1.47	$\overline{\text{OCMe}_2\text{CH}_2\text{CHMeOP}}(\text{S})\text{SC}_6\text{H}_4\text{NHC(O)Ph}$ 1.52 70	55.30 (56.02)	5.36 (5.41)	15.00 (15.72)	—
8.	$-\text{CH}_2\text{CH}_2\text{CHMe}-$ 1.28	Ph 1.75	$\overline{\text{OCH}_2\text{CH}_2\text{CHMeOP}}(\text{S})\text{SC}_6\text{H}_4\text{NHC(O)Ph}$ 1.98 82	53.75 (53.83)	4.68 (4.75)	16.02 (16.87)	—

¹H NMR SPECTRA

The ¹H NMR spectra of these compounds show characteristic resonance for all the different rings protons present in the molecule. A broad singlet has been observed in the region δ 5.5 – 6.6 ppm (Table II) which have been assigned to secondary amine (-NH) proton. A multiplet at δ 6.8 – 7.1 ppm has been observed which is ascribed to benzoyl protons; while *s*-phenyl protons give resonance signal as a multiplet at δ 7.4 – 7.6 ppm.

³¹P NMR SPECTRA

³¹P NMR spectra of these derivatives show single resonance signal in the region δ 98.88 – 87.19 ppm (Table II). In comparison to dithiophosphoric acid, the resonance signal of acetanilide (benzanilide) derivatives of alkylene dithiophosphates show down field shifting (δ 5 – 10 ppm). On the basis of above observations, the mode of chemical bonding in these compounds appears to; P(S) – S – C.

EXPERIMENTAL

Stringent precautions were taken to exclude moisture during the experimental manipulations. Solvents were dried by standard methods. *p*-bromoacetanilid (benzanilide)^[18] and alkylene dithiophosphates^[1] were prepared by the methods reported in the literature. Sulphur was estimated gravimetrically as barium sulphate (Messenger's method)^[18]. Nitrogen was estimated by kjeldahl's method^[18]. Molecular weights were determined with a "Knauer Vapor Pressure Osmometer" using chloroform solution at 45°C. Infrared spectra were recorded in nujol mull (4000 – 200 cm⁻¹) on Perkin -Elmer 577 spectrophotometer. Carbon and hydrogen analyses were performed on a perkin Elmer CHNS/O analyzer. ¹H NMR spectra were recorded in CDCl₃ solution on a 90 MHz JEOL FX 90Q spectrometer using TMS as an internal reference. ³¹P NMR spectra were recorded in CHCl₃ using H₃PO₄ as an external reference.

The compounds were synthesized in similar manner, the experimental details of a representative compound is being described below. Analytical results are summarised in Table III.

Preparation of $\text{OCMe}_2\text{CMe}_2\text{OP(S)SC}_6\text{H}_4\text{NHC(O)Me}$

A weighed amount of p-bromoacetanilide (1.13 g) was treated with ammonium tetramethyl ethylene dithiophosphate (1.21 g) in benzene (~45 ml). The reaction mixture was refluxed for ~28 hrs. The reaction is fast in the presence of strong base (EtONa) and completes within ~10 hrs of refluxing in benzene. The NH_4Br precipitated was filtered off and the excess of solvent was removed under reduced pressure. The product obtained was light yellow sticky solid. The compound on analysis show; C, 48.00; H, 5.72; S, 18.01% Calcd. for $\text{OCMe}_2\text{CMe}_2\text{OP(S)SC}_6\text{H}_4\text{NHC(O)Me}$: C, 48.69; H, 5.80; S, 18.55%. The above procedure was adopted for all the other reactions. Relevant data are given in Table III.

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