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Straightforward Synthesis of a New Series of α-(Arylamino thiocarbonyloxy) Hydrocarbylphosphonates

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ABSTRACT

A convenient, straightforward, two-step reaction of α-hydroxyhydrocarbylphosphonates with arylisothiocyanates in the presence of catalytic amounts of sodium methoxide in 1,2-dichloroethane as solvent produced various new α-(arylamino thiocarbonyloxy) hydrocarbylphosphonates in excellent yields. Their structures have been confirmed by their IR, ^{1}H NMR and ^{31}P NMR spectra and by elemental analysis. The preliminary antisepsis activity and protein activity of some of the compounds were identified.

KEYWORDS

Phosphonates, arylisothiocyanates, α-hydroxyhydrocarbylphosphonates, synthesis, activity.

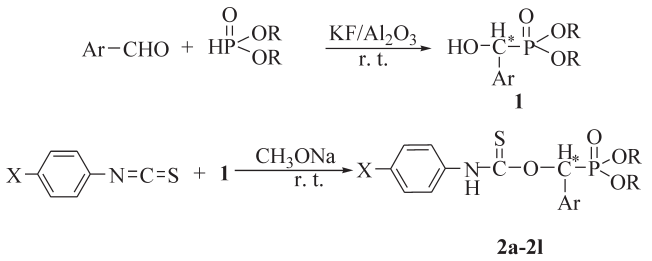
1. Introduction

Phosphonates constitute an important class of organophosphorus compounds and are useful in many applications from organic synthesis to agriculture applications as pesticides and plant growth regulating reagents. Besides that, α-hydroxy phosphonates can be converted into other α-substituted phosphonates.[1,2] In the last decade, research on phosphonates has mainly focussed on six structure types[3,4] of which α-oxohydrocarbylphosphonate was a typical one.[5,6] Furthermore, α-hydroxy alkyl phosphonates have become increasingly important for their biological activity.[7–9] They are also convenient intermediates in the synthesis of other substituted phosphonates.[10,11] Based on the research of our predecessors,[12–15] we designed and synthesized a new series of α-(arylamino thiocarbonyloxy) hydrocarbylphosphonates. The structures were confirmed by IR and ^{1}H NMR spectroscopy and elemental analysis; some compounds were also confirmed by their ^{31}P NMR spectra. Here, the bioactivities of some of these new compounds with respect to antisepsis and plant growth regulating activities are reported.

2. Results and Discussion

As shown in Scheme 1, α-hydroxyhydrocarbylphosphonate **1** was prepared by the reaction of equimolar amounts of an aldehyde and a phosphite.[16–18] Neutral alumina and potassium fluoride (no dehydration was necessary) were used to facilitate the reaction.[19] The reaction proceeded on the surface of the catalyst (the mixture of alumina and potassium fluoride) at room temperature. This method had a fast reaction rate, was easy to manipulate and gave high yields with no noticeable side reactions. In the preparation of **2** (Scheme 1), the catalyst appeared to play a major role. In the absence of sodium methoxide, the yield was between 20% and 30%, compared with yields of 74% to 90% in the presence of the catalyst.

Aryl isothiocyanates are easily obtained through proper preparation methods,[20,21] and have important applications in synthesis.[22] Furthermore, due to the thermal instability of aryl isothiocyanates, a trimerization reaction occurred if the reaction was heated (Scheme 2). This polymerization reaction was extraordinarily rapid, and the trimer was isolated as a pale yellow resinoid.[12]

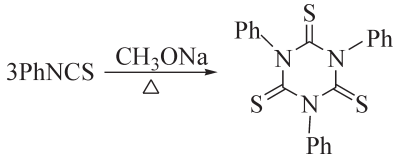


Scheme 1

To avoid the trimerization reaction, the sodium methoxide and α-hydroxyhydrocarbylphosphonate were mixed in the solvent (1, 2-dichloroethane) at room temperature. Aryl isothiocyanate was then added slowly to the mixture to reduce the side reaction.

All compounds (**2a–2l**) exhibit characteristic IR absorptions for N-H, P=O and C=S groups. In the ^{1}H NMR spectra, the protons on the benzene ring appear at δ 7.20 to 7.60 ppm. Because the hydrogen on the α-carbon (in **2a–2l**, the α-carbon is chiral and is indicated with an asterisk) is coupled to the phosphorus atom, it shows up as a doublet, and the coupling constant and chemical shift are approximately δ 6.85 ppm and 13.0 Hz. In the ^{31}P NMR spectrum, the four-coordinate phosphorus is affected by one asymmetric atom in the structure of the products (**2a–2l**), and the phosphorus signal appears as two peaks. In the elemental analysis, all the results are consistent with the theoretical values.

In the test of antisepsis activity, the product **2a** was analysed by observational measurement and quantitative measurement. *Escherichia coli* and *Staphylococcus aureus* were tested. Both the



Scheme 2

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Table 1 Results of observational measurements for product **2a**.

Bacterium	Diameter of bacteriostasis circle/cm
E. coli	0.70
S. aureus	0.60

results of observational measurement and quantitative measurement were followed, namely the diameter of the bacteriostasis circle and the suitable conditions of concentration. As can be seen from Tables 1 and 2, the product **2a** exhibited definite bacteriostasis for *Escherichia coli*. When the product concentration was 1000 mg L^{-1}, it inhibited the growth of bacteria, and when the product concentration was reduced to 500 mg L^{-1}, partial bacteria were observed. Lastly in the 250 mg L^{-1} range, no antisepsis activity was observed. The antisepsis activities of other compounds form part of an ongoing study.

For the preliminary plant growth regulating studies,[4,18] we used the products **2a**, **2b**, **2c**, **2d** and **2e** for chrysanthemum rootage (see Table 3), and the products **2f, 2g, 2h**, **2i**, **2j**, **2k** and **2l** for chrysanthemum leafage (see Table 4). The first five products all exhibited definite rootage, especially product **2a**. The efficiency of the last seven products for leafage growth is comparatively low.

3. Experimental

Melting points were uncorrected. IR spectra were recorded in KBr on a Digilab FTS-40 spectrophotometer. ^{1}H NMR spectra were measured on a Bruker DPX-400 spectrometer using TMS as internal standard and $CDCl_3$ as solvent. ^{31}P NMR spectra were measured using a Bruker DPX–162 spectrometer using TMS as internal standard, 85% phosphoric acid as external standard, and $CDCl_3$ as solvent. Elemental analyses were performed using a PE-2400 CHN elemental analyser.

3.1. General Procedure for 2a–2l (Scheme 1), taking 2a as an Example

The 1,2-dichloroethane solution of *p*-bromophenyl isothiocyanate (0.532 g, 2.5 mmol) was slowly added to a solution of diethyl α-hydroxy-α-phenyl phosphonate (0.61 g, 2.5 mmol) and sodium methoxide (0.02 g, 0.37 mmol) in 1,2-dichloroethane (10 mL). The mixture was kept for 30 min at room temperature with stirring, and the reaction was monitored by TLC. The reaction mixture was then dried with anhydrous sodium sulphate, the solvent was distilled under reduced pressure and the crude product was obtained. The purity of the crude product was analysed by TLC and separated on silica gel (eluent: petroleum ether 60–90 °C/ethyl acetate, 3:2). Diethyl α-(*p*-bromophenylaminothiocarbonyloxy)-α-(phenyl)methylphosphonate **2a** was obtained, and the yield was 85% (see Table 5).

3.1.1. *Diethyl* α-(p-*bromophenylaminothiocarbonyloxy*)-α-(*phenyl*) *methyl phosphonate* (**2a**): white crystals; IR (KBr): $\bar{\nu}$ 3165 (N-H), 1593, 1538, 1243 (P=O), 1136 (C=S), 1051 (C-O-C), 741 (P-O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.00 (s, 1H, NH), 7.43 (m, 5H, -C_6H_5), 7.28 (m, 4H, -C_6H_4), 6.90 (d, 1H, $^2J_{PCH}$ = 13.6 Hz, PCH), 3.98 (q, 4H, ^{3}J = 7.6 Hz, 2 ×OCH_2), 1.25 (t, 6H, ^{3}J = 7.6 Hz, 2 ×CH3). Analysis: calcd for $C_{18}H_{21}NO_4PSBr$: C, 47.16; H, 4.59; N, 3.06; found: C, 47.41; H, 4.32; N, 2.95. ^{31}P NMR: δ 17.988, 16.829 ppm.

3.1.2. *Dimethyl* α-(p-*bromophenylaminothiocarbonyloxy*)-α-(*phenyl*)*methyl phosphonate* (**2b**): pale yellow crystals; IR (KBr): $\bar{\nu}$ 3187 (N-H), 1600, 1548, 1255 (P=O), 1128 (C=S), 1042 (C-O-C), 769 (P-O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.97 (s, 1H, NH), 7.60 (m, 5H, -C_6H_5), 7.08 (m, 4H, -C_6H_4), 6.90 (d, 1H, $^2J_{PCH}$ = 13.6 Hz, PCH), 3.72 (s, 6H, 2 ×OCH_3). Analysis: calcd for $C_{16}H_{17}NO_4PSBr$: C, 44.65; H, 3.95; N, 3.26; found: C, 44.87; H, 4.13; N, 3.11. ^{31}P NMR: δ 19.965, 18.843 ppm.

3.1.3. *Diisopropyl* α-(p-*bromophenylaminothiocarbonyloxy*)-α-(*phenyl*)*methyl phosphonate* (**2c**): pale yellow crystals; IR (KBr): $\bar{\nu}$ 3160 (N-H), 1594, 1542, 1259 (P=O), 1134 (C=S), 1014 (C-O-C), 748 (P-O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.05 (s, 1H, NH), 7.43 (m, 5H, -C_6H_5), 7.32 (m, 4H, -C_6H_4), 6.84 (d, 1H, $^2J_{PCH}$ = 14.0 Hz, PCH), 4.61 (m, 2H, ^{3}J = 5.6 Hz, 2 ×OCH), 1.25 (d, 12H, ^{3}J = 5.6 Hz, 4 ×CH_3). Analysis: calcd for $C_{20}H_{25}NO_4PSBr$: C, 49.38; H, 5.14; N, 2.88; found: C, 49.10; H, 5.36; N, 3.20. ^{31}P NMR: δ 17.745, 16.926 ppm.

3.1.4. *Diisopropyl* α-(p-*bromophenylaminothiocarbonyloxy*)-α-(p-*chlorophenyl*) *methyl phosphonate* (**2d**): pale yellow crystals; IR (KBr): $\bar{\nu}$ 3176 (N-H), 1595, 1545, 1231 (P=O), 1123 (C=S), 1017 (C-O-C), 767 (P-O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.80 (s, 1H, NH), 7.39 (m, 4H, -C_6H_4), 7.29 (m, 4H, -C_6H_4), 6.78 (d, 1H, $^2J_{PCH}$ =

Table 2 Results of quantitative measurements for product **2a**.

Bacterium	Concentration/mg L^{-1} and growth of bacteria						
E. coli	1 000.00 – – –	500.00 – – +	250.00 + + +	125.00 + + +	62.50 + + +	31.25 + + +	15.63 + + +

Note: – indicates no growth; + indicates growth.

Table 3 Plant growth regulating activity of compounds **2a–2e.**

Compound	Concentration/mg L^{-1}	Ratio of chrysanthemum rootage
2a	35	73
2b	35	59
2c	35	50
2d	35	61
2e	35	48

Table 4 Plant growth regulating activity of compounds **2f–2l.**

Compound	Concentration/mg L^{-1}	Ratio of chrysanthemum leafage
2f	35	1.54
2g	35	2.38
2h	35	0.75
2i	35	1.85
2j	35	1.00
2k	35	0.41
2l	35	0.15

Table 5 Reaction times, yields and melting points of compounds **2a–2l.**

Compound	R	Ar	X	Reaction time/h	Yield/%	M.p./°C
2a	Et	C_6H_5	Br	0.5	85	120~122
2b	Me	C_6H_5	Br	3	74	126~128
2c	i-Pr	C_6H_5	Br	0.5	80	137~138
2d	i-Pr	4-ClC_6H_4	Br	2	82	139~141
2e	Et	4-$CH_3C_6H_4$	Br	3	77	120~121
2f	i-Pr	2-ClC_6H_4	Br	3.5	76	143~145
2g	Et	C_6H_5	EtO	0.5	85	91~93
2h	Me	C_6H_5	EtO	1	80	140~141
2i	i-Pr	C_6H_5	EtO	0.5	90	119~121
2j	Et	4-ClC_6H_4	EtO	1	82	130~132
2k	Et	4-$CH_3C_6H_4$	Cl	3	78	106~108
2l	i-Pr	4-ClC_6H_4	Cl	2.5	85	108~110

13.6 Hz, PCH), 4.55 (q, 2H, ^3J = 6.0 Hz, 2 ×OCH), 1.20 (d, 12H, ^3J = 6.0 Hz, 4 ×CH_3). Analysis: calcd for $C_{20}H_{25}NO_4PSBr$: C, 46.10; H, 4.61; N, 2.69. Found: C, 46.29; H, 4.78; N, 2.89. ^{31}P NMR: δ 15.432, 14.829 ppm.

3.1.5. *Diethyl* α-(p-*bromophenylaminothiocarbonyloxy*)-α-(p-*methyl phenyl*) *methyl phosphonate* (**2e**): pale yellow crystals, IR (KBr): $\bar{\nu}$ 3171 (N-H), 1599, 1543, 1233 (P=O), 1135 (C=S), 1022 (C-O-C), 772 (P-O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.20 (s, 1H, NH), 7.38 (dd, 4H, ^3J = 8.0 Hz, -C_6H_4), 7.14 (m, 4H, -C_6H_4), 6.88 (d, 1H, $^2J_{PCH}$ = 13.2 Hz, PCH), 4.05 (q, 4H, ^3J = 6.8 Hz, 2 ×CH_2), 2.90 (s, 3H, CH_3), 1.25 (t, 6H, ^3J = 6.8 Hz, 2 ×CH_3). Analysis: calcd. for $C_{18}H_{21}NO_5PSCl$: C, 50.28; H, 4.88; N, 3.27; found: C, 50.01; H, 4.62; N, 3.44. ^{31}P NMR: δ18.188, 17.481 ppm.

3.1.6. *Diisopropyl* α-(p-*bromophenylaminothiocarbonyloxy*)-α-(o-*chlorophenyl*) *methyl phosphonate* (**2f**): pale yellow crystals; IR (KBr): $\bar{\nu}$ 3178 (N-H), 1596, 1545, 1244 (P=O), 1130 (C=S), 1025 (C-O-C), 763 (P-O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.00 (s, 1H, NH), 7.33 (m, 4H, -C_6H_4), 7.25 (m, 4H, -C_6H_4), 6.85 (d, 1H, $^2J_{PCH}$ = 13.6 Hz, PCH), 4.35 (q, 2H, ^3J = 5.6 Hz, 2 × OCH), 1.15(d, 12H, ^3J = 5.6 Hz, 4 ×CH_3). Analysis: calcd. for $C_{20}H_{25}NO_4PSBr$: C, 46.10; H, 4.61; N, 2.69; found: C, 45.89; H, 4.35; N, 2.48.

3.1.7. *Diethyl* α-(p-*ethoxyphenylaminothiocarbonyloxy*)-α-(*phenyl*)*methyl phosphonate* (**2g**): pale yellow crystals; IR (KBr): $\bar{\nu}$ 3156 (N-H), 1591, 1537, 1263 (P=O), 1138 (C=S), 1044 (C-O-C), 738 (P-O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.75 (s, 1H, NH), 7.35 (m, 5H, -C_6H_5), 7.50 (m, 4H, -C_6H_4), 6.88 (d, 1H, $^2J_{PCH}$ = 9.2 Hz, PCH), 4.00 (q, 4H, ^3J = 6.8 Hz, 2 × OCH_2), 1.30 (t, 6H, ^3J = 6.8 Hz, 2 × CH_3). Analysis: calcd. for $C_{20}H_{26}NO_5PS$: C, 56.74; H, 6.10; N, 3.35; found: C, 56.39; H, 5.73; N, 3.11. ^{31}P NMR: δ 18.186, 16.829 ppm.

3.1.8. *Dimethyl* α-(p-*ethoxyphenylaminothiocarbonyloxy*)-α-(*phenyl*)*methyl phosphonate* (**2h**): pale yellow crystals; IR (KBr): $\bar{\nu}$ 3175 (N-H), 1610, 1538, 1246 (P=O), 1124 (C=S), 1053 (C-O-C), 740 (P-O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.25 (s, 1H, NH), 7.40 (m, 5H, -C_6H_5), 6.96 (d, 1H, $^2J_{PCH}$ = 12.4 Hz, PCH), 6.85 (m, 4H, -C_6H_4), 4.40 (q, 2H, ^3J = 6.0 Hz, OCH_2), 3.65 (s, 6H, 2 × OCH_3), 1.27 (t, 3H, ^3J = 6.0 Hz, CH_3). Analysis: calcd. for $C_{18}H_{22}NO_5PS$: C, 54.67; H, 5.55; N, 3.53; found: C, 54.39; H, 5.24; N, 3.71.

3.1.9. *Diisopropyl* α-(p-*ethoxyphenylaminothiocarbonyloxy*)-α-(*phenyl*)*methyl phosphonate* (**2i**): white crystals; IR (KBr): $\bar{\nu}$ 3188 (N-H), 1604, 1545, 1231 (P=O), 1120 (C=S), 1027 (C-O-C), 753 (P-O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.55 (s, 1H, NH), 7.57 (m, 4H, -C_6H_4,), 7.30 (m, 5H, -C_6H_5), 6.87 (d, 1H, $^2J_{PCH}$ = 14.0 Hz, PCH), 4.60 (m, 2H, ^3J = 5.6 Hz, 2 × CH), 4.00 (q, 2H, ^3J = 6.8 Hz, OCH_2), 1.40 (t, 3H, ^3J = 6.8 Hz, 4 × CH_3), 1.10 (dd, 12H, ^3J = 5.6 Hz, CH_3). Analysis: calcd. for $C_{22}H_{30}NO_5PS$: C, 58.55; H, 6.60; N, 3.08; found: C, 58.78; H, 6.46; N, 2.87.

3.1.10. *Diethyl* α-(p-*chlorophenyl*)-α-(p-*ethoxyphenylaminothiocarbonyloxy*) *methyl phosphonate* (**2j**): white crystals; IR (KBr): $\bar{\nu}$ 3175 (N-H), 1600, 1540, 1240 (P=O), 1136 (C=S), 1044 (C-O-C), 770 (P-O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.85 (s, 1H, NH), 7.45 (m, 4H, -C_6H_4), 7.35 (m, 4H, -C_6H_4), 6.85 (d, 1H, $^2J_{PCH}$ = 14.0 Hz, PCH), 4.05 (q, 4H, ^3J = 6.8 Hz, 2 ×OCH_2), 1.23 (t, 6H, ^3J = 6.8 Hz, 2 ×CH_3). Analysis: calcd for $C_{20}H_{25}NO_5PSCl$: C, 52.43; H, 5.47; N, 3.08; found: C, 52.18; H, 5.25; N, 2.81.

3.1.11. *Diethyl* α-(p-*chlorophenylaminothiocarbonyloxy*)-α-(p-*methylphenyl*) *methyl phosphonate* (**2k**): pale yellow crystals; IR (KBr): $\bar{\nu}$ 3177 (N-H), 1599, 1546, 1227 (P=O), 1132 (C=S), 1017 (C-O-C), 749 (P-O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.70 (s, 1H, NH), 7.40 (m, 4H, -C_6H_4), 7.16 (m, 4H, -C_6H_4), 6.84 (d, 1H, $^2J_{PCH}$ = 13.2 Hz, PCH), 4.00 (s, 6H, 2 ×OCH_3), 2.30 (s, 3H, CH_3). Analysis: calcd. for $C_{20}H_{25}NO_4PSCl$: C, 50.30; H, 5.21; N, 2.92; found: C, 53.51; H, 5.03; N, 3.26.

3.1.12. *Diisopropyl* α-(p-*chlorophenyl*)-α-(p-*chlorophenylaminothiocarbonyloxy*) *methyl phosphonate* (**2l**): white crystals; IR (KBr): $\bar{\nu}$ 3188 (N-H), 1599, 1546, 1231 (P=O), 1136 (C=S), 1048 (C-O-C), 765 (P-O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.30 (s, 1H, NH), 7.40 (m, 4H, -C_6H_4), 7.30 (m, 4H, -C_6H_4), 6.78 (d, 1H, $^2J_{PCH}$ = 14.0 Hz, PCH), 4.45 (m, 2H, ^3J = 6.0 Hz, 2 ×CH), 1.27 (d, 12H, ^3J = 6.0 Hz, 4 ×CH_3). Analysis: calcd. for $C_{20}H_{25}NO_4PSCl_2$: C, 50.30; H, 5.21; N, 2.92; found: C, 50.49; H, 5.10; N, 2.74. ^{31}P NMR: δ 19.735, 18.886 ppm.

4. Conclusion

In conclusion, we have synthesized a new series of α-(arylamino thiocarbonyloxy) hydrocarbylphosphonates. The operation is simple, and the yield is quite high (74% to 90%). Besides, the preliminary plant growth regulating and antisepsis studies of some compounds had a significant activity.

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