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Synthesis of Phosphonic Acid Containing Thiadiazole

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ABSTRACT: *A series of phosphonic acid, 1,3,4-thiadiazol-2-amine-N-alkyl have been synthesized by the reaction of 2-amine thiadiazole, different aldehydes (or ketone), and phosphorous acid via the melting method or the solvent method. These compounds have been characterized by IR, ^{1}H NMR, ^{31}P NMR, and elemental analysis. Results showed that compounds were reacted via the solvent method in better yields.* © 2008 Wiley Periodicals, Inc. Heteroatom Chem 19:140–143, 2008; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20395

INTRODUCTION

Corrosion inhibitors are widely used in industry to reduce the corrosion rate of metals, which is caused due to the contact with aggressive environments. Their protective action is based on the formation of a metal–inhibitor complex film on the metal surface. Many phosphonic acids have been used as water treatment reagents [1,2]. As early as 1970, phosphonate was successfully used as a reagent in the water treatment of the brewery by Hass Geffers Cologue [3]. In addition, phosphonic acids may act as inhibitors for metal dissolution due to the chelating action and the formation of a physical blocking barrier on the metal surface. Many kinds of phosphonic acid including EDTMP, HDTP, NTP, and HEDP [4], have been developed and applied in the rare metal extraction [5], corrosion inhibition of metals, etc.

Heterocyclic compounds, especially those containing nitrogen, sulfur, or oxygen can form a complex film on the metal surface due to the presence of lone-pair of electrons and/or aromatic rings [6]. These compounds include benzotriazole [7,8], thioimidazole [9], pyrimidines [10], etc. Thus, they are often used to protect metals from corrosion [11,12]. It is known that phosphonic acids containing heterocycle are effective inhibitors for metals [13–15].

Corrosion inhibition by phosphonic acids and heterocyclic compounds prompted us to prepare a new kind of compound with a high-effective inhibition for metal corrosion. In this paper, a series of phosphonic acids containing heterocycle were synthesized by different methods.

RESULTS AND DISCUSSION

Phosphonic acids containing heterocycle were synthesized (Scheme 1) by the reaction of 2-amine thiadiazole, different aldehydes (or ketone), and phosphorous acid via different methods.

Phosphorous acid reacted with 2-amine thiadiazole and aldehydes (formaldehyde and butyraldehyde) in the presence of concentrated hydrochloric acid by boiling the solution to afford **a** and **b** (Scheme 2) in 21–26% yields. The color of solid **a** and **b** is khaki. The structures of **a** and **b** have been characterized spectroscopically, and their data are listed in Table 2. The gross formula, $C_3H_6N_3O_3SP$, of **a** was confirmed by the mass spectrum, which exhibited

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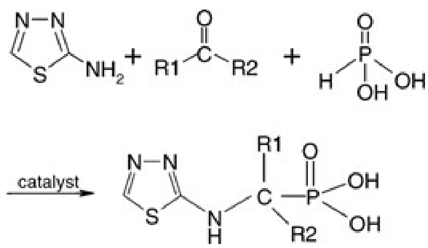
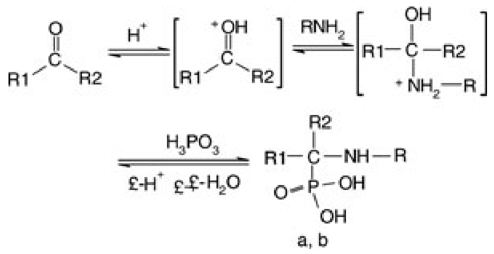


SCHEME 1

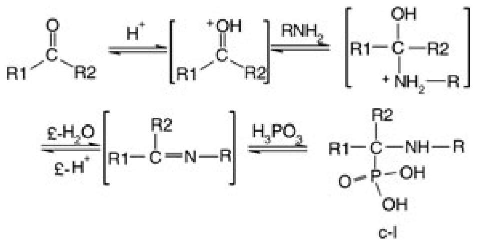


SCHEME 2

the molecular ion at m/z 195. The IR spectrum of **a** revealed peaks at 3395 cm^{-1} (N—H), 1218 cm^{-1} (P=O), 2678 cm^{-1} (P—OH), and 1666 cm^{-1} (C=N). The ^{1}H NMR spectrum exhibited a multiplet at 4.21 4.42 (m, 1H, NH), a doublet at 3.91 (d, 2H, CH$_2$P), and two kinds of singlet at 7.92 (s, 1H, =CH) and 2.49 (s, 2H, OH). The ^{31}P NMR spectrum showed a singlet peak: δ_P 8.12.

Compounds **c–l** (Scheme 3) were obtained in tetramethylenesulfone solvent at 170°C–180°C by equimolecular addition of reactants. Furthermore, **c–l** were also prepared by the reaction of phosphorous acid, 2-amine thiadiazole, and aldehydes (or ketone) without solvent at 190°C–200°C.

The results are listed in Table 1. The structures of the products were confirmed by IR, ^{1}H NMR, ^{31}P NMR, MS, and elemental analysis, and their data are listed in Table 2. Compound **c** (taken as a representative example) gave correct elemental analyses, and the IR spectrum of **c** showed the absorption bands of NH at 3400 cm^{-1}, Ph—C at 3044 cm^{-1}, P=O at 1243 cm^{-1}, P—OH at 2560 cm^{-1}, C=N at 1690 cm^{-1}, and C=C at 1450 cm^{-1}. Its ^{1}H NMR revealed signals of =CH at $\delta = 8.32$ ppm, CHP at $\delta = 4.68$ ppm, NH at $\delta = 4.47$ ppm, OH at $\delta = 2.45$ ppm, Ar—H at $\delta = 7.23$, 7.60 ppm. Moreover, the ^{31}P NMR of **c** showed signals at 12.42. Its mass spectrum showed a molecular ion peak, as the base peak at m/z 271.



SCHEME 3

EXPERIMENTAL

Melting points were determined with a model X4 apparatus and were uncorrected. MS were measured on a Finnigan Trace MS spectrometer. ^{1}H NMR spectra and ^{31}P NMR spectra were recorded on a Varian Mercury 400 spectrometer, and resonance is given in ppm (δ) relative to TMS. IR was measured on a Perkin-Elmer Spectrum-2000 Fourier infrared spectrum apparatus. Elemental analysis was recorded on a Vario EL III elemental analysis instrument.

Preparation of **a** *and* **b**

A mixture of 2-amine thiadiazole (0.05 mol) and phosphorous acid (0.05 mol) in concentrated hydrochloric acid (5 mL) was stirred and heated. Aldehyde (0.06 mol) was added dropwise at 80°C. The mixture was refluxed for 2–4 h. The solution was allowed to cool to room temperature and was neutralized by 20% NaOH to pH 2–3. The precipitate was removed by filtration. The precipitated solid was recrystallized from acetic acid/water to obtain **a** and **b**.

Preparation of **c–l**

Method A (Solvent Method). Tetramethylenesulfone (20 mL) was added in a three-necked flask and heated. Phosphorous acid (0.05 mol), 2-amine thiadiazole (0.05 mol), and toluene-*p*-sulfonic acid (0.02 mol) were added at 80°C. Aldehyde (or ketone) (0.06 mol) was then added dropwise to the mixture. When the addition was complete, the reactant was stirred at 120°C for 10 min. The mixture was heated to 170–180°C and kept for 30 min and then cooled. Water was added. The solid product was collected by filtration and recrystallized from acetic acid/water to yield **c–l**.

Method B (Melting Method). To a mixture of 2-amine thiadiazole (0.05 mol), phosphorous acid (0.05 mol), and toluene-*p*-sulfonic acid (0.02 mol) was slowly added aldehyde (or ketone) (0.06 mol). The reaction mixture was heated to 190–200°C for 30 min and then cooled. The solid was washed by water. The product so obtained was collected by filtration and recrystallized from acetic acid/water to yield **c–l**.

TABLE 1 Preparation of Phosphonic Acid, 1,3,4-Thiadiazol-2-Amine-*N*-Alkyl **a–l**

	R₁	*R₂*	*Formula*	*Yield (%) Solvent (Melting)*	*MP (°C)*
a*	H	H	$C_3H_6N_3O_3SP$	21	187–188
b*	H	*n*-C_3H_7	$C_6H_{12}N_3O_3SP$	26	169–170
c	H	Ph	$C_9H_{10}N_3O_3SP$	72 (50)	254–256
d	H	*p*-OHC_6H_4	$C_9H_{10}N_3O_4SP$	79 (52)	>300
e	H	*p*-$OCH_3C_6H_4$	$C_{10}H_{12}N_3O_4SP$	82 (55)	152–154
f	H	*o*-OHC_6H_4	$C_9H_{10}N_3O_4SP$	67 (42)	288–290
g	H	*m, p*-ClC_6H_3	$C_9H_8N_3O_3SPCl_2$	65 (32)	232–234
h	H	*p*-ClC_6H_4	$C_9H_9N_3O_3SPCl$	66 (37)	167–169
i	H	*p*-$NH_2C_6H_4$	$C_9H_{11}N_4O_3SP$	81 (56)	296–298
j	H	*o*-BrC_6H_4	$C_9H_9N_3O_3SPBr$	70 (40)	142–144
k	H	*m*-$NO_2C_6H_4$	$C_9H_9N_4O_5SP$	73 (44)	264–266
l	CH_3	Ph	$C_{10}H_{12}N_3O_3SP$	60 (37)	216–217

TABLE 2 The Elemental Analyses, IR, MS, ^{1}H NMR, and ^{31}P NMR Data of Phosphonic Acid, 1,3,4-Thiadiazol-2-Amine-*N*-Alkyl **a–l**

	Anal. %, (calc.)	*IR(cm^{-1})*	*MS (m/z)*	*^{1}H NMR (δ, ppm)*	*^{31}P NMR (δ, ppm)*
a	C, 18.35 (18.46); H, 2.96 (3.08); N, 21.42 (21.54)	3395, 1218, 2678, 1666	195	7.92 (s, 1H, =CH), 4.21–4.42 (m, 1H, NH), 2.49 (s, 2H, OH), 3.91 (d, 2H, CH_2P)	8.12
b	C, 30.26 (30.40); H, 4.95 (5.06); N, 17.59 (17.72)	3420, 1231, 2586, 1675	237	7.96 (s, 1H, =CH), 4.24 (d, 1H, NH), 2.49 (s, 2H, OH), 3.61–3.83 (m, 1H, CHP)	19.05
c	C, 39.71 (39.85); H, 3.55 (2.69); N, 15.38 (15.50)	3400, 3044, 1243, 2560, 1690, 1450	271	8.32 (s, 1H, =CH), 4.68 (d, 1H, CHP), 4.47 (d, 1H, NH), 2.45 (s, 2H, OH), 7.23–7.60 (m, 5H, Ar—H)	12.42
d	C, 37.75 (37.63); H, 3.39 (3.48); N, 14.55 (14.63)	3500, 3040, 1240, 2591, 1688, 1438	287	8.52 (s, 1H, =CH), 4.38 (d, 1H, CHP), 2.44 (s, 2H, P—OH), 5.20 (s, H, Ar—OH), 6.91–7.54 (m, 4H, Ar—H)	13.46
e	C, 39.81 (39.87); H, 3.93 (3.99); N, 13.89 (13.95)	3400, 3059, 1210, 2560, 1665, 1447	301	8.48 (s, 1H, =CH), 5.18 (d, 1H, CHP), 2.43 (s, 2H, P—OH), 3.60 (s, 3H, OCH_3), 7.11–7.46 (m, 4H, Ar—H)	10.60
f	C, 37.80 (37.63); H, 3.40 (3.48); N, 14.58 (14.63)	3411, 3032, 1250, 2650, 1655, 1452	287	8.11 (s, 1H, =CH), 4.58 (d, 1H, CHP), 2.44 (s, 2H, P—OH), 5.25 (s, H, Ar—OH), 7.16–7.46 (m, 4H, Ar—H)	23.37
g	C, 31.81 (31.76); H, 2.30 (2.35); N, 12.43 (12.35)	3408, 3032, 1245, 2680, 1674, 1460	340	8.23 (s, 1H, =CH), 5.06 (d, 1H, CHP), 4.45 (d, 1H, NH), 2.45 (s, 2H, P—OH), 6.71–7.26 (m, 3H, Ar—H)	21.15
h	C, 35.40 (35.35); H, 3.20 (3.27); N, 13.81 (13.75)	3415, 3051, 1252, 2670, 1670, 1463	305	8.46 (s, 1H, =CH), 4.96 (d, 1H, CHP), 4.43 (d, 1H, NH), 2.45 (s, 2H, P—OH), 6.95–7.48 (m, 4H, Ar—H)	12.88
i	C, 37.74 (37.62); H, 3.9 1 (3.85); N, 19.49 (19.58)	3380, 3039, 1210, 2596, 1695, 1435	286	8.15 (s, 1H, =CH), 4.79 (d, 1H, CHP), 4.52 (s, 2H, NH_2), 2.43 (s, 2H, P—OH), 6.88–7.54 (m, 4H, Ar—H)	16.76
j	C, 30.91 (30.86); H, 2.81 (2.86); N, 12.03 (12.00)	3430, 3046, 1245, 2623, 1670, 1457	349	8.65 (s, 1H, =CH), 5.21 (d, 1H, CHP), 4.42 (d, 1H, NH), 2.45 (s, 2H, P—OH), 7.13–7.68 (m, 4H, Ar—H)	14.38
k	C, 34.22 (34.17); H, 2.81 (2.85); N, 17.68 (17.72)	3415, 3035, 1218, 2691, 1680, 1459	316	8.85 (s, 1H, =CH), 4.97 (d, 1H, CHP), 4.48 (d, 1H, NH), 2.50 (s, 2H, P—OH), 7.98–8.43 (m, 4H, Ar—H)	17.88
l	C, 41.96 (42.11); H, 4.08 (4.21); N, 14.61(14.74)	3427, 3080, 1221, 2742, 1657, 1471	285	8.52(s, 1H, =CH), 1.87(d, 3H, CH_3), 4.47 (d, 1H, NH), 2.45 (s, 2H, P—OH), 7.55–7.88 (m, 5H, Ar—H)	13.72

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