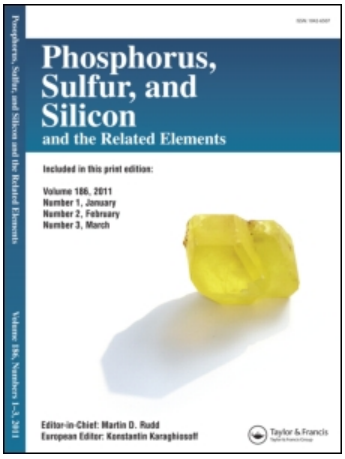

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HYDROXY AND/OR CARBOXY SUBSTITUTED PHOSPHONIC AND BISPHOSPHONIC ACIDS USABLE AS CORROSION AND SCALE INHIBITORS

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2-Dihydroxyphosphonyl-2-hydroxy-propionic acid (DHHPA), 1,4-bis[(dihydroxyphosphonyl)hydroxymethyl]benzene (BDHB) and 2,3-bis(dihydroxyphosphonyl)-1,4-butanedioic acid (BDBA) were synthesized by acid catalyzed hydrolysis of the corresponding substituted phosphonates or bisphosphonates. The structure of these compounds was confirmed by elemental analysis as well as by infrared (IR) and proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy. They can be used as corrosion and scale inhibitors.

INTRODUCTION

Phosphonic or bisphosphonic acids containing hydroxy and/or carboxy substituents have valuable properties as ferrous corrosion inhibitors and scale control additives for circulating water systems. They, along with polyelectrolytes, belong to the most effective scale inhibitors. These inhibitors are able to retard or to block the growth process, even if added in concentrations far below the stoichiometric quantity normally needed for coordination of the cations in solution. The inhibitors apparently exert their influence directly upon the crystal surface.

In connection with our interest in the preparation of new useful organophosphorus compounds[1–4] we carried out the synthesis and characterization of three substituted phosphonic or bisphosphonic acids prepared by acid catalyzed hydrolysis of the corresponding phosphonates or bisphosphonates. It was shown that they exhibit a considerable corrosion and scale inhibiting effect.[5]

RESULTS AND DISCUSSION

The overall reaction sequences for the synthesis of the substituted phosphonic or bisphosphonic acids are outlined in Scheme 1.

More particularly, the reaction of ethyl pyruvate with an equimolar amount of diethyl phosphite afforded 2-diethoxyphosphonyl-2-hydroxy-propionic acid ethyl ester. This reaction was carried out in the absence of a solvent by heating the

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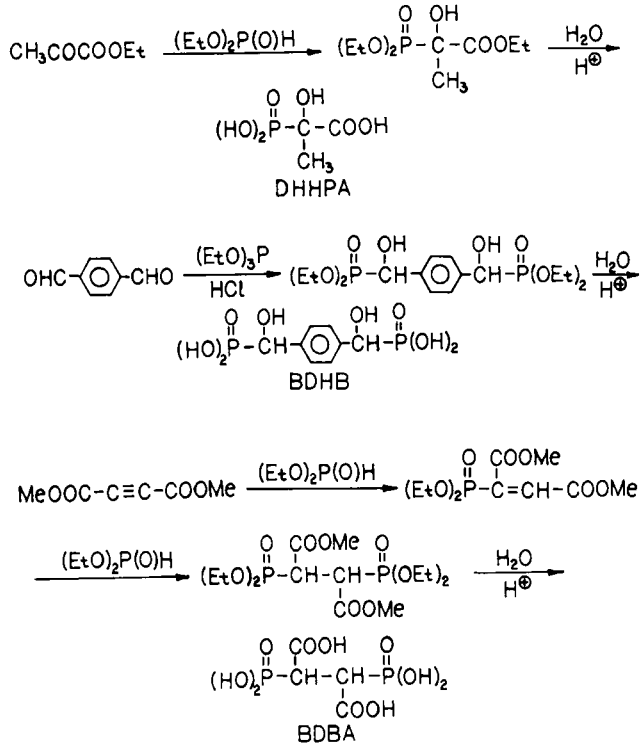

SCHEME 1

mixture of the reagents at 70°C for 90 hours. Under these conditions no isomerization of the reaction product to the corresponding phosphate was observed. It has been reported[6] that 2-diethoxyphosphonyl-2-hydroxy-propionic acid ethyl ester was thermally unstable and isomerized to the corresponding phosphate by heating at 155–190°C for 3 hours.

In the present case the reaction between ethyl pyruvate and diethyl phosphite was monitored by ^{1}H-NMR measurements of the reaction mixture. Figure 1 shows the ^{1}H-NMR spectra of the reaction mixture obtained without applying heating (top) as well as after heating at 70°C for 22 hours (middle) and 90 hours (bottom). It can be seen that the singlet at 2.07 δ assigned to $\underline{CH_3}COCOOEt$ was reduced with the progress of the chemical reaction. In addition, a doublet ($J_{PCCH} = 16$ Hz) associated with these methyl protons of the reaction product appeared at 1.30 δ. The right leg of this doublet overlapped with the left leg of the triplet at 1.05 δ assigned to the $\underline{CH_3}CH_2O$ protons. The reaction was completed when the singlet at 2.07 δ disappeared. Furthermore, the with D_2O exchangeable proton of the singlet at 5.48 δ shows the presence of the hydroxyl group.

The reaction product, 2-diethoxyphosphonyl-2-hydroxy-propionic acid ethyl ester, was obtained as a viscous undistillable liquid. It was hydrolyzed by refluxing its solution in concentrated hydrochloric acid for 8 hours. Shorter refluxing periods of this solution afforded a partially hydrolyzed product.

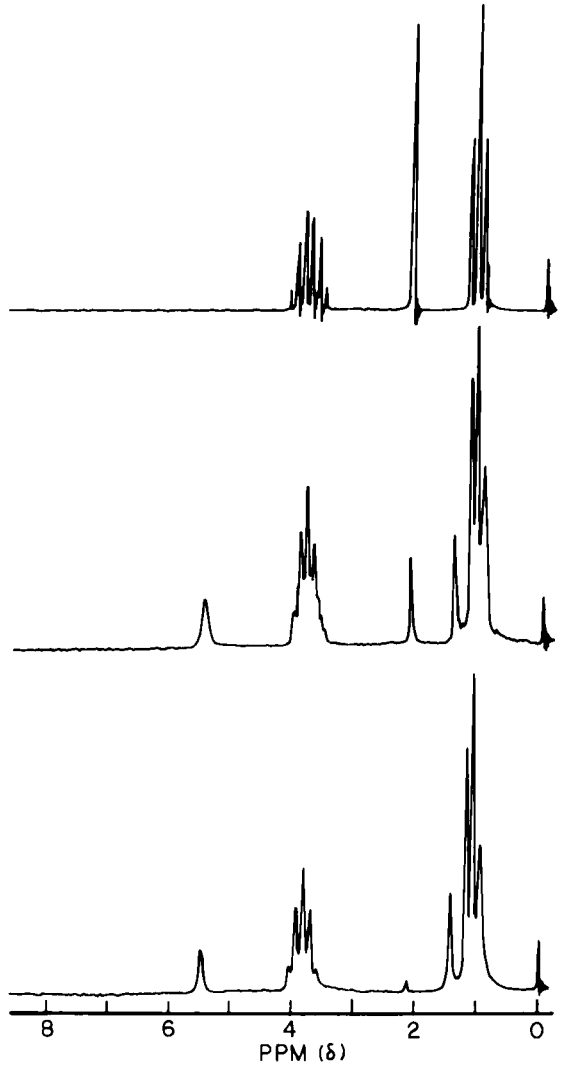

FIGURE 1 ^{1}H-NMR spectra of ethyl pyruvate and diethyl phosphite mixture obtained without applying heating (top) as well as after heating at 70°C for 22 hours (middle) and 90 hours (bottom).

DHHPA was obtained in nearly quantitative yield after removal of the volatile components.

Salt of 2-phosphonyl-2-hydroxy-propionic acid prepared from pyruvic acid and diethyl phosphite has been used as detergent builder.[7] A different preparation method of DHHPA has been reported by treating $CH_3COCOOH$ with PCl_3, next by adding glacial CH_3COOH followed by hydrolysis.[8] DHHPA has been functioned as an Fe sequestration agent from pH 6 to 11.[8] In addition, DHHPA has been used as a component for several photographic developers.[9–12]

The IR spectrum of DHHPA showed characteristic absorption bands at 3350–3150 cm^{-1} (alcoholic OH), 3000–2600 cm^{-1} (carboxylic OH and P—OH),

1755 cm^{-1} (C=O) and 1265 cm^{-1} (P=O). The ^{1}H-NMR spectrum of DHHPA obtained from D_2O solution exhibited only a doublet (J_{PCCH} = 16 Hz) at 1.56 δ assigned to the methyl protons. The other protons of DHHPA were exchangeable with D_2O and therefore did not show signals.

BDHB was prepared by acid catalyzed hydrolysis of 1,4-bis[(diethoxyphosphonyl)hydroxymethyl]benzene (Scheme 1). The latter was synthesized by reacting 1,4-benzenedicarboxaldehyde with triethyl phosphite in the presence of anhydrous hydrogen chloride.[13] The synthesis of BDHB was undertaken because of its structural features. It should be noted that an analogous compound 1,2-dihydroxy-1,2-bis(dihydroxyphosphonyl)ethane,[1] $(HO)_2P(O)CH(OH)CH(OH)P(O)(OH)_2$, has been shown to be a very useful complexing agent[14] and effective scale inhibitor.[15] Salts of BDHB and other analogous bisphosphonic acids can be used as catalysts for manufacturing polyisocyanurate plastics.[16]

The most important absorption bands which appeared in the IR spectrum of BDHB were at 3600–3200 cm^{-1} (alcoholic OH), 2700–2500 cm^{-1} (P—OH), 1580 and 1445 cm^{-1} (aromatic) and 1240 cm^{-1} (P=O). The ^{1}H-NMR spectrum of BDHB in D_2O solution showed a singlet at 7.33 δ assigned to the aromatic protons and a doublet (J_{PCH} = 13 Hz) at 4.93 δ associated with the PCH protons.

The last reaction sequence of Scheme 1 outlines the synthesis route of BDBA. Particularly, acetylenedicarboxylic acid dimethyl ester (1 mole) reacted with diethyl phosphite (2 mole)[17]. The reaction was carried out by heating the reagent mixture without utilizing a solvent. The progress of this reaction was followed by IR measurements of the reaction mixture. The reaction was completed when the absorption bands at 2430 and 2140 cm^{-1} attributed to the P—H and C≡C stretching vibrations, respectively, disappeared. The unreacted starting materials were removed from the reaction mixture by distillation under reduced pressure. The adduct was obtained as a viscous undistillable liquid. It was hydrolyzed in the presence of concentrated hydrochloric acid.

The synthesis of BDBA by acid catalyzed hydrolysis of the corresponding bisphosphonate has been disclosed in a patent.[18] BDBA has been used as builder for organic detergents,[18] as a component for photographic developers,[19–21] as agent for preventing incrustation from salt-containing water[22] and finally in oral compositions for calculus retardation.[23]

Several characteristic absorption bands appeared in the IR spectrum of BDBA were at 3200–2560 cm^{-1} (carboxylic OH and P—OH), 1740 cm^{-1} (C=O) and 1305 cm^{-1} (P=O). The ^{1}H-NMR spectrum of BDBA obtained from D_2O solution showed only a doublet (J_{PCH} = 12 Hz) at 3.5 δ associated with the PCH protons.

EXPERIMENTAL

Materials. Ethyl pyruvate, 1,4-benzenedicarboxaldehyde and acetylene dicarboxylic acid dimethyl ester (Aldrich) were used as supplied. Dimethyl phosphite (Merck) was distilled under reduced pressure. Triethyl phosphite and *p*-dioxane (Merck) were purified by refluxing with sodium and fractional distillation.

Instrumentation. Infrared (IR) spectra were recorded on a Perkin–Elmer 710B spectrophotometer with nujol or KBr pellets or NaCl cells. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded on a Varian T-60A spectrometer at 60.0 MHz and at 30°C, normal probe temperature. Chemical shifts (δ) are given in parts per million. Tetramethylsilane and 3-trimethylsilylpropane sulfonate were used as an internal standard in DMSO-d_6 and D_2O solutions, respectively. Melting points were determined on an Electrothermal melting point apparatus IA6304 and are uncorrected.

2-*Dihydroxyphosphonyl*-2-*hydroxy-propionic acid* (*DHHPA*). Ethyl pyruvate 98% (7.12 g, 60 mmol) and diethyl phosphite (8.28 g, 60 mmol) were introduced in a flask equipped with a magnetic stirrer and a condenser. The mixture was stirred and heated at 70–75°C for 90 h. A small amount of unreacted starting materials was subsequently removed from the reaction mixture by distillation under reduced pressure (0.9 mm Hg). 2-Diethoxyphosphonyl-2-hydroxy-propionic acid ethyl ester was obtained as a viscous undistillable liquid (13.50 g, 93%). IR (neat) cm^{-1}: 3480–3250 (OH stretching), 2960 and 2926 (C—H stretching), 1744 (C=O stretching), 1408 (OH deformation), 1280 (C—O—C stretching), 1257 (P=O) and 1070–995 (P—O—C). ^{1}H-NMR (neat) δ: 5.48 (s, 1H, OH), 3.83 (m, 6H, O$\underline{CH_2}CH_3$), 1.30 (d, J_{PCCH} = 16 Hz, 3H, PC$\underline{CH_3}$), 1.05 (t, 9H, OCH$_2\underline{CH_3}$).

2-Diethoxyphosphonyl-2-hydroxy-propionic acid ethyl ester (13.50 g, 55.8 mmol) was dissolved in 10 ml of 36% hydrochloric acid and refluxed for 4 h under stirring. To this solution additional 10 ml of 36% hydrochloric acid were added and refluxing was continued for other 4h. After removal of the volatile components in a rotary evaporator DHHPA was obtained as a white solid (9.30 g, 98%). Recrystallizations from tetrahydrofurane-ether (1:2 vol/vol) gave an analytical sample having mp 145–147°C (decomposition).

Anal. Calcd for $C_3H_7O_6P$:C, 21.19%; H, 4.15%.
Found: C, 21.26%; H, 4.18%.

1,4-*Bis*[(*dihydroxyphosphonyl*)*hydroxymethyl*]*benzene* (*BDHB*). A mixture of powdered 1,4-benzenedicarboxaldehyde 98% (14.37 g, 105 mmol), *p*-dioxane (35 ml) and triethyl phosphite (38.39 g, 231 mmol) were introduced in a three-necked flask equipped with a magnetic stirrer, thermometer, gas inlet and gas trap. Into the stirred suspension hydrogen chloride was bubbled and the temperature of the reaction mixture was maintained between 20–30°C by means of external cooling. Hydrogen chloride addition dissolved at first the suspended 1,4-benzenedicarboxaldehyde and subsequently a large amount of white solid was separated. During the hydrogen chloride addition the yellow color of dialdehyde gradually disappeared. The hydrogen chloride addition was discontinued when it did not cause an exothermic reaction and no more solid product was separated (~30 min). The reaction mixture was subsequently stirred at room temperature for 30 min, filtered and the solid washed twice with *p*-dioxane and twice with ether to give 1,4-bis[(diethoxyphosphonyl)hydroxymethyl]benzene (36.5 g, 85%). It was purified by recrystallizations from dimethyl sulfoxide (mp 216–218°C). IR (KBr) cm^{-1}: 3270 (OH stretching), 3030, 1493 and 670 (aromatic), 1408 (OH deformation), 1228 (P=O) and 1078–987 (P—O—C). ^{1}H-NMR (DMSO-d_6) δ: 7.73 (s, 4H, aromatic), 5.15 (d, J_{PCH} = 13 Hz, 2H, PCH), 4.07 (m, 8H, O$\underline{CH_2}CH_3$) and 1.20 (t, 12H, OCH$_2\underline{CH_3}$).

1,4-Bis[(diethoxyphosphonyl)hydroxymethyl]benzene (3.85 g, 9.4 mmol) was dissolved in 10 ml of 36% hydrochloric acid and refluxed for 2 h under stirring. To this solution additional 10 ml of 36% hydrochloric acid were added and refluxing was continued for other 2 h. The solution was subsequently concentrated in a rotary evaporator to yield BDHB (2.64 g, 92%). An analytical sample having mp 199–202°C (decomposition) was obtained by recrystallizations from methanol-ether (1:2 vol/vol).

Anal. Calcd for $C_8H_{12}O_8P_2$: C, 32.23%; H, 4.06%
Found: C, 32.25%; H, 4.10%.

2,3-*Bis*(*dihydroxyphosphonyl*)-1,4-*butanedioic acid* (*BDBA*). Acetylenedicarboxylic acid dimethyl ester 99% (4.30 g, 30 mmol) and diethyl phosphite (8.29 g, 60 mmol) were introduced in a flask equipped with a magnetic stirrer and a condenser. The mixture was stirred and heated at 70–75°C for 100 h. A small amount of unreacted starting materials was removed from the reaction mixture by distillation under vacuum (0.3 mm Hg). 2,3-Bis(diethoxyphosphonyl)-1,4-butanedioic acid dimethyl ester was obtained as a viscous undistillable liquid (11.91 g, 95%). IR (neat) cm^{-1}: 2960–2930 (C—H stretching), 1746 (C=O), 1308–1273 (P=O and C—O—C stretching) and 1067–990 (P—O—C). ^{1}H-NMR (neat) δ: 4.33–3.87 (m, 10H, O$\underline{CH_2}CH_3$ and PCH), 3.68 (s, 6H, COOCH$_3$), 1.28 (t, 12H, OCH$_2\underline{CH_3}$).

2,3-Bis(diethoxyphosphonyl)-1,4-butanedioic acid dimethyl ester (7.07 g, 16.9 mmol) was dissolved in 15 ml of 36% hydrochloric acid and refluxed for 6 h under stirring. To this solution additional 15 ml

of 36% hydrochloric acid were added and refluxing was continued for another 6 h. The solution was subsequently concentrated in a rotary evaporator to yield BDBA (4.40 g, 94%). An analytical sample having mp 196–198°C (decomposition) was obtained by recrystallizations from methanol-ether (1:3 vol/vol).

Anal. Calcd for $C_4H_8O_{10}P_2$: C, 17.28%; H, 2.90%.
Found: C, 17.32%; H, 2.85%.

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