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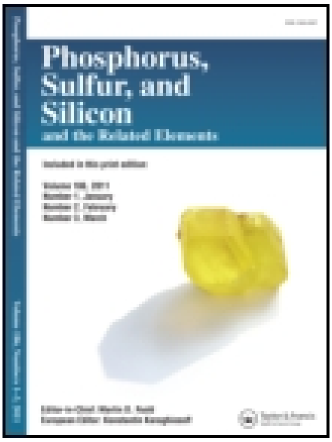

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Rapid One-Pot Synthesis of Alkane-α,ω-Diylbisphosphonic Acids from Dihalogenoalkanes Under Microwave Irradiation

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RAPID ONE-POT SYNTHESIS OF ALKANE-α,ω-DIYLBISPHOSPHONIC ACIDS FROM DIHALOGENOALKANES UNDER MICROWAVE IRRADIATION

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A one-pot, two-step synthesis of alkylenebisphosphonic acids from dihalogenoalkanes was performed under microwave irradiation. The reaction is very rapid and convenient for the synthesis of small samples of alkylenebisphosphonic acids.

Keywords Alkane-α,ω-diylbisphosphonic acids; microwave irradiation; one-pot synthesis; xylene-α,α'-bisphosphonic acids

INTRODUCTION

The classical Arbusov synthesis of phosphonates starting from halide derivatives is accelerated considerably under microwave irradiation.[1] In the same way, microwaves are known to accelerate hydrolyses, and they are used successfully for the hydrolysis of proteins or polysaccharides to form amino acids and monsaccharides.[2] The hydrolysis of phosphonates to phosphonic acids by hydracids is also accelerated by microwave irradiation. In the aim of preparing minor amounts of diphosphonic acids to study the preparation of phosphonates as hybrid materials, we have developed a one-pot method for the Arbusov reaction followed by hydrolysis under microwave irradiation. The diphosphonates and phosphonic acids represent organic–inorganic hybrid material precursors.[3–6] They also have anticorrosion[7–10] and antiscaling properties.[11] They are known as excellent coordinating compounds of metallic ions and are frequently used in liquid–liquid extraction processes, particularly for the concentration and purification of actinides, lanthanides, and other polyvalent ions.[12–15]

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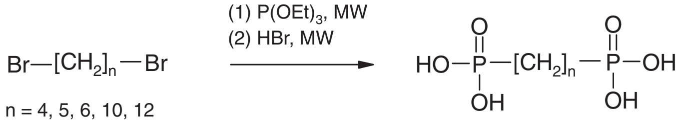
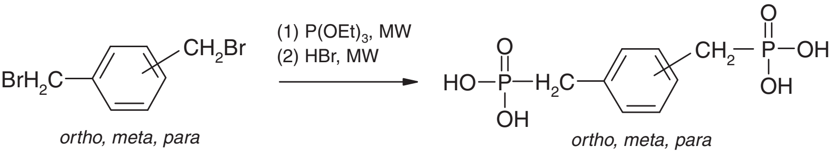
FAST AND EASY SYNTHESIS OF DIPHOSPHONIC ACIDS

Halide derivatives react with an excess of triethyl phosphite under microwave irradiation. In a mono-mode reactor, the reaction is complete within 10 min. Excesses of phosphites and alkyl halides are evaporated under vacuum. The mixture is hydrolyzed by a hydrobromic acid solution during 10 min under microwave irradiation, and the obtained diphosphonic acid is crystallized in water.

We have used α,ω-dibromoalkanes for the preparation of alkane-α,ω-diylbisphosphonic acids (Scheme 1) and α,α'-dibromoxylenes as starting materials for the preparation of xylene-α,α'-bisphosphonic acids (Scheme 2).



Scheme 1 One-pot synthesis of alkane-α,ω-diylbisphosphonic acids from α,ω-dihalides.



Scheme 2 One-pot synthesis of xylene-α,α'-bisphosphonic acids.

The reaction was particularly fast and efficient, and made it possible to prepare very pure diphosphonic acids without distillation or chromatography. It was not necessary to operate under an inert atmosphere. A minute amount of phosphite is transformed into phosphonate, which hydrolyzed in water to the soluble phosphonic acid. We have also tested various hydracids while following the reaction by sampling and ^{31}P NMR analysis. The following order of hydrolysis rates is observed: HI > HBr > HCl.[16] Unfortunately the use of hydroiodic acid is accompanied by the formation of a small quantity of iodine by air oxidation, coloring the final phosphonic acid. Thus, hydrobromic acid is preferable for the hydrolysis step.

EXPERIMENTAL

Reagents and Materials

The reagents used in the present syntheses, 1,4-dibromobutane, 1,5-dibromopentane, 1,6-dibromohexane, 1,10-dibromodecane, 1,12-dibromododecane, α,α'-dichloro-*ortho*-xylene, α,α'-dibromo-*meta*-xylene, α,α'-dibromo-*para*-xylene, triethyl phosphite, aqu. HBr (54%), methanol, and acetone (analytical grade), were purchased from Fluka (Switzerland). The infrared spectra (ν, cm^{-1}) were recorded on a Perkin Elmer ATR spectrometer. Samples were analyzed by NMR spectroscopy on a Bruker B 400 multinuclear spectrometer (δ in ppm, J in Hz). Samples of the products were diluted in D_2O in the presence of Na_2CO_3. Microwave irradiation reactions were performed in a microwave oven Synthewave 402 (Prolabo) working with a frequency of 2450 MHz. The reactions were performed in a 3.5 cm diameter Pyrex tube fitted with a condenser.

Butane-1,4-diylbisphosphonic acid was obtained from 1,4-dibromobutane (20 mmol, 2.4 mL) and triethyl phosphite (40 mmol, 6.9 mL) under MW irradiation (170 W, 5 min). HBr (80 mmol, 12 mL) was rapidly added to the obtained product, and the mixture was again irradiated (140 W, 5 min). The liquids were evaporated in a vacuum. The resulting solid was crystallized in water/methanol (95:5) and dried to yield 55% of white crystals. Mp >230°C. ^{1}H NMR: 1.55 (m, 4H), 1.82 (m, 2H), 3.55 (t, $^2J_{HP} = 6.84$, 2CH$_2$-P). ^{31}P NMR: 22.8. ^{13}C NMR: 11.15, 25.5 (d, $^2J_{CP} = 120$, 2CH$_2$-P), 34.5. IR: 3000–2840 (OH), 1460 (δ CH$_2$), 1170 (P=O), 1020 (ν_{as} P-OH), 940 (ν_s P-OH).

Pentane-1,5-diylbisphosphonic acid[17] was obtained from 1,5-dibromopentane (20 mmol, 2.8 mL) and triethyl phosphite (40 mmol, 6.9 mL) under MW irradiation (170 W, 6 min). HBr (80 mmol, 12 mL) was rapidly added to the obtained product, and the mixture was again irradiated (140 W for 4 min). The liquids were evaporated in a vacuum. The resulting solid was crystallized in water/methanol (95:5) and dried to yield 64% of white crystals. Mp >240°C. ^{1}H NMR: 1.5 (m, 4H), 1.8 (m, 2H), 3.5 (t, $^2J_{HP} = 6.84$, 2CH$_2$-P). ^{31}P NMR: 23.2. ^{13}C NMR: 11.25, 26.5 (d, $^2J_{CP} = 120$, 2CH$_2$-P), 35.7. IR: 3000–2850 (OH), 1465 (δ CH$_2$), 1178 (P=O), 1026 (ν_{as} P-OH), 941 (ν_s P-OH).

Hexane-1,6-diylbisphosphonic acid was obtained from 1,6-dibromohexane (20 mmol, 7 mL) and triethyl phosphite (40 mmol, 6.9 mL) under MW irradiation (170 W, 5 min). Crystallization in water/acetone (5:95) gave a yield of 89%. Mp >240°C, lit.[18]: Mp 206–208°C. ^{1}H NMR: 1.59 (m, 4H), 1.84 (m, 4H), 3.09 (t, $^2J_{HP} = 6.75$, 2CH$_2$-P). ^{31}P NMR: 27.1. ^{13}C NMR: 22.9, 26.74 (d, $^2J_{CP} = 117.6$, 2CH$_2$-P), 31.97, 35.58. IR: 3000–2850 (OH), 1445 (δ CH$_2$), 1130 (P=O), 1044 (ν_{as} P-OH), 946 (ν_s P-OH).

Decane-1,10-diylbisphosphonic acid[19] was synthesized from 1,10-dibromodecane (20 mmol, 6.19 g) and triethyl phosphite (40 mmol, 6.9 mL) under MW irradiation (170 W, 5 min). Crystallization in water/methanol (95:5) gave a yield of 54%. Mp 200°C. ^{1}H NMR: 1.25 (m, 8H), 1.75 (m, 4H), 1.81 (m, 4H), 3.42 (t, $^2J_{HP} = 6.9$, 2CH$_2$-P). ^{31}P NMR: 23.5. ^{13}C NMR: 24.1, 27.36, 28.3 (d, $^2J_{CP} = 120.7$, 2CH$_2$-P), 28.74, 30.86, 32.15, 33.0, 35.4. IR: 3000–2850 (OH), 1463.9 (δ CH$_2$), 1134.6 (P=O), 1020.7 (ν_{as} P-OH), 948.7 (ν_s P-OH).

Dodecane-1,12-diylbisphosphonic acid was obtained from 1,12-dibromododecane (10 mmol, 3.42 mL) and triethyl phosphite (20 mmol, 3.5 mL) under MW irradiation (170 W, 5 min). Crystallization in water/methanol (95:5) gave a yield of 45%. Mp 220°C. ^{1}H NMR: 1.13 (m, 12H), 1.25 (m, 4H), 1.80 (m, 4H), 3.41 (t, $^2J_{HP} = 6.7$, 2CH$_2$-P). ^{31}P NMR: 23.5. ^{13}C NMR: 24.2, 28.4 (d, $^2J_{CP} = 125.8$, 2CH$_2$-P), 28.97, 30.49, 30.97, 31.25. IR: 3000–2850 (OH), 1464 (δ CH$_2$), 1133 (P=O), 1019 (ν_{as} P-OH), 946 (ν_s P-OH).

ortho-Xylene-α,α'-diphosphonic acid was obtained from α,α'-dichloro-*ortho*-xylene (11.5 mmol, 1.0 g) and triethyl phosphite (23 mmol, 3.9 mL) under MW irradiation (170 W, 5 min). The obtained oil crystallizes in water/acetone (5:95) to yield 40%. Mp 230°C.[20] ^{1}H NMR: 2.97 (t, $^2J_{HP} = 8.96$, 2CH$_2$-P), 7.12 (m, 2H, H$_{ar}$), 7.29 (m, 2H, H$_{ar}$). ^{31}P NMR: 18.9. ^{13}C NMR: 33.49 (d, $^2J_{CP} = 123.76$, 2CH$_2$-P), 125.0, 130.5, 136.0. IR: 3000–2850 (OH), 2189 (CH$_{ar}$), 1453 (δ CH$_2$), 1140 (P=O), 1065 (ν_{as} P-OH), 933 (ν_s P-OH).

meta-Xylene-α,α'-diphosphonic acid[21] was obtained from α,α'-dibromo-*meta*-xylene (20 mmol, 5.44 g) and triethyl phosphite (40 mmol, 6.9 mL) under MW irradiation (170 W, 3 min). Crystallization in water/acetone (5:95) gave a yield of 82%. Mp 240°C.[21] ^{1}H NMR: 3.10 (t, $^2J_{HP} = 9.8$, 2CH$_2$-P), 7.16 (m, 3H, H$_{ar}$), 7.27 (m, 1H, H$_{ar}$).

^{31}P NMR: 20.2. ^{13}C NMR: 35.43 (d, $^2J_{CP} = 125.77$, 2CH$_2$-P), 127, 128.24, 130.5, 135.9. IR: 3000–2850 (OH), 2200 (CH$_{ar}$), 1442 (δ CH$_2$), 1160 (P=O), 1100 (ν_{as} P-OH), 930 (ν_s P-OH).

para-Xylene-α,α′-diphosphonic acid[22] was obtained from α,α′-dibromo-*para*-xylene (20 mmol, 5.44 g) and triethyl phosphite (40 mmol, 6.9 mL) under MW irradiation (170 W, 3 min). Crystallization in water/methanol (95:5) gave a yield of 55%. Mp 190°C.[22] ^{1}H NMR: 2.75 (t, $^2J_{HP} = 9.77$, 2CH$_2$-P), 7.20 (m, 4H$_{ar}$). ^{31}P NMR: 17.8. ^{13}C NMR: 36.4 (d, $^2J_{CP} = 122.66$, 2CH$_2$-P), 127.75, 130.1, 137.1, 138.5. IR: 3000–2850 (OH), 2284 (CH$_{ar}$), 1422 (δ CH$_2$), 1124 (P=O), 1037 (ν_{as} P-OH), 941(ν_s P-OH).

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