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Synthesis, Characterization and Performance of a New Type of Alkylene Triphenyl Double Quaternary Phosphonium Salt*

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ABSTRACT

By Bimolecular Nucleophilic Substitution, four new types of alkylene triphenyl double quaternary phosphonium salt were synthesized respectively by using triphenylphosphine, 1,3-dibromopropane, 1,6-dibromohexane, 1,10-dibromodecane, 1,12-dibromododecane as raw materials and using DMAC as the solvent, under a certain temperature and reaction time. The productivity is 58% - 83%. The molecular structures of the products were characterized by IR, NMR and elemental analysis. The sterilizing effect of 1,6-hexylidene triphenyl double phosphonium bromide (HTDPB) and 1,12-dodecylidene triphenyl double phosphonium bromide (DoTDPB) was evaluated by using extinct dilution method. The experimental result shows that the sterilizing effect of DoTDPB is better than the effect of HTDPB under the same drug concentration and contact time. When the concentration of DoTDPB was 20 mg/L and the contact time was 0.5 h, the sterilizing rate of DoTDPB used to kill saprophytic bacteria (TGB), sulfate-reducing bacteria (SRB) and iron bacteria (IB) was 95.56%, 84% and 99.58% respectively.

Keywords: Alkylene Triphenyl Phosphonium; Double Quaternary Phosphonium Salt; Bactericide; Synthesis; Performance

1. Introduction

One traditional way to prevent microbes from breeding in water is adding bactericide in water. If people use the same kind of bactericide frequently, microbes will get resistance to drugs. That will decreases the sterilizing effect of bactericide, and increases the application amount of bactericide and the cost of water treatment, so to make a new type of high-effeciency bactericide has been a research hotspot among domestic and overseas researchers. Quaernary phosphonium salt and double quaernary phosphonium salt are one type of new, high-effeciency and broad-spectrum bactericide [1-3], which will not produce foam after being used in water and exist in the interface and water body. The sulfonated triphenyl phosphonium has the effect of resisting tumour [4], so it is evaluated highly.

Four new types of alkylene triphenyl double quaternary phosphonium salt were synthesized respectively by Bimolecular Nucleophilic Substitution and using triphenyl phosphine, 1,3-dibromo propane, 1,6-dibro mohexane, 1,10-dibromodecane and 1,12-dibromododecane as raw materials. Their synthetic route is in **Figure 1**.

The molecular structures of products were characterized by using IR, NMR and element analysis. The sterilizing effect of 1,6-hexylidene triphenyl double phosphonium bromide (HTDPB) and 1,12-dodecylidene triphenyl double phosphonium bromide (DoTDPB) was tested by using extinct dilution method.

2. Experimental Part

2.1. Reagents and Instruments

Reagents: Triphenylphosphine, 1,3-dibromomopropane, 1,6-dibromohexane, 1,10-dibromodecane, 1,12-dibromododecane and N,N-dimethylacetamide are all analytical reagents. Industrial circulating cooling water samples are from a petrochemical corporation in Guangzhou.

Instruments: PE-2400 CHNS elementalanalyser (PerkinElmer of Shanghai); NICOLET-380 infrared spectrometer (Thermo Electron Corporation); XT41-00B

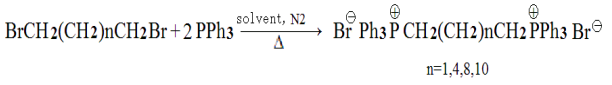

Figure 1. The synthetic route of alkylene triphenyl double quaternary phosphonium salt.

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micromelting point apparatus (Keyi photoelectric instrument factory of Beijin); thermometers; Bruker AVANCE III HD 500 NMR spectrometer; 722 ultraviolet and visible spectrophotometer(INESA).

2.2. The Synthesis of Bactericide

2.2.1. The Synthesis of 1,12-Dodecylidene Triphenyl Double Phosphonium Bromide (DoTDPB)

1,12-dibromododecane (3.28 g, 0.01 mol) and triphenylphosphine (5.78 g, 0.022 mol) were added in a three-necked bottle with a thermometer, a condensation tube and the entrance of N_2. DMAC (12 ml) was used to dissolve reactants. Under the protection of N_2, the reaction proceeded at 150˚C for 20 h. The product was obtained by using reduced perssure distillation after the reaction. Then, it was dissolved in some distilled water and the aqueous phase was extracted thrice with petroleum ether. We obtained the liquid product (DoTDPB) by using rotary evaporation in the end. The productivity was 82.6%.

2.2.2. The Synthesis of 1,10-Decylidene Triphenyl Double Phosphonium Bromide (DeTDPB)

The experimental method was similar to the method in the part 1.2.1. 1,10-dibromodecane (2.44 g, 0.01 mol) and triphenylphosphine (5.78 g, 0.022 mol) reacted under the same condition like the part 1.2.1 for 18 h. And then, we obtained the liquid product (DeTDPB). The productivity was 82.8%.

2.2.3. The Synthesis of 1,6-Hexylidene Triphenyl Double Phosphonium Bromide (HTDPB)

The experimental method was similar to the method in the part 1.2.1. 1,6-dibromohexane (2.44 g, 0.01 mol) and triphenylphosphine (5.24 g, 0.02 mol) reacted under the same condition like the part 1.2.1. Then, we obtained the solid product (HTDPB). It was recrystallized by using the solvent which was comprised of ethanol (1 mol) and acetone (1 mol). The melting point of the product is 324˚C - 326˚C and the productivity was 74.5%.

2.2.4. The Synthesis of 1,3-Propylidene Triphenyl Double Phosphonium Bromide (PTDPB)

Under the protection of N_2, triphenylphosphine (5.78 g, 0.022 mol), 1,3-dibromomopropane(2.02 g, 0.01 mol) and DMAC (20 mL) were mixed to react at 120˚C - 125˚C for 10 h. After the rection, the precipitate in the solvent were filtered out and dissolved in the distilled water (210 ml). The insoluble matters in the distilled water were filtered out, and the aqueous phase was evaporated by using rotry evaporation. The residual solids was recrystallized by using the same solvent mentioned at the part 1.2.3 and dried in vacua untill their weight was constant. The melting point of the product is 350˚C - 352˚C and the productivity was 57.7%.

2.3. Bactericidal Experiments

By using MPN [5] to measure the change of bacterial concentration of water samples, the sterilizing effect of bactericide was tested. The water samples used in the bactericidal experiments was from a petrochemical corporation in Guangzhou. The bacteria used in the bactericidal experiments were saprophytic bacteria (TGB), sulfate-reducing bacteria (SRB) and iron bacteria (IB).

2.4. The Determination of the Phosphorus Content of Products

The total phosphorus content of products disposed by using microwave digestion was determined by using ammonium molybdate spectrophotometric method [6]. The phosphorus content of products was calculated by using the formula (1).

$$p(\%) = \left(G \times 10^{-3} / W\right) \times 100 \quad (1)$$

G (μg)—The phosphorus content of tested products;
W (mg)—The weight of products.

2.5. The Determination of Dissociative Bromine

A certain amount of triphenyl double quaternary phosphonium salt was added in a 250 mL conical flask and dissolved in distilled water under being heated and stirred. When the temperature of the liquid fell to the room temperature, 1ml potassium chromate solution (5%) was added in the liquid. After that, the liquid was titrated with silver nitrate standard solution until brick-red precipitate appeared. The wasting volumes of silver nitrate standard solution were recorded. The percentage content of dissociative bromine was calculated by using formula (2).

$$\eta = \frac{79.904\,\mathrm{CV}}{\mathrm{W}} \times 100\% \quad (2)$$

V (ml)—The wasting volume of $AgNO_3$ standard solution during titration;
C (mol/L)—The concentration of $AgNO_3$ standard solution;
W (mg)—The weight of samples.

3. The Results of Experiments and Discussion

3.1. The Results of Elemental Analysis

Figure 2 is phosphorus standard curve. The linear equation is $Y = 51.3A - 0.1794$, $R_2 = 0.9997$. The bromine content of products was tested by using the method in part 1.5. The results of elemental analysis about C, H, P, Br are in **Table 1**.

According to the datas in **Table 1**, we can see that the

theorelical values and test values of elemental content of four products are nearly equal.

3.2. The Results of IR

The characteristic absorption peaks of four products were detected by using potassium bromide pressed-disk technique. The result is in **Table 2**.

From those characteristic peaks, the main functional groups of products were confirmed.

3.3. The Results of NMR

The conditions of tests: CD3OD (solvent), 25˚C (temperature), TMS (internal standard).

The results of 1HNMR and 13CNMR about four products are in **Table 3** and **Table 4**.

According to the experimental results of NMR, the inference about the molecular structures of four products is correct.

3.4. The Results of Sterilization Experiment

When bactericide concentration was 20 mg/L and contact time was 1 h, the effect of killing saprophytic bacteria (TGB), sulfate-reducing bacteria (SRB) and iron bacteria (IB) with two types of quaternary phosphonium salt was tested, and the results are in **Table 5**.

From **Table 5**, we see that two products have good effect of killing IB, and their sterilizing rate is all more than 99% under the experimental conditions.

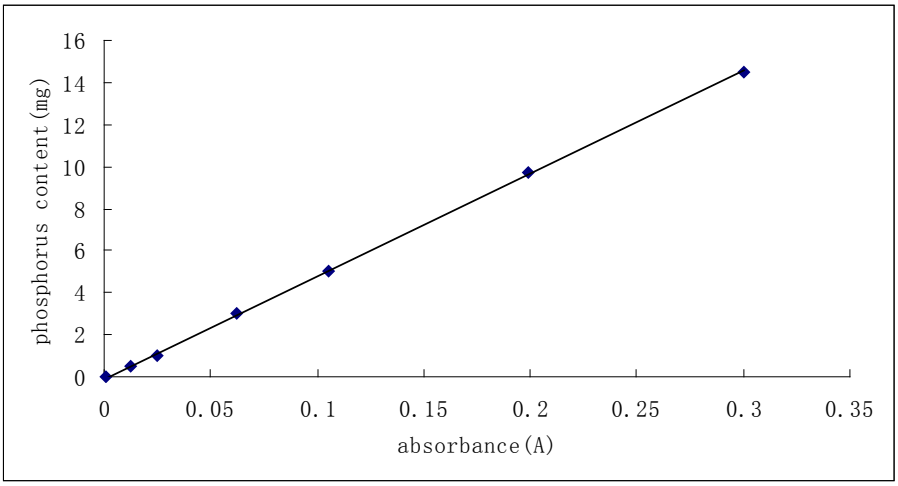

Figure 2. The standard curve of phosphorous.

Table 1. The results of elemental analysis about four types of double quarternary phosphonium salt.

Products	C (%)		H (%)		P (%)		Br (%)	
DoTDPB $C_{48}H_{54}P_2Br_2$	67.61 (*a*)	67.57 (*b*)	6.38	6.34	7.26	7.15	18.74	18.49
DeTDPB $C_{46}H_{50}P_2Br_2$	67.00	66.97	6.11	6.10	7.51	7.56	19.38	19.24
HTDPB $C_{42}H_{42}P_2Br_2$	65.64	65.61	5.51	5.55	8.06	7.99	20.80	20.85
PTDPB $C_{39}H_{36}P_2Br_2$	64.48	64.39	4.99	5.04	8.53	8.50	22.00	21.41

a—Theorelical values; *b*—Test values.

Table 2. The infrared characteristic absorption peaks of products.

Products	The infrared characteristic absorption peaks/cm^{-1}
DoTDPB	2985 ~ 2875 (The stretching vibration of CH_2); 1646, 1488(The vibration of benzene ring); 850 (The stretching vibration of C-P)
DeTDPB	2927 ~ 2855 (The stretching vibration of CH_2); 1635, 1585, 1464 (The vibration of benzene ring); 995 (The stretching vibration of C-P)
HTDPB	2975 ~ 2845 (The stretching vibration of CH_2); 1686, 1483 (The vibration of benzene ring); 750 (The stretching vibration of C-P)
PTDPB	2932 ~ 2865 (The stretching vibration of CH_2); 1656, 1463 (The vibration of benzene ring); 795 (The stretching vibration of C-P)

Table 3. The results of 1HNMR about four products.

Products	The chemical shift in ^{1}HNMR/δ (ppm)
DoTDPB	δ = 7.67 ~ 7. 99 (30H) (The chemical shift of H on benzene ring); δ = 3.63 ~ 3.68 (4H) (The chemical shift of H on CH_2 that is connected with P); δ = 1.73 ~ 1.79 (4H) (The chemical shift of H on CH_2 that is separated by one C from P); δ = 1.64 ~ 1.71 (4H) (The chemical shift of H on CH_2 that is separated by two C from P); δ = 1.37 ~ 1.38 (4H) (The chemical shift of H on CH_2 that is separated by three C from P); δ = 1.27 ~ 1.30 (8H) (The chemical shift of other H);
DeTDPB	δ = 7.77 ~ 7. 94 (30H) (The chemical shift of H on benzene ring); δ = 3.42 ~ 3.48 (4H) (The chemical shift of H on CH_2 that is connected with P); δ = 1.66 ~ 1.71 (4H) (The chemical shift of H on CH_2 that is separated by one C from P); δ = 1.54 ~ 1.59 (4H) (The chemical shift of H on CH_2 that is separated by two C from P); δ = 1.28 ~ 1.36 (8H) (The chemical shift of other H);
HTDPB	δ = 7.76 ~ 7. 93 (30H) (The chemical shift of H on benzene ring); δ = 3.45 ~ 3.49 (4H) (The chemical shift of H on CH_2 that is connected with P); δ = 1.66 (8H) (The chemical shift of H on CH_2 that is separated by one C from P);
PTDPB	δ = 7.78 ~ 7. 96 (30H) (The chemical shift of H on benzene ring); δ = 3.54 ~ 3.75 (4H) (The chemical shift of H on CH_2 that is connected with P); δ = 2.21 ~ 2.28 (2H) (The chemical shift of H on CH_2 that is separated by one C from P);

Table 4. The results of 13CNMR about four products.

Products	The chemical shift in ^{13}CNMR/δ (ppm)
DoTDPB	δ = 129.9 ~ 136.1 (The chemical shift of C on benzene ring); δ = 119.4 ~ 129.9 (The chemical shift of C that is connected with P); δ = 29.5 ~ 31.3 (The chemical shift of C that is separated by one C from P); δ = 21.6 ~ 23.4 (The chemical shift of other C);
DeTDPB	δ = 131.5 ~ 140.1 (The chemical shift of C on benzene ring); δ = 119.7 ~ 120.4 (The chemical shift of C that is connected with P); δ = 29.9 ~ 35.4 (The chemical shift of C that is separated by one C from P); δ = 22.5 ~ 26.9 (The chemical shift of other C);
HTDPB	δ = 131.5 ~ 136.3 (The chemical shift of C on benzene ring); δ = 119.6 ~ 120.3 (The chemical shift of C that is connected with P); δ = 30.6 ~ 30.7 (The chemical shift of C that is separated by one C from P); δ = 22.5 ~ 23.3 (The chemical shift of other C);
PTDPB	δ = 131.5 ~ 136.5 (The chemical shift of C on benzene ring); δ = 119.2 ~ 119.9 (The chemical shift of C that is connected with P); δ = 33.0 ~ 33.2 (The chemical shift of C that is separated by one C from P);

Table 5. The effect of killing TGB, SRB and IB with products.

Products	The sterilizing rate (%)		
	TGB	SRB	IB
HTDPB	91.11%	62%	99.29%
DoTDPB	95.56%	84%	99.58%

4. Conclusion

1) The molecular structures of four types of double quaternary phosphonium salt sythesised with triphenyl phosphine, 1,3-dibromopropane, 1,6-dibromohexane, 1,10-dibromodecane and 1,12-dibromododecane by Bimolecular Nucleophilic Substitution are confirmed by using element analysis, IR and NMR.

2) The results of sterilizing experiments can indicate that the sterilizing effect of 1,12-dodecylidene triphenyl double phosphonium bromide (DoTDPB) is better than 1,6-hexylidene triphenyl double phosphonium bromide (HTDPB). The best conditions of sterilization are that the concentration of products is 20 mg/L and the contact time is 1 h. The sterilizing rate of killing TGB, SRB and IB with 1,12-dodecylidene triphenyl double phosphonium bromide (DoTDPB) were 95.56%, 84% and 99.58% respectively.

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