Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Preparation of Zirconium (Benzyldiethylammonio-Methylphosphonate Chloride) and Ptc Reactions

Xiang-Kai Fu [a] & Shu-Ying Wen [a]
[a] Department of Chemistry, Southwest-China Normal University, Chongqing, Sichuan, People's Republic of China, 630715

To cite this article: Xiang-Kai Fu & Shu-Ying Wen (1995): Preparation of Zirconium (Benzyldiethylammonio-Methylphosphonate Chloride) and Ptc Reactions, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 25:16, 2435-2442

To link to this article: http://dx.doi.org/10.1080/00397919508015447

SYNTHETIC COMMUNICATIONS, 25(16), 2435-2442 (1995)

PREPARATION OF ZIRCONIUM (BENZYLDIETHYLAMMONIO-METHYLPHOSPHONATE CHLORIDE) AND PTC REACTIONS

Xiang-Kai Fu* and **Shu-Ying Wen**

Department of Chemistry, Southwest-China Normal University,
Chongqing, Sichuan, People's Republic of China 630715

Abstract: Zirconium (benzyldiethylammoniomethylphosphonate chloride)phosphate $Zr(HPO_4)_{2-x}(O_3PCH_2N^+Et_2CH_2ph \cdot Cl^-)_x \cdot H_2O$, ($0.25 < x < 0.75$, ZBEPC-ZP) were prepared for the first time and characterized by IR andelemental analyses. ZBEPC-ZP catalyzed some typical PTC reactions in L/S/L phases were carried out to give good results. ZBEPC-ZP can be easily separated from the reaction mixture and recovered about 70-100 %, and can be reused and did not show any change in activity after 10 cycles.

Polymer supported phase transfer catalyst called "triphase catalysis", which were usually chemically immobilized on a cross-linked polystyrene, or silica gel, is potentially of wide application in synthesis research and still being actively developed since the catalysts are easily to be filtered out from the reaction mixture or can be reused for many times.[1]

Some insoluble acid salts of phosphoric or phosphonic acids of tetravalent metals such as Zr, Ti, Sn(IV) and Th et al, could be formed in a layered crystalline structure, which could present site for anchoring active groups. In addition, they provided the organo groups on all of the apparent and interlamellar surfaces whether they are crystalline, semicrystalline or amorphous.[2] They were potentially available as absorbents and adsorbents, ion exchangers, chaleting agents and catalysts. Besides, the material are chemically and thermally stable and nontoxic.[3] We have reported the preparation of a-zirconium phosphate-ferric chloride complex and its catalytic reactions,[4] the zirconium sulphophenylphosphonate catalyzed reactions.[5] Both have fairly good acidic catalytic activity, and can be recovered and reused.

Here we report the preparation of a quite new triphase catalyst zirconium (benzyldiethylammoniomethylphosphonate chloride)-phosphate $Zr(HPO_4)_{2-x}\cdot(O_3PCH_2N^+Et_2CH_2ph\cdot Cl^-)_x\cdot H_2O$. ($0.25 < x < 0.75$ ZBEPC-ZP), in which the quarternary ammonium groups were fixed on $Zr(HPO_4)_2H_2O$. The preparation procedure is outlined as following:

$$Et_2NCH_2PO(OEt)_2 \xrightarrow[CH_3CN,\ reflux]{phCH_2Cl} \underset{2}{phCH_2Et_2N^+CH_2PO(OEt)_2Cl^-}$$

$$+ \underset{3}{phCH_2Et_2N^+CH_2P(OEt)O_2^-} + \underset{4}{phCH_2Et_2N^+CH_2PO(OEt)(OCH_2ph)\cdot Cl^-}$$

$$+ \underset{5}{phCH_2Et_2N^+CH_2P(OCH_2ph)O_2^-} + \underset{6}{phCH_2Et_2N^+CH_2P(OCH_2ph)_2Cl^-}$$

$$2 + 3 + 4 + 5 + 6 \xrightarrow[reflux]{HCl} \underset{7}{phCH_2Et_2N^+CH_2PO_3H_2Cl^-}$$

$$+ \underset{8}{phCH_2Et_2N^+CH_2PO_3H^-}$$

$$7 + 8 \xrightarrow[H_2O]{H_3PO_4^-,ZrOCl_2 8H_2O} \underset{ZBEPC-ZP\ 9}{Zr(HPO_4)_{2-x}(O_3PCH_2N^+Et_2CH_2ph\cdot Cl^-)x\cdot H_2O}$$

Diethyl N,N-diethylaminomethylphosphonate 1 was prepared by a procedure described in earier literature.[6] It is extremely stable, and can't be hydrolyzed with concentrated hydrochloride acid or sodium hydroxide solution. The quarternisation of the tertiary amine in compound 1 was simultaneously carried out with the transesterification of the phosphate, and a mixture consisting of quarternized ammoniometylphosphonate 2, 4, 6 and quarternized ammoniometylphosphonate betain 3 and 5 may be resulted.[7] Hydrolyzing the mixture of 2,3, 4,5 and 6 with refluxing concentrated hydrochloride acid, a mixture of benzyldiethylammoniometylphosphonic acid chloride 7 and its betaine 8 may be obtained.

The mixture of compounds 7 and 8 can be used directly to prepare the triphase catalyst ZBEPC-ZP 9.

ZBEPC-ZP 9 is a white powder sometimes with slight yellow color, insoluble either in water or in organic solvents. ZBEPC-ZP catalyzed reactions such as preparation of thiocyanate, ether formation, ester from halide and carboxylate and addition of dichlorocarbene in L/S/L phases were carried out to give nice catalytic activity. The catalyst can be separated, recovered and reused.

EXPERIMENTAL

IR spectra were recorded on a PK 60000 FTIR spectrometer for KBr tablets, ^{1}H NMR were run on a Varian EM 360L spectrometer in D_2O or $CDCl_3$. Elemental analyses were performed by a PE 2400 instrument, MS were obtained on a QP 1000A MS-GC instrument. All the reagents were used as received from suppliers.

1 Quarternization of 1.

A mixture of 1 (0.2 mol, 44.6 g) and benzylchloride (0.25mol, 31.7 g) in40 ml CH_3CN was reflxing with stirring for 5 days. After acetonitrile was distilled out with reduced pressure, a brown thicky residue was redissolved in 50 ml water, and was extracted with 30 ml ethyl acetate. Evaperation of the water under vacuum to gave 59.9 g products which were proved to be compound 3 with small amount of 2 and 5 by the MS and ^{1}HNMR, and not easy to be separated.

Vmax: 3406, 2981, 1653, 1457, 1395, 1228, 1081, 1049, 946, 758, 567, 517, 473 cm-1. δ H: 7.15 -7.5(m, 5H ,Ar), 4.4-4.6(m, 2H ,Ar-CH_2),3.65-4.2(m, 2H ,O-CH_2), 3.15-3.4(d, 2H ,P-CH_2), 2.85-3.25(m, 4H ,N-CH_2), 1.15-1.4(t, 6H , CH_3), 1.05-1.3 (t, 3H ,CH_3), ppm.

M/Z: 350(M^+ of 2), 347(M^+ of 5), 346($M-1^+$ of 5), 285(M^+ of 3), 91(phCH_2), 90(C_6H_5CH), 84(Et_2NC), 77(C_6H_5).

2 Hydrolyzation of 3 .

41.0 g compound 3 (not be purified) was added 35 ml concentrated hydrochloride acid, heated to reflux for overnight. After adding 10 ml of water, the mixture was extracted with 30 ml chloroform. Then, the water and hydrochloride in the aqueous phase was evaporated under vacuum to give 34.6 g brown thick residue which was compound 8, with some 7 and water. The residue was difficult to be separated or purified, because of easy to be decomposed.

Vmax: 3584, 2978, 1651, 1534, 1510, 1460, 1365, 1209, 1161, 1084, 982, 897, 721, 536, 503, 461 cm-1.

δ H: 7.15-7.55(m, 5H ,Ar), 4.4-4.7(m, 2H ,Ar-CH_2), 3.0-3.35 (d, 2H ,CH_2-P), 2.65-3.55(m, 4H ,N-CH_2), 0.9-1.4(m, 6H ,CH_3) ppm.

M/Z: 257(M^+ of 8), 258($M+1^+$ of 8), 256($M-1^+$ of 8), 147(Et_2NCPO_2), 133(Et_2NCH_2PO), 132(Et_2NCHPO), 85(Et_2NCH), 72(Et_2N), 91, 90 and 77 as above.

3 Amorphous ZBEPC-ZP 9.

A solution of 0.05 mol $ZrOCl_2 \cdot 8H_2O$(16.1 g) in 100 ml water was heated to 60° c. Stirrihg was commanced, and 10.5 g compound 8 (not be purified) in 100 ml water was added, and temperature was raised to reflux for overnight and the solution was then concentrated to less than 50 ml. Then, 100 ml of water and 0.07 mol NaH_2PO_4 in 200 ml water were added with stirring. Immediately, a white precipitate was formed, and kept the temperature between 60° to 80° c for 8 to 12 h. The slurry was filtered and washed with water until the filtrate pH > 5. The solid product was dried at 110° c to a constant weight 20.7 g. If Zr(IV) was 100 % pricipitated, x=0.58.

$Zr(HPO_4)1.42 \cdot (O_3PCH_2N^+Et_2CH_2ph \cdot Cl^-)_{0.58} \cdot H_2O$,

C 10.31, H 2.83, N 1.70 %; found: C 10.56, H 2.95, N 1.86 %.

Vmax: 2990, 2955, 1651, 1462, 1386, 1034, 775, 721, 594, 517, 457cm^{-1}.

Change the amount of compound 8 and NaH_2PO_4 used, different x arround 0.5 for ZBEPC-ZP were obtained. IR were as same as x = 0.58 , and the elemental analyses were almost consistent with the weight of the products.

4 PTC reactions with ZBEPC-ZP 9.

4.1 Thiocyanate from halide.

0.1 mol RX , 50 ml toluene, 0.15 mol KSCN, 30 ml water and 2.5g ZBEPC-ZP were used for typical PTC reaction procedure, workup and distillation to give the alkyl thiocyanate.

4.2 Ester from benzylchloride and carboxylates.

0.1 mol benzylchloride, 50 ml toluene, 0.15 mol sodium or potasium carboxylate, 30 ml water and 3.0 g of ZBEPC-ZP were stirred and refluxed for 15-24h, general workup and distillation.

4.3 Methyl ether and ethyl ether formation.

Standard PTC reaction procedure was carried out with 0.1 mol alcohol, 50 ml of petroleum ether (bp. 60-90° c) 0.2 mol NaOH, 10 ml H_2O and 2.5 g ZBEPC-ZP, 0.13 mol dimethyl or diethyl sulfate at 45° c.

4.4 Preparation of phenol ether.

0.1 mol phenol, 60 ml of toluene, 0.15 mol NaOH, 0.13 mol BuBr, 10 ml water and 2.5 g ZBEPC-ZP were used for normal PTC reaction procedure at 80° c.

4.5 Addition of dichlorocarbene.

0.1 mol styrene or cyclohexene, 60 ml chloroform, 0.35 mol NaOH, 15 ml water and 3.0 g ZBEPC-ZP were stirred and heated at 50° c for 8 to 12 h, normal workup and distillation.

RESULTS AND DISSCUSSION

The conditions and yields of the PTC reaction with ZBEPC ZP were listed in Table 1.

1 ZBEPC-ZP gave well PTC activity for all the reactions in section 4.1 - 4.5 of experimental part. If the spacer arm between N and P was lengthened with more CH_2 units, like polymer-bound PTC catalysts, it would improve their PTC activity. [8]

Table 1 Triphase Catalytic Reactions With ZBEPC-ZP

Reaction	Reaction temperature (°c)	Time (h)	Highest Yield (%)
$BuBr + KSCN \longrightarrow BuSCN$	85	6	87.8
$phCH_2Cl + KSCN \longrightarrow phCH_2SCN$	92	6	90.1
$CH2{=}CHCH_2Cl + KSCN \longrightarrow CH2{=}CHCH_2SCN$	40	24	70.2
$phCH_2Cl + AcOK \longrightarrow AcOCH_2ph$	88	15	82.5a
$phCH_2Cl + AcONa \longrightarrow AcOCH_2ph$	90	16	79.3a
$phCH_2Cl + C_2H_5COONa \longrightarrow C_2H_5COOCH_2ph$	88	16	81.1a
$phCH_2Cl + phCOONa \longrightarrow phCOOCH_2ph$	90	24	77.5a
$phCH_2OH + Me_2SO_4 \longrightarrow phCH_2OMe$	42	8	80.1
$phCH_2CH_2OH + Me_2SO_4 \longrightarrow phCH_2CH_2OMe$	42	8	81.3
$n\text{-}C_8H_{17}OH + Me_2SO_4 \longrightarrow n\text{-}C_8H_{17}OMe$	42	10	82.6
$phCH_2OH + Et_2SO_4 \longrightarrow phCH_2OEt$	45	10	78.5
$n\text{-}C_8H_{17}OH + Et_2SO_4 \longrightarrow n\text{-}C_8H_{17}OEt$	45	10	82.4
$phOH + BuBr \longrightarrow phOBu$	80	12	81.5
$p\text{-}CH_3C_6H_4OH + BuBr \longrightarrow p\text{-}CH_3C_6H_4OBu$	80	12	80.7
$p\text{-}CH_3OC_6H_4OH + BuBr \longrightarrow p\text{-}CH_3OC_6H_4OBu$	80	12	78.3
$C_6H_5CH{=}CH_2 + CHCl_3 + NaOH \longrightarrow$	45	8	83.2
$cyclohexene + CHCl_3 + NaOH \longrightarrow$	45	12	78.5

a. About 5 - 10 % benzyl alcohol was also obtained.

2 Crtstalline layered zirconium phosphate contains on its lamellar surface a hexagonal array of hydroxyl groups spaced about 0.53 nm apart. This lead to an arear per site of 0.24 nm^2, which is quite suitable as a cross sectional limit for a fixed active organo groups.[9] Therefore, x should not beyond about 0.8 or so, otherwise too many organo groups would be crowded each other and hindered PTC reactions. This is something like cross-linked polystyrene supported quarternary ammmonium salts, with the ring substitution increased from 20 % to 46-76 %, the PTC activity sharply dropped.[10]

3 The catalyst can be easily recovered, just filtered out, washed with water. Usually for the thiocyanate reaction and the ester from halide which were in neutral medium, the catalyst can be recovered almost 100 %. For the ether formation which were not in very strong alkaline medium, the catalyst can be got back 80-95 % ; and for the addition of dichlorocarbene which were in large ammount of caustic alkaline medium, the catalyst can be obtained back about 70-85 %.

4 ZBEPC-ZP can be reused more than 10 times for almost all the reactions mentioned above and without loss of their activity.

ACKNOWLEDGEMENT: This project is supported by the NATIONAL NATUREAL SCIENCE FUNDATION OF P. R. CHINA.

REFERENCES

[1] S.L.Regen, *Angew.Chem.Int.Ed.Engl*.,1979,6,421.

[2] P.M.Digiacomo, M.B.Dines and V.E.Parziale, Eur Patent 10,366.

[3] A.Clearfield and D.S.Thukur, *Applied Catalysis*,1986,26,1.

[4] B.-K. Luo, Xiang-Kai Fu and Q.-Y. Lei, *Ion change and Adsorption*(ch),1993, 9, 124.

[5] Xiang-Kai Fu, B.-K. Luo and Q.-Y. Lei, *Chinese J. of Applied Chemistry*,1991, 8(5),6. CA:116,105253b(1992).

[6] E.K.Fields, *J.Am.Chem.Soc*.,1952, 74, 1528.

[7] D.Redmore and W.Groves, U.S. Patent 4,420,399.

[8] J B.Brown and J.A.Jenkins, *J.Chem.Soc.,Chem. Commun*., 1976,458.

[9] M.B.Dines and P.M.Digiacomo, *Inorg Chem*.,1981,20,92.

[10] S.L.Regen, *J.Am.Chem.Soc.*,1976,98,6270.

(Received in The Netherlands 14 June 1994)