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Nonhydrolytic sol–gel routes to layered metal(IV) and silicon phosphonates

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Three nonhydrolytic routes to methyl and phenylphosphonates have been developed involving the systems: (i) MCl_4–$RPO(OR)_2$ or $M(OR)_4$–$RPOCl_2$ ($M=Si$, Ti); (ii) MCl_4–$RPOCl_2$–ether ($M=Sn$, Ti, Zr); (iii) MCl_4–$RPOCl_2$–alcohol ($M=Sn$, Ti, Zr). It is noteworthy that use of nonhydrolytic conditions opens a route to water-sensitive silicon phosphonates. In most cases the phosphonates were obtained as gels. The poorly crystalline materials obtained after drying were characterised by solid-state NMR spectroscopy and their layered structure could be shown by powder X-ray diffraction. However a higher degree of crystallinity could be obtained under solvothermal conditions, either by the direct alcoholysis of chloride precursors with *tert*-butanol (2-methylpropan-2-ol), or by a simple postsynthesis treatment in *tert*-butanol.

Introduction

Layered materials based on phosphonates of tetravalent metal ions, combined or not with phosphates or phosphites, are currently of great interest as new hybrid inorganic–organic molecular sieves and catalysts.[1–4] Metal(IV) phosphonates are readily obtained by reacting phosphonic acids with metal halides or oxohalides. However, if rapid precipitation is not prevented, mainly amorphous products are yielded, in which case a crystallisation stage is required. Heat treatment in concentrated phosphoric acid solution is generally used to crystallise phosphates, but this method cannot be applied to phosphonates owing to the restricted solubility of phosphonic acids in water. Generally titanium and zirconium fluorocomplexes, readily formed by the addition of HF to the precursor solutions, afford samples with a high degree of crystallinity, because their slow decomposition in the presence of phosphonic acids constitutes a controlled process. Indeed zirconium phenylphosphonate, $Zr(O_3PPh)_2$, may be prepared from ZrF_6^{2-}. Powder X-ray diffraction showed the layered structure of $Zr(O_3PPh)_2$, akin to that of $\alpha-$zirconium phosphate $Zr(O_3POH)_2{\cdot}H_2O$, with the phenyl groups alternating above and below the mean plane of the zirconium atoms, which are octahedrally bridged by the phosphonate groups.[5,6]

However, treatment in hydrofluoric acid combines the drawbacks of a long reaction time and the problems derived from use of HF. Some attempts to circumvent this process by changing metal precursors have been reported. Thus, $Ti(OH)_4$, $TiCl_4$ complexed with H_2O_2, and $TiCl_3$ have been tested as alternative starting materials in the synthesis of titanium phenylphosphonates.[7–9] The $TiCl_3$–$PhP(O)OH_2$ system, involving subsequent oxidation under oxygen, seems the most auspicious for obtaining crystalline titanium phenylphosphonates, although it does not appear to be applicable to other metals.

Our concern here is whether the novel nonhydrolytic sol–gel methods that we have recently developed in the field of network oxides[10] can be extended as alternative routes to layered metal(IV) phosphonates. In these methods the formation of oxide linkages is based on the thermal condensation between halide and alkoxide groups, with the elimination of alkyl halide:

$$\equiv M-X+\equiv M-OR\rightarrow\equiv M-O-M\equiv+R-X \qquad (1)$$

Mixtures of halide and alkoxide precursors may be used, or alternatively the alkoxyl groups may be generated *in situ* by the action of alcohol or dialkyl ether on halides:

$$\equiv M-X+ROH\rightarrow\equiv M-OR+HX$$

or

$$\equiv M-X+ROR\rightarrow\equiv M-OR+RX \qquad (2)$$

These reactions are usually carried out at 100–150 °C in sealed tubes; under such conditions the process most likely combines the effects of nonhydrolytic condensations and solvothermal treatment. Depending on the nature of the oxygen donor (alkoxide, ether or alcohol), various ultrastructures may be achieved in the material which in turn induce various crystallisation behaviours. Thus, by preparing TiO_2 precursors by different nonhydrolytic sol–gel methods, based on the etherolysis or alcoholysis of titanium tetrachloride at 110 °C, it is possible either to delay significantly the anatase-to-rutile transformation, or conversely to obtain directly the rutile phase, whereas the reaction of *tert*-butanol gives rise to the unexpected formation of brookite.[11] Moreover, nonhydrolytic sol–gel methods have been successfully applied to the synthesis of silicates, such as SiO_2–Al_2O_3 and SiO_2–ZrO_2 which were found to be homogeneous on the molecular scale.[12,13]

In this work we set out to investigate various nonhydrolytic routes to layered phosphonates of Ti, Zr, Sn and Si involving three kinds of oxygen donors: alkoxides, ethers and alcohols. The influence of a postsynthesis treatment in alcohol on the structure of phosphonates has been studied in additional experiments.

Experimental

Preparation of metal phosphonates

Commercially available starting materials were used as received [$TiCl_4$, $Ti(OPr^i)_4$, $MePOCl_2$ and $PhPOCl_2$ from Aldrich; $ZrCl_4$ from Janssen]. Diisopropyl phenylphosphonate was prepared by the alcoholysis of $PhPOCl_2$ with propan-2-ol in the presence of triethylamine. Ethers, alcohols and CH_2Cl_2 were distilled from appropriate drying agents prior to use. All manipulations were carried out under inert atmosphere by using standard vacuum-line and glovebox techniques.

In all cases the reaction mixture (solution or suspension) was prepared at 0 °C (exothermic reactions occurred in most cases) in a Schlenk tube under argon, and was then transferred into a glass tube which was frozen in liquid nitrogen and sealed under vacuum prior to heating at the desired temperature in a thermostatically controlled oven. It is worth recalling that the pressure reached at a given temperature in a sealed vessel depends on the degree of filling, that is the volume of the reaction vessel that was originally filled. The volume of the liquid phase and the vapour pressure over the solution grow with temperature. There is a critical degree of filling which if exceeded gives rise to complete filling of the tube at some temperature below the critical temperature: at this stage a slight variation of the temperature results in a sharp change of the pressure. In practice, filling factors of about 30% and thick-walled glass tubes were used in this work.

Three typical experiments are given here. In the first one $Ti(OPr^i)_4$ (1.60 g; 4 mmoles) was added to a solution of $PhPO(Cl)_2$ (2.05 g; 8 mmoles) in CH_2Cl_2 (5 ml) chilled to 0 °C. An orange solution was obtained which gave a light yellow gel after 5 h heating at 110 °C; this gel turned white after 91 h further heating. In the second example diisopropyl ether (2.5 ml; 18 mmoles) was added to a solution of $TiCl_4$ (0.87 g; 5 mmoles) and $PhPOCl_2$ (1.68 g; 9 mmoles) in CH_2Cl_2 (5 ml) at 0 °C. Gelation occurred after 24 h heating at 110 °C; the gel remained yellow after 82 h further heating. In the third example $TiCl_4$ (0.5 ml; 5 mmoles) was dissolved in CH_2Cl_2 (3.5 ml). The addition of *tert*-butanol (1.7 ml; 18 mmoles) brought about the exothermic evolution of HCl and the formation of a light yellow precipitate. $PhPOCl_2$ (1.3 ml; 9 mmoles) was then added, leading to the dissolution of the precipitate. The yellow solution rapidly turned green and thickened. A white gel was obtained after 24 h heating at 110 °C.

In all cases the solids obtained were filtered off, washed with small aliquots of CH_2Cl_2 and dried under vacuum at 110 °C for 3 h before further characterisation.

Characterisation techniques

Elemental analyses were performed by the Service Central d'Analyses du CNRS at Vernaison, France: Si, Sn, Ti and Zr contents were determined by inductively coupled plasma (ICP) from aqueous solutions, and C and H contents by high temperature combustion and infrared spectroscopy, and chlorine content by potentiometric titration. The oxygen content was calculated by difference.

Thermal analyses were performed at a heating rate of 10 K min^{-1} heating rate in a 20/80 mixture of oxygen and nitrogen. Specific surface areas were determined by the Brunauer–Emmett–Teller (BET) method, using nitrogen adsorption–desorption isotherms recorded on an Micromeritics ASAP 2400 analyser (the estimated error being within 5%). X-Ray powder diffraction (XRD) patterns were recorded with Cu-Kα radiation using a Seifert MZ IV diffractometer.

The ^{29}Si and ^{13}C solid-state NMR data were collected on a Bruker ASX 200 spectrometer (500–1000 scans), with a 7 mm MAS NMR probe (3 kHz spinning frequency), using cross-polarisation sequences (5–10 ms contact time) and recycle delays of 2 s and 5 s, respectively. The ^{31}P and the ^{119}Sn NMR data were collected on a Bruker ASX 200 and a Bruker FT-AM 300 apparatus, respectively, with a 7 mm MAS NMR probe (3 and 5 kHz spinning frequencies, respectively), using a proton high-power decoupling sequence, $\pi/4$ pulse and 10 s recycle delay. Tetramethylsilane was used as an external reference for ^{13}C and ^{29}Si chemical shifts, tetramethyltin as an external reference for ^{119}Sn chemical shifts and 85% aqueous H_3PO_4 as an external reference for ^{31}P chemical shifts.

Results

Preparation of titanium phosphonates

Nonhydrolytic sol–gel processing was implemented for three types of systems: (i) $TiCl_4$–$RPO(OR)_2$ or $Ti(OR)_4$–$RPOCl_2$; (ii) $TiCl_4$–$RPOCl_2$–ether; (iii) $TiCl_4$–$RPOCl_2$–alcohol. The stoichiometry required an equal number of alkoxyl and chloride functional groups. Thus, the idealised equations of the reactions corresponding to a P/Ti ratio of 2 were:

$$TiX_4 + 2\ RP(O)Y_2 \rightarrow Ti(O_3PR)_2 + 4\ R'Cl \qquad (3)$$

where X = OR′ or Cl, Y = Cl or OR′;

$$TiCl_4 + 2\ RP(O)Cl_2 + 4\ R'OX \rightarrow Ti(O_3PR)_2 + 4\ R'Cl + 4\ XCl \qquad (4)$$

where X = R′ or H

However in the case of the alcoholysis route the degree of condensation was found to be much greater when an excess of alcohol was used.

All phosphonates were obtained as gels of colour varying from white to yellow. Tables 1 and 2 summarise the characteristics of the solids obtained after drying. In Table 1 empirical formulae are tentatively drawn from elemental analyses (in which the oxygen contents are deduced by difference), assuming that the organic moiety attached to phosphorus (methyl or phenyl) is retained. Subsequently the excess of carbon is attributed to the presence of residual alkoxyl groups, and the number of residual OR groups per Ti atom is calculated. The discrepancy observed between the amounts of residual alkoxyl and chloride functional groups is difficult to rationalise. Moreover in some cases the oxygen content turns out to be in excess in comparison with the theoretical formula, most likely because of the presence of hydroxyl groups. Consequently the

Table 1 Titanium phosphonates: synthesis conditions, elemental analysis (oxygen contents calculated by difference), calculated and experimental mass losses

reagents[a]	conditions	composition [theoretical]	tentative formula [theoretical]	$\Delta m/m$ from formula (%)	$\Delta m/m^b$ from TGA (%)
$TiCl_4 + 2\ PhPO(OPr^i)_2$	110 °C; 96 h solvent CH_2Cl_2	$TiP_{1.95}O_{8.72}C_{16.22}H_{16.42}Cl_{0.36}$ $[TiP_2O_6C_{12}H_{10}]$	$Ti[O_{3.75}PPh(OPr^i)_{0.72}Cl_{0.18}]_{1.95}$ $[Ti(O_3PPh)_2]$	53 [38.4]	44.4
$Ti(OPr^i)_4 + 2\ PhPOCl_2$	110 °C; 96 h solvent CH_2Cl_2	$TiP_{2.18}O_{6.77}C_{13.73}H_{12.78}Cl_{0.40}$ $[TiP_2O_6C_{12}H_{10}]$	$Ti[O_{2.83}PPh(OPr^i)_{0.26}Cl_{0.18}]_{2.18}$ $[Ti(O_3PPh)_2]$	46.7 [38.4]	42.8
$Ti(OPr^i)_4 + 2\ PhPOCl_2$	150 °C; 26 h solvent CH_2Cl_2	$TiP_{1.99}O_{5.37}C_{11.88}H_{10.04}Cl_{0.26}$ $[TiP_2O_6C_{12}H_{10}]$	$Ti(O_{2.87}PPhCl_{0.13})_{1.99}$ $[Ti(O_3PPh)_2]$	37.9 [38.4]	35.8
$Ti(OPr^i)_4 + 2\ MePOCl_2$	150 °C; 40 h solvent CH_2Cl_2	$TiP_{2.03}O_{6.07}C_{2.33}H_{6.95}Cl_{0.14}$ $[TiP_2O_6C_2H_6]$	$Ti[O_{2.94}PMe(OPr^i)_{0.05}Cl_{0.07}]_{2.03}$ $[Ti(O_3PMe)_2]$	10.4 [6.0]	7.1
$TiCl_4 + 2\ PhPOCl_2 + 4\ Pr^i_2O$	110 °C; 96 h	$TiP_{2.1}O_{5.95}C_{12.75}H_{12.81}Cl_{1.35}$ $[TiP_2O_6C_{12}H_{10}]$	$Ti[O_{2.71}PPh(OPr^i)_{0.12}Cl_{0.64}]_{2.1}$ $[Ti(O_3PPh)_2]$	47.4 [38.4]	42.5
$TiCl_4 + 2\ PhPOCl_2 +$ excess Bu^tOH	110 °C; 24 h solvent Bu^tOH	$TiP_{2.16}O_{6.55}C_{12.98}H_{11.47}Cl_{0.06}$ $[TiP_2O_6C_{12}H_{10}]$	$Ti[O_{2.92}PPh(OBu^t)_{0.11}Cl_{0.03}]_{2.16}$ $[Ti(O_3PPh)_2]$	43.0 [38.4]	40.8
$TiCl_4 + 2\ MePOCl_2 +$ excess Bu^tOH	110 °C; 168 h solvent Bu^tOH	$TiP_{2.03}O_{6.03}C_{2.1}H_{5.71}Cl_{0.01}$ $[TiP_2O_6C_2H_6]$	$Ti(O_3PMe)_{2.03}$ $[Ti(O_3PMe)_2]$	6.0 [6.0]	—

[a] Ph = phenyl; Me = methyl. [b] Thermogravimetric analysis to 1000 °C in air.

Table 2 Titanium phosphonates: characterisation by ^{31}P and ^{13}C solid-state NMR spectroscopy, XRD and BET measurement

sample derived from ...	^{31}P NMR chemical shift (ppm) [literature][7,8]	^{13}C NMR chemical shift (ppm)	interlayer spacing from XRD/Å [literature][1,7,8]	BET surface area/ $m^2\ g^{-1}$
$Ti(OPr^i)_4 + 2\ MePOCl_2$	8.5	9.8 (broad doublet)	9.4 [amorphous]	—
$Ti(OPr^i)_4 + 2\ PhPOCl_2$	−4.0 [−4.0]	131.9; 127.7	15.9 [15.0]	350
$TiCl_4 + 2\ PhPOCl_2 + 4\ Pr^i_2O$	−3.3 [−4.0]		15.1 [15.0]	—
$TiCl_4 + 2\ PhPOCl_2 +$ excess Bu^tOH	−4.0 [−4.0]	131.9; 127.7	15.8 [15.0]	281
$TiCl_4 + 2\ MePOCl_2 +$ excess Bu^tOH	9.0	12.9 (J_{PC} 155 Hz)	9.1 [amorphous]	—

calculation of the degree of condensation from the amounts of Cl and OR residual groups is not reliable.

However the degree of condensation can be estimated by comparing the weight loss measured by thermogravimetric analysis (TGA) with the value calculated from the theoretical reaction (the formation of pyrophosphate TiP_2O_7 was checked by X-ray diffraction):

$$Ti(O_3PPh)_2 \rightarrow TiP_2O_7 + \text{gases} \qquad (5)$$

Moreover, although cross-polarization NMR experiments are not quantitative, the presence or absence of signals due to residual OR groups in the ^{13}C CP MAS NMR spectra [*e.g.* for residual OPr^i: 22.8 ppm (CH_3) and 72.5 ppm (CH)] gives a qualitative appraisal of the completion of the condensation reactions. Thus the spectrum given in Fig. 1 confirms that the sample derived from the $Ti(OPr^i)_4$–$2PhPOCl_2$ system was efficiently condensed after 26 h heating at 150 °C in CH_2Cl_2, as expected from the elemental analysis and the TGA weight loss. Note that the ^{31}P MAS NMR spectrum indicates several resonances between 0 and 20 ppm, whereas the single signal at −4 ppm, typical of $Ti(O_3PPh)_2$,[7,8] would be the only one expected. This point will be discussed below.

X-Ray powder diffraction patterns indicated low angle reflections characteristic of layered compounds. The interlayer spacing appeared to be in agreement with the literature (Table 2).[1,7,8] However the samples were found to be very poorly crystalline. Fig. 2 displays the powder X-ray diffraction patterns of titanium phenylphosphonates arising from the alcoholysis of $TiCl_4$–$2PhPOCl_2$ mixtures with various alcohols: ethylene glycol, ethanol, butan-2-ol and 2-methylpropan-2-ol. The use of *sec*-butyl and *tert*-butyl alcohol appeared to improve the crystallinity. An even higher efficiency was achieved with Bu^tOH in the case of methylphosphonate [Fig. 3(a) and (c)]. Consequently further experiments were carried out to test the influence of a postsynthesis treatment in alcohol on the structure of the phosphonates. A slight positive effect was observed by treating the sample arising from the $Ti(OPr^i)_4$–$2MePOCl_2$ system in Bu^tOH at 110 °C for 7 days [Fig. 3(b)]. Furthermore this tendency was clearly confirmed in the case of phenylphosphonate (Fig. 4).

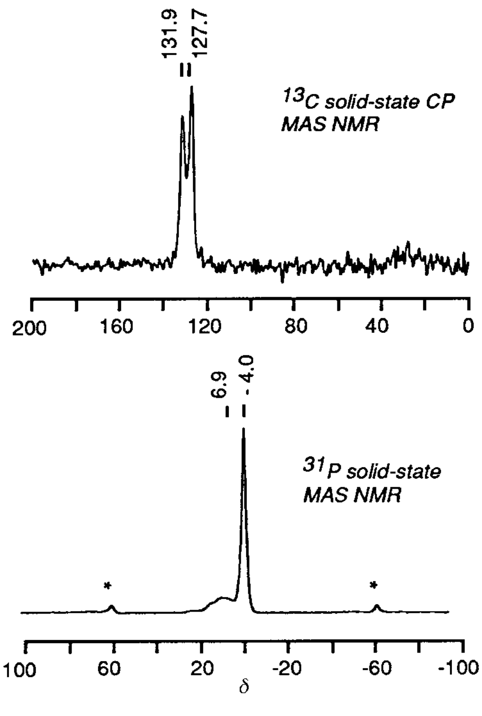

Fig. 1 ^{13}C CP MAS NMR and ^{31}P MAS NMR spectra of the sample arising from the system $Ti(OPr^i)_4$–$2PhPOCl_2$ (26 h heating at 150 °C in CH_2Cl_2) (spinning side bands marked by asterisks)

Preparation of zirconium and tin phosphonates

In view of the fact that etherolysis and alcoholysis of $TiCl_4$–2 $RP(O)Cl_2$ mixtures appeared simple and convenient routes to

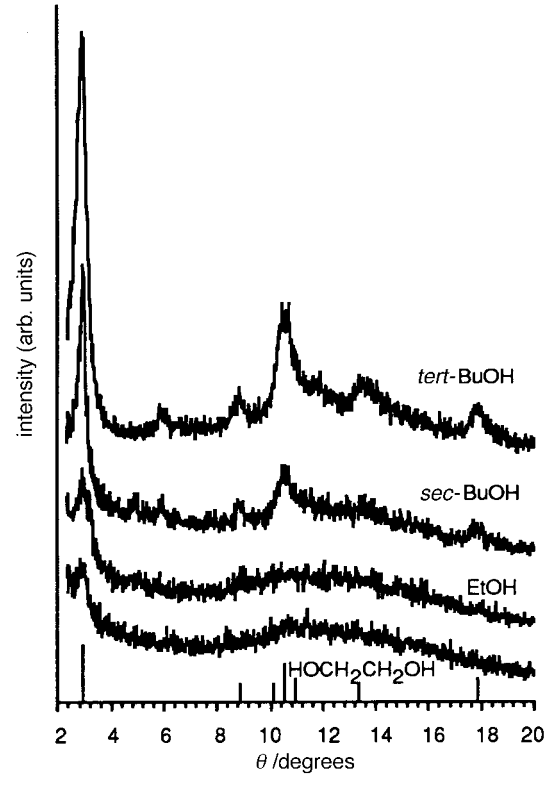

Fig. 2 XRD powder patterns of the phenylphosphonate samples arising from the alcoholysis of the $TiCl_4$–$PhPOCl_2$ system with ethylene glycol, ethanol, butan-2-ol, *tert*-butyl alcohol [the main reflections of crystalline $Ti(O_3Ph)_2$ are given for information from ref. 7]

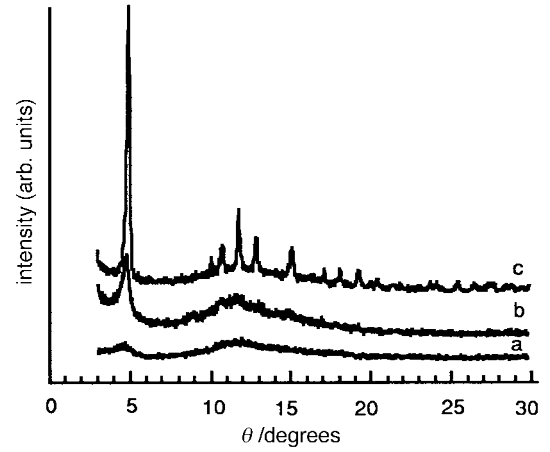

Fig. 3 Comparison of the XRD powder patterns of the titanium methylphosphonate samples (a) as prepared from the $Ti(OPr^i)_4$–$2MePOCl_2$ system; (b) after the post-synthesis solvothermal treatment in Bu^tOH (110 °C; 7 days); (c) as prepared by the alcoholysis route (Bu^tOH)

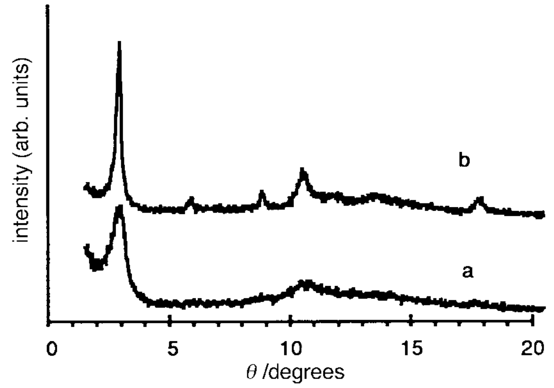

Fig. 4 Comparison of the XRD powder patterns of the titanium phenylphosphonate sample (a) as prepared from the condensation of chloride and alkoxide precursors; (b) after the post-synthesis solvothermal treatment in Bu^tOH (110 °C; 7 days)

phosphonates, these nonhydrolytic synthesis methods were extended to zirconium and tin. Indeed the etherolysis of $ZrCl_4$–$2\,RP(O)Cl_2$ and $SnCl_4$–$2\,RP(O)Cl_2$ mixtures with $Pr^i{}_2O$ led successfully to phenyl and methylphosphonates. Gels were obtained, except in the case of tin phenylphosphonate which was isolated as a brown precipitate. The elemental analysis results are supported by the TGA data (Table 3).

Fig. 5 shows that the ^{31}P MAS NMR spectra of the zirconium phenylphosphonate samples prepared either by etherolysis at 110 °C or by the classical hydrolytic route [from an

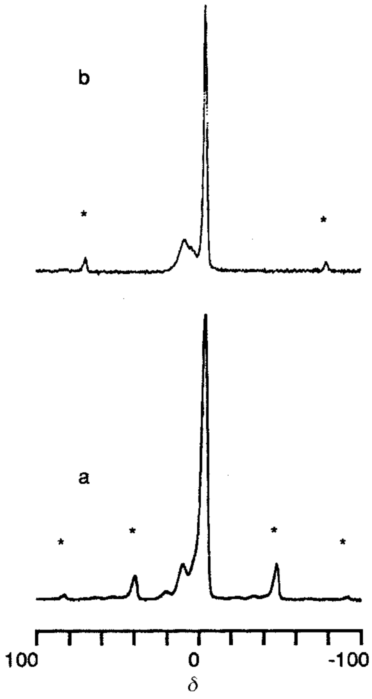

Fig. 5 Comparison of the ^{31}P MAS NMR spectra of zirconium phenylphosphonate samples prepared by (a) the nonhydrolytic route and (b) the hydrolytic route (spinning side bands marked by asterisks)

aqueous solution of $ZrOCl_2$ and $PhP(O)OH_2$, at room temperature] are not very different. The ^{31}P MAS NMR spectra of tin phosphonates (Fig. 6) arising from the etherolysis route may be deconvoluted into two signals: at 17.6 ppm (15 Hz FWHM; 81% relative area) and 14.4 ppm (3.6 Hz FWHM; 19% relative area) for the phenylphosphonate; at 10.3 ppm (8.5 Hz FWHM; 33% relative area) and 4.6 ppm (3.4 Hz FWHM; 67% relative area) for the methylphosphonate. Moreover the ^{119}Sn MAS NMR spectra indicated in both cases only one resonance at -222.9 ppm corresponding to a six-co-ordinated tin atom.

Note that in the case of phenylphosphonates (Table 4), the ^{13}C CP MAS NMR spectra indicated the formation of isopropylphenyl groups bonded to phosphorus, corresponding to aromatic electrophilic substitution byreaction of the phenyl groups with Pr^iCl in the presence of Friedel–Crafts catalytic species (such as $ZrCl_4$ and $SnCl_4$). The presence of bulkier alkylated phenyl groups provides an explanation for the expanded interlayer spacing inferred from XRD data (17.2 and 16.1 Å as compared to about 15.5 Å expected from the literature).[2,14,15]

The alcoholysis of mixtures of $ZrCl_4$ or $SnCl_4$ with two

Table 3 Zirconium and tin phosphonates arising from the etherolysis of chloride precursors: synthesis conditions, elemental analyses (oxygen contents calculated by difference), calculated and experimental mass losses

reagents[a]	conditions	composition [theoretical]	tentative formula [theoretical]	$\Delta m/m$[b] from TGA (%)	$\Delta m/m$ from formula (%)
$ZrCl_4+2\,PhPOCl_2+4\,Pr^i{}_2O$	110 °C; 92 h solvent CH_2Cl_2	$ZrP_{1.89}O_{6.44}C_{13.08}H_{15.05}Cl_{0.56}$ $[ZrP_2O_6C_{12}H_{10}]$	$Zr[O_{2.4}PPh(OPr^i)_{0.3}Cl_{0.3}]_{1.89}$ $[Zr(O_3PPh)_2]$	40.3	40.4 [34.3]
$ZrCl_4+2\,MePOCl_2+4\,Pr^i{}_2O$	150 °C; 24 h solvent CH_2Cl_2	$ZrP_{2.05}O_{6.12}C_{2.53}H_{8.24}Cl_{1.19}$ $[ZrP_2O_6C_2H_6]$	$Zr[O_{2.96}PMe(OPr^i)_{0.07}Cl_{0.57}]_{2.05}$ $[Zr(O_3PMe)_2]$	19.1	20.5 [5.0]
$SnCl_4+2\,PhPOCl_2+4\,Pr^i{}_2O$	150 °C; 92 h solvent CH_2Cl_2	$SnP_{2.23}O_{6.64}C_{13.33}H_{12.62}Cl_{0.64}$ $[SnP_2O_6C_{12}H_{10}]$	$Sn(O_{2.98}PPhCl_{0.64})_{2.23}$ $[Sn(O_3PPh)_2]$	36.8	40.2 [32.1]
$SnCl_4+2\,MePOCl_2+4\,Pr^i{}_2O$	150 °C; 1 month solvent CH_2Cl_2	$SnP_{2.05}O_{7.61}C_{2.81}H_{9.75}Cl_{0.94}$ $[SnP_2O_6C_2H_6]$	$Sn[O_{2.42}PMe(OPr^i)_{0.12}Cl_{0.46}]_{2.05}$ $[Sn(O_3PMe)_2]$	18	23.2 [4.6]
$SnCl_4+2\,PhPOCl_2+$excess Bu^tOH	110 °C; 98 h solvent Bu^tOH	$SnP_{1.73}O_{6.95}C_{10.77}H_{10.14}Cl_{0.34}$ $[SnP_2O_6C_{12}H_{10}]$	$Sn[O_{3.96}PPh(OBu^t)_{0.05}Cl_{0.64}]_{1.73}$ $[Sn(O_3PPh)_2]$	35	32.7 [32.1]

[a] Ph = phenyl; Me = methyl. [b] Thermogravimetric analysis to 1000 °C in air.

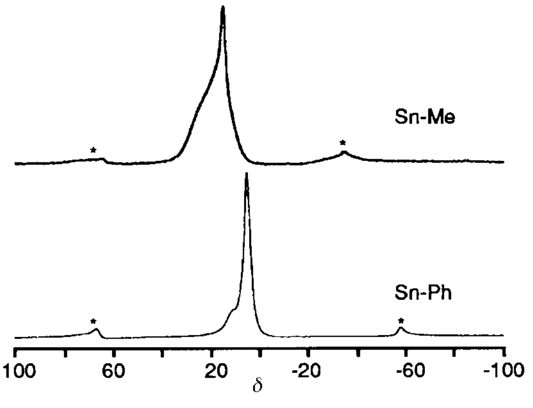

Fig. 6 ^{31}P MAS NMR spectra of tin methylphosphonate (referred to as Sn-Me) and tin phenylphosphonate (referred to as Sn-Ph) prepared by the etherolysis route (Pr^i_2O) (spinning side bands marked by asterisks)

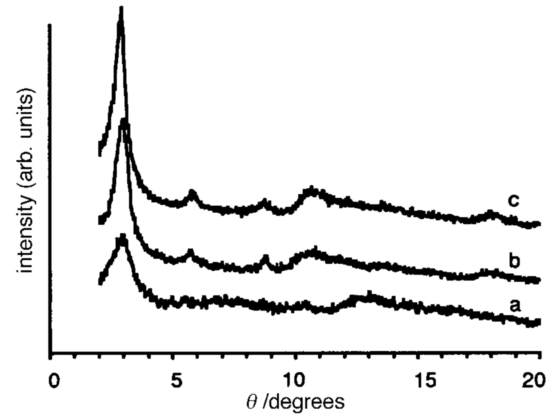

Fig. 7 Comparison of the XRD powder patterns of the tin phenylphosphonate samples (a) as prepared by the etherolysis route (Pr^i_2O); (b) as prepared by the alcoholysis route (Bu^tOH); (c) after the solvothermal treatment in Bu^tOH (110 °C; 7 days)

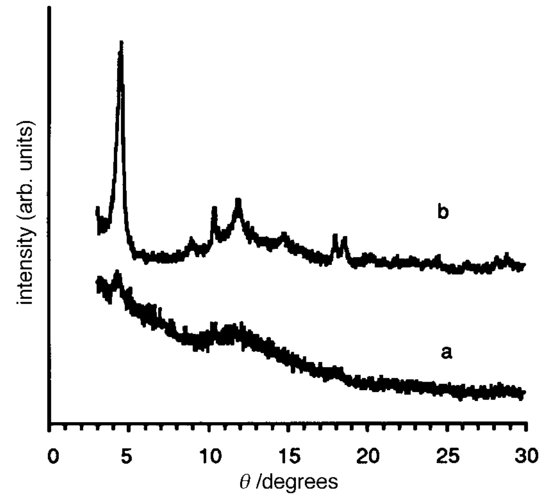

Fig. 8 Comparison of the XRD powder patterns of the tin methylphosphonate samples (a) after the solvothermal treatment in Bu^tOH (110 °C; 7 days); (b) as prepared by the etherolysis route (Pr^i_2O)

equivalents of phenyl or methylphosphonic chlorides was performed with an excess of Bu^tOH. This method failed in one case: no solid was formed from the $SnCl_4$–$MeP(O)Cl_2$ system after heating at 150 °C for one week. Nevertheless in other cases white gels were obtained after 98 h heating at 110 °C. However no improvement in crystallinity was observed in the case of zirconium (zirconium methylphosphonate was again found to be amorphous). On the other hand, Fig. 7(a) and (b) show the moderately improved crystallinity of the tin phenylphosphonate sample.

As in the case of the titanium derivatives the influence of an additional solvothermal treatment on the crystallinity of samples arising from the etherolysis route was investigated [Fig. 7(c) and 8]. The effect was clearly positive in the case of tin methylphosphonate, as shown in Fig. 8.

Preparation of silicon phosphonates

The aprotic condensation between tetraethoxysilane (TEOS) and dichloromethyl or phenyl-phosphonates appeared as a convenient route to the silicon derivatives owing to the availability of TEOS. Table 5 gives the elemental analyses of the precipitates obtained after heating without solvent for a few hours at 150 °C in sealed tubes (no gelation was observed in these cases, while a translucent gel was obtained by allowing tetrachlorosilane and two equivalents of dichlorophenylphosphonate react with an excess of Bu^tOH at 110 °C for 98 h). The solids appeared to be sensitive to air moisture. However, despite several X-ray diffraction scans under anaerobic conditions, no reproducible patterns typical of layered structures were found. On the other hand ^{29}Si MAS NMR spectroscopy (Table 6) indicated that, in both cases, all the silicon was hexacoordinated, with chemical shifts around −212 ppm ($Si[OP]_6$ sites), which is typical of silicon–phosphate bonding.[16,17] It is worth noticing that the octahedral co-ordination of silicon, instead of tetrahedral co-ordination ($Si[OP]_4$ sites would be expected at *ca.* −120 ppm), is consistent with the layered structure of α-phosphonates. However, even though the ^{31}P MAS NMR spectrum of the methylphosphonate sample showed only one signal at −5 ppm, two phosphorus sites were found in the phenylphosphonate sample, at −2.5 and −14.4 ppm. Note that in both cases, new signals appeared after a few days standing in air, at 30.2 ppm for the former, at

Table 4 Zirconium and tin phosphonates arising from the etherolysis or alcoholysis of chloride precursors: characterisation by ^{31}P and ^{13}C solid-state NMR spectroscopy, XRD and BET measurement

sample arising from ...	^{31}P NMR chemical shift[a] [literature][14]	^{13}C NMR chemical shift	interlayer spacing from XRD/Å [literature]	BET surface area/$m^2\ g^{-1}$
$ZrCl_4 + 2\ PhPOCl_2 + 4\ Pr^i_2O$	−4.6 (also 7.2 and 20) [−4.7]	broad signal around 128.5 (also 148.4; 33.6; 23.5)	17.2 [15.5][2,14]	290
$ZrCl_4 + 2\ MePOCl_2 + 4\ Pr^i_2O$	10.7 (also 19.9) [27]	12.3 (broad doublet)	amorphous	—
$SnCl_4 + 2\ PhPOCl_2 + 4\ Pr^i_2O$	4.6 (also a broad signal at 10.3)	128.3; 131.9 (also 148.8; 34.0; 22.8)	16.1 [15.4][15]	—
$SnCl_4 + 2\ PhPOCl_2 + \text{excess}\ Bu^tOH$	5.1	128.1; 131.9	15.0 [15.4][15]	229
$SnCl_4 + 2\ MePOCl_2 + 4\ Pr^i_2O$	14.4 and 17.6 (broad signal)	14.0	10.4	—

Table 5 Silicon phosphonates: synthesis conditions, elemental analysis (oxygen contents calculated by difference), calculated and experimental mass losses

reagents[a]	conditions	composition [theoretical]	tentative formula [theoretical]
$Si(OEt)_4 + 2\ MePO(Cl)_2$	150 °C; 16 h	$SiP_{1.79}O_{5.77}C_{2.11}H_{7.64}Cl_{0.02}$ $[SiP_2O_6C_2H_6]$	$Si[O_{3.04}PMe(OEt)_{0.18}Cl_{0.01}]_{1.79}$ $[Si(O_3PMe)_2]$
$Si(OEt)_4 + 2\ PhPOCl_2$	150 °C; 16 h	$SiP_{2.03}O_{6.65}C_{12.39}H_{12.56}Cl_{0.40}$ $[SiP_2O_6C_{12}H_{10}]$	$Si[O_{3.22}PPh(OEt)_{0.05}Cl_{0.2}]_{2.03}$ $[Si(O_3PPh)_2]$

[a] Ph = phenyl; Me = methyl.

6.9 and 17.5 ppm for the latter, most likely resulting from hydrolysis of P—O—Si bonds.

Discussion

Three nonhydrolytic routes to phosphonates have been investigated, including the condensation between alkoxide and chloride precursors, the etherolysis of chloride mixtures and the alcoholysis of them. The elemental analysis indicates a phosphorus to metal(IV) ratio around 2.

^{31}P MAS NMR shows broad signals shifted downfield relative to one sharp resonance (Fig. 1 and 5) [however in sample $Sn(O_3PMe)_2$ the sharp resonance is minor (Fig. 6)]. The chemical shifts of the sharp signals agree well with the data reported for crystalline metal phosphonates (Tables 2 and 4). The broad resonances may be ascribed to $PhP(OM)_{3-x}X_x$ units, with X = OR, Cl or OH. Another possibility is the presence of pyrophosphate P—O—P bonds; nevertheless, unlike silanols, P—OH groups do not condense readily. However ^{31}P NMR is quite sensitive to variations of bond angle, and these resonances may also correspond to $PhP(OM)_3$ sites in slightly distorted geometries,[18] which is consistent with the poor crystallinity of the samples.

As mentioned above, the chemical shifts of the sharp signals agree well with the literature. Nevertheless one exception is for zirconium methylphosphonate (Table 4). It is interesting to discuss this exception. Fig. 9 displays the change in ^{31}P NMR chemical shifts of Sn, Ti, Zr phosphonates from those of the parent acids (methyl or phenylphosphonic acids); our values are self-consistent, in contrast with the one calculated for the compound previously reported as zirconium methylphosphonate (here referred to as Zr-Me). The discrepancy observed for the latter value suggests that it was erroneously ascribed to a compound of that formula in the literature.[14,19] Indeed, in our hands the reported preparation of Zr-Me led to a sample containing 1.1 fluorine atom per zirconium atom, based on the elemental analysis. Conversely, when the classical crystallisation treatment in aqueous HF was applied to our nonhydrolytic compound, a high fluorine content was again found. In both cases, the presence of fluorine in the formula was associated with the appearance of a ^{31}P NMR resonance around 27 ppm. Accordingly, in our opinion, this resonance must be related to fluorophosphonate species.

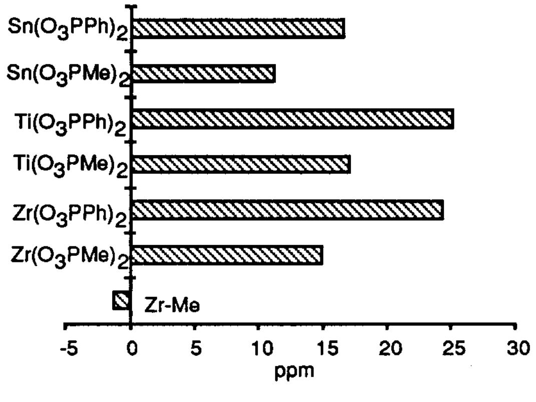

Fig. 9 Displacements of the ^{31}P NMR chemical shifts of the present phosphonates from the parent acids, compared to that of the compound previously reported as zirconium methylphosphonate (here referred to as Zr-Me)

The synthesis of silicon compounds deserves special attention. No silicon phosphonate has been reported so far, probably because Si—O—P bonds are sensitive to hydrolysis. In phosphosilicates the difficulty in forming Si—O—P bonds to any large extent in the first stages of gelation is a drawback in controlling the composition of the final material[16,17,20] [however the direct reaction of P_2O_5 with $Si(OEt)_4$ has been recently reported to give a promising improvement[21]]. Our results suggest that the nonhydrolytic sol–gel route will permit circumvention of this problem.

It is worth underlining that, in general, the metal(IV) phosphonates synthesised by the nonhydrolytic sol–gel route were obtained as gels. This may be regarded as an advantage with regard to shaping, *e.g.* for thin-film and coating applications. On the other hand the compounds were found to be poorly crystalline, although in most cases they were unambiguously characterised as layered solids by powder X-ray diffraction, with interlayer distances in agreement with the literature. However a higher degree of crystallinity could be afforded either by direct alcoholysis with *tert*-butanol, or by postsynthesis treatment in *tert*-butanol. Nevertheless in both cases some questions remain unanswered about the role of tert-butanol.

It has been reported that the composition of the precipitate initially formed in the reaction of *tert*-butanol with $TiCl_4$ does not correspond to the expected formula $TiCl_2(OR)_2{\cdot}ROH$[11] (it should be recalled that Bu^tOH was added to $TiCl_4$ in the first stage, and $RPOCl_2$ subsequently; see Experimental). The elemental analysis (found C 4.68%, Cl 18.66%, Ti 36.65%) corresponds better to the hydroxide $TiCl_{0.68}(OBu^t)_{0.127}(OH)_{3.19}$ or oxotitanate $TiCl_{0.68}(OBu^t)_{0.127}O_{1.59}$. The weight losses, $\Delta m/m$, calculated from these formulae are 41% and 25%, respectively, the experimental value (38%) being rather close to the former. The formation of hydroxyl groups may be accounted for by the occurrence of reaction (6) (liberation of Bu^tCl) instead of reaction **(7)** (liberation of HCl), owing to the increased cationic character on the tertiary carbon group which favours the nucleophilic attack of chloride:

$$\equiv TiCl + Bu^tOH \rightarrow \equiv TiOH + Bu^tCl \tag{6}$$

$$\equiv TiCl + Bu^tOH \rightarrow \equiv TiOBu^t + HCl \tag{7}$$

The presence of numerous hydroxyl groups in the precursor most probably affects the kinetics of the condensation reactions with chlorophosphonates in the direct alcoholysis route.

On the other hand it is difficult to rationalise how *tert*-butanol acts on crystallisation in the postsynthesis treatment. Many studies have indicated that the structure and texture of the solids are strongly influenced by the properties of the solvent in sol–gel processing or, more generally, in solvothermal syntheses (which may be carried out in a similar manner in sealed glass tubes in the 100–200 °C temperature range).[22] In fact such solvent properties as polarity, ability to donate or

Table 6 Silicon phosphonates: characterisation by ^{31}P, ^{13}C and ^{29}Si solid-state NMR spectroscopy

sample derived from ...	^{31}P NMR chemical shift	^{13}C NMR chemical shift	^{29}Si NMR chemical shift
$Si(OEt)_4 + 2\ MePOCl_2$	-5.0	13.5 (also 35.1; 60.0)	-212.9
$Si(OEt)_4 + 2\ PhPOCl_2$	-2.5; -14.4	131.2; 128.4	-211.9

Table 7 Autoprotolysis constant, relative permittivity and dipole moment (in Debye units) of various alcohols (from ref. 23)

	pK	ε/dm^3 mol^{-1} cm^{-1}	μ/D
Bu^{t}OH	19.0	10.90	1.66
Bu^{s}OH		16.56	
EtOH	19.1	24.55	1.66
ethylene glycol	14.2	37.70	
H_2O	14.0	78.39	1.85

accept lone pairs of electrons, softness and viscosity govern the solubility and transport behaviour of the ions involved in heterogeneous liquid–solid reactions. However the data collected in Table 7[23] indicate that *tert*-butanol possesses a low relative permittivity compared to those of other alcohols, and it may be regarded as a quasi-aprotic solvent, considering its low autoprotolysis constant. In our opinion *tert*-butanol acts less as a solvent and more by consuming the residual chlorides thus completing the condensation reactions.

Conclusion

In summary, the present work demonstrates that layered phosphonates of metal(IV) (titanium, zirconium and tin) can be synthesised by using a nonhydrolytic sol–gel approach, either by condensation between chloride and alkoxide precursors, or by etherolysis (or alcoholysis) of chlorides mixtures. Moreover the nonhydrolytic conditions open a route to water-sensitive silicon phosphonates.

In most cases the phosphonates were obtained as gels, leading to poorly crystalline materials on drying. However a higher degree of crystallinity could be achieved under solvothermal conditions, either by the direct alcoholysis of chloride precursors with *tert*-butanol, or by a simple postsynthesis treatment in *tert*-butanol. It is worth underlining that this crystallisation route avoids the contamination of phosphonates with fluoride, as may occur in the classical HF way.

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References

1 P. M. DiGiacomo, M. B. Dines and V. E. Parziale, *Patent* WO 80/00703 A (Occidental Research Corp.), 17 April 1980.
2 A. Clearfield, J. D. Wang, Y. Tian, E. Stein and C. Bhardwaj, *J. Solid State Chem.*, 1995, **117**, 275.
3 G. Alberti, M. Casciola, U. Costantino and R. Vivani, *Adv. Mater.*, 1996, **8**, 291.
4 K. P. Olivera-Pastor, P. Maireles-Torres, E. Rodriguez-Castellon, A. Jimenez-Lopez, T. Cassagneau, D. Jones and J. Rozière, *Chem. Mater.*, 1996, **8**, 1758.
5 G. Alberti, U. Costantino, S. Alluli and N. Tomassini, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1113.
6 D. M. Poojary, H. L. Hu, F. L. Campbell III and A. Clearfield, *Acta Crystallogr., Sect. B*, 1993, **49**, 996.
7 E. Jaimez, Ph. D. Dissertation, University of Oviedo, Spain, 1994.
8 E. Jaimez, A. Bortun, G. B. Hix, J. R. Garcia, J. Rodriguez and R. C. T. Slade, *J. Chem. Soc., Dalton Trans.*, 1996, 2285.
9 M. A. Villa-Garcia, E. J. Jaimez, A. Bortun, José R. Garcia and J. Rodriguez, *J. Porous Mater.*, 1995, **2**, 293.
10 (*a*) S. Acosta, P. Arnal, R. J. P. Corriu, D. Leclercq, P. H. Mutin and A. Vioux, *Mater. Res. Soc. Symp. Proc.*, 1994, **346**, 43; (*b*) for a recent review on nonhydrolytic sol–gel, see A. Vioux, *Chem. Mater.*, 1997, **9**, 2292.
11 P. Arnal, R. J. P. Corriu, D. Leclercq, P. H. Mutin and A. Vioux, *J. Mater. Chem.*, 1996, **6**, 1925.
12 S. Acosta, R. J. P. Corriu, D. Leclercq, P. H. Mutin and A. Vioux, *Mater. Res. Soc. Symp. Proc.*, 1994, **346**, 345.
13 M. Andrianainarivelo, R. J. P. Corriu, D. Leclercq, P. H. Mutin and A. Vioux, *J. Mater. Chem.*, 1996, **6**, 1665.
14 K. Segawa, A. Sugiyama and Y. Kurusu, *Stud. Surf. Sci. Catal.*, 1991, **60**, 73.
15 M. E. Medeiros and O. L. Alves, (*a*) *J. Mater. Chem.*, 1992, **2**, 1075; (*b*) *Thermochim. Acta*, 1994, **241**, 33.
16 S. P. Szu, L. C. Klein and M. Greenblatt, *J. Non-Cryst. Solids*, 1992, **143**, 21.
17 B. I. Lee, *J. Mater. Res.*, 1996, **11**, 134.
18 C. Schmutz, P. Barboux, F. Ribot, F. Taulelle, M. Verdaguer and C. Fernandez-Lorenzo, *J. Non-Cryst. Solids*, 1994, **170**, 250.
19 K. Segawa, N. Kihara and H. Yamamoto, *J. Mol. Catal.*, 1992, **101**, 213.
20 J. C. Schrotter, A. Cardenas, M. Smaihi and N. Hovnanian, *J. Sol–Gel Sci. Technol.* 1995, **4**, 195.
21 Q. Wang, W. D. Samuels, G. J. Exarhos, B. I. Lee and Z. Cao, *J. Mater. Chem.*, 1998, **8**, 165.
22 W. S. Sheldrick and M. Wachhold, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 206.
23 C. Reichardt, *Solvents and solvent effects in organic chemistry*, 2nd edn., VCH, Weinheim, 1988.

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