



Triphasic catalyst systems based on surfactant/clay composites

Facile synthesis of cyano, thiocyno and hydroxy compounds using a triphasic catalyst

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Summary

Benzyl halides undergo cyanation, thiocyanation and hydroxylation reactions under the influence of triphasic catalysts. The utility of a variety of surfactants, namely cetyltrimethyl-, tetrabutyl-, tetraethyl- and tetramethylammonium chlorides, pillared clays and 18-crown-6 intercalated clay has been demonstrated in these nucleophilic substitution reactions. Furthermore, we noticed that these clay-catalysed reactions are insensitive towards the size of the surfactants used.

Introduction

Cation-exchanged montmorillonites, clay-supported reagents and pillared clays find extensive applications in organic synthesis under milder reaction conditions.¹⁻⁶ These modified clay materials, unlike other conventional catalysts, enjoy considerable advantages such as ease of handling, recyclability, low cost, and easier modulation of acidity levels by suitable exchange of cations thus contributing to the main theme of 'Green Chemistry'. Our interest in modified clay materials and their applications in organic functional group transformations,⁶ prompted us to explore the preparation of benzyl cyanides, thiocyanides and alcohols by employing triphasic catalysts.

Several organic polymers⁷⁻¹² or inorganic solid supports¹³⁻¹⁶ that contain immobilized organocations such as quaternary ammonium ions have been used as triphasic catalysts.¹⁷ These inorganic solid supports, including clays,^{14,15} zeolites¹⁶ and metal oxides,¹³ have been used in place of polymers but they generally suffer from disadvantages of low reactivity or structural instability under sustained reaction conditions. Though similar catalytic reactivities can be expected from organic-functionalized silica and alumina, they require relatively elaborate preparative procedures involving the use of silane coupling agents that covalently bind the onium ion to the oxide surface. In contrast, organo-clay assemblies may be readily prepared and enjoy improved catalytic longevity. Thus, clay-based new materials for improved triphasic catalysis are desirable.

The earlier significant contribution of Cornelius and Laszlo entailed the utilization of a commercially available quaternary ammonium montmorillonite (Thixogel VP, a product from Sud-Chemie/AG) to catalyze the formation of symmetrical formaldehyde acetals from organic *gem*-dihalides and alcohols.¹⁴ Almost

any organo-clay entity may be expected to function as a triphasic catalyst because of the general hydrophobicity of these materials and their ability to bind ion pairs. In our case, organo-clays form thin membrane-like assemblies at the interface of a hexane-in-water emulsion. Emulsion formation by certain quaternary ammonium clays has been recognized previously in the use of these materials as oil well drilling fluids,¹⁸ but little is known concerning the mechanism. Lin and Pinnavaia have studied the cyanation of 1-bromopentane employing several quaternary ammonium ion exchange forms of hectorite as a triphasic catalyst.¹⁹

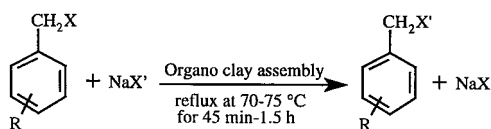
Results and discussion

We have prepared modified clays by introducing 3-aminopropyltriethoxysilane^{6a} and also surfactants^{6b} into the clay interlayer and have used these materials in some useful organic transformations. The efficiency of surfactant-pillared clays to act as a dispersed solid phase in a triphasic catalyst system¹⁹ prompted us to study other practically useful reactions using organo-clay assemblies. Herein, we report that benzyl cyanides, thiocyanides and alcohols are easily accessible from the corresponding benzyl halides and sodium cyanide, thiocyanide and hydroxide respectively (Scheme 1). The recovered mass balance is > 90%.

In a control experiment, using only reactants in the absence of catalyst, the reaction is found to be very slow and also results in the generation of a large number of byproducts (Table 1, entry 9). In another experiment, benzyl bromide is found to produce a number of white polymeric byproducts^{2b} (entry 10) when natural montmorillonite K10 clay is used. In our initial explorations, the reaction rate at room temperature is found to be very slow but could be accelerated meaningfully under refluxing conditions.

Green Context

Benzylic halides can be converted to a range of synthetically useful derivatives by the use of triphasic catalytic systems based on surfactant/clay composites. Catalytic activity seems to be related to the formation of an emulsion, which stably disperses the catalysts. *DJM*



R = 2-Me, 3-Me, 4-Me, 4-NO₂; X = Br, Cl; X' = CN, SCN, OH

Scheme 1

The reaction does not occur in the absence of the catalyst. For each reaction system described in Table 1, the organo-clay assembly formed a thin membrane like film at the interface of a hexane-in-water emulsion. However, in the case of unmodified montmorillonite K10 clay, neither the emulsion formation nor any catalytic activity is observed. When only the pillaring solution is used and the experiment is performed in a biphasic catalysis, the conversion is more efficient, an observation corroborated by earlier work.¹⁹ Such a decrease in catalytic efficiency upon onium ion immobilization is a general feature of triphasic

catalysis. Next, we set out to analyse the effect of the surfactant's size on the catalytic effectiveness of these reactions. The conversion efficiency essentially remains unchanged as a result of these changes indicating the relative insensitivity of the reaction towards the surfactant size. Although the approach has been explored earlier,¹⁹ we have employed much smaller and more symmetrical surfactants (TBAC, TEAC and TMAC) wherein the generality of the reaction is established with relatively inexpensive and less lachrymatory substrates such as benzyl chlorides rather than bromides.¹⁹ Interestingly, the catalyst can be reused without loss of activity; we have reused the recovered clay twice with reproducible results (entries 32 and 33, Table 1).

In the case of a substrate bearing an electron-withdrawing group, the reaction proceeds expeditiously with rapid consumption of the starting material. However, the reaction invariably leads to the formation of complex byproducts that are devoid of the desired cyanated material according to GC-MS analysis (Hewlett-Packard model 5890 gas chromatograph with a mass spectrometer).

The ability of crown ethers and cryptands to intercalate in smectites is well known.²⁰ They form very stable polydentate

Table 1 Preparation of benzyl cyanides, thiocyanides and alcohols from benzyl halides using organo-clay assemblies as triphasic catalysts^a

Entry	Catalyst	Substrates		Product yield (%)	
				RC ₆ H ₄ CH ₂ X'	Others
1	TMAC-pillared	C ₆ H ₅ CH ₂ Br	NaCN	86	—
2	TMAC-pillared	2-MeC ₆ H ₄ CH ₂ Br	NaCN	84	—
3	TMAC-pillared	3-MeC ₆ H ₄ CH ₂ Br	NaCN	80	—
4	TMAC-pillared	4-MeC ₆ H ₄ CH ₂ Br	NaCN	89	—
5	TMAC-pillared	C ₆ H ₅ CH ₂ Br	NaSCN	89	—
6	TMAC-pillared	2-MeC ₆ H ₄ CH ₂ Br	NaSCN	87	—
7	TMAC-pillared	3-MeC ₆ H ₄ CH ₂ Br	NaSCN	83	—
8	TMAC-pillared	4-MeC ₆ H ₄ CH ₂ Br	NaSCN	89	—
9	— ^b	C ₆ H ₅ CH ₂ Cl	NaCN	13	40
10	K10-montmorillonite clay	C ₆ H ₅ CH ₂ Cl	NaCN	13	41
11	Pillaring solution ^c	C ₆ H ₅ CH ₂ Cl	NaCN	85	8
12	CTAC-pillared	C ₆ H ₅ CH ₂ Cl	NaCN	82	—
13	CTAC-pillared ^d	C ₆ H ₅ CH ₂ Cl	NaCN	15	—
14	TBAC-pillared	C ₆ H ₅ CH ₂ Cl	NaCN	79	—
15	TEAC-pillared	C ₆ H ₅ CH ₂ Cl	NaCN	79	—
16	TMAC-pillared	C ₆ H ₅ CH ₂ Cl	NaCN	80	—
17	CTAC-pillared ^e	C ₆ H ₅ CH ₂ Cl	NaCN	79	—
18	CTAC-pillared ^f	C ₆ H ₅ CH ₂ Cl	NaCN	80	—
19	18-Crown-6-clay	C ₆ H ₅ CH ₂ Cl	NaCN	87	—
20	18-Crown-6 solution ^g	C ₆ H ₅ CH ₂ Cl	NaCN	95	—
21	CTAC-pillared	C ₆ H ₅ CH ₂ Cl	NaOH	89	—
22	TBAC-pillared	C ₆ H ₅ CH ₂ Cl	NaOH	84	—
23	TEAC-pillared	C ₆ H ₅ CH ₂ Cl	NaOH	79	—
24	TMAC-pillared	C ₆ H ₅ CH ₂ Cl	NaOH	77	—
25	TMAC-pillared	C ₆ H ₅ CH ₂ Br	NaOH	84	—
26	TMAC-pillared	2-MeC ₆ H ₄ CH ₂ Br	NaOH	84	—
27	TMAC-pillared	3-MeC ₆ H ₄ CH ₂ Br	NaOH	80	—
28	TMAC-pillared	4-MeC ₆ H ₄ CH ₂ Br	NaOH	89	—
29	18-Crown-6-clay	C ₆ H ₅ CH ₂ Cl	NaOH	89	—
30	TMAC-pillared	4-NO ₂ C ₆ H ₄ CH ₂ Cl	NaCN	Complex product formation	—
31	TMAC-pillared	4-NO ₂ C ₆ H ₄ CH ₂ Br	NaCN	Complex product formation	—
32	TMAC-pillared ^h	C ₆ H ₅ CH ₂ Cl	NaCN	80	—
33	TMAC-pillared ^h	C ₆ H ₅ CH ₂ Cl	NaCN	80	—

^a Reaction time 45 min under refluxing conditions except *m*-methylbenzyl halides (1.5 h). ^b Blank experiment. ^c 0.1 ml of 0.15 M pillaring solution (CTAC). ^d Room temperature, 7 h. ^e CTAC-pillared (0.05 g) clay. ^f CTAC-pillared (0.2 g) clay. ^g 0.1 ml of 0.1 M solution of 18-crown-6. ^h Recycled clay (used twice).

coordination compounds in the interlayer space, replacing water molecules which belong to the hydration sphere of the exchangeable cations. Consequently, we decided to conduct the reaction by substituting 18-crown-6 in place of surfactants in the organo-clay assembly. The reaction turned out to be equally facile with this crown ether-clay material.

In summary, the efficiency of triphasic catalysts in the facile syntheses of benzyl cyanides, thiocyanides and alcohols is demonstrated. This method provides a relatively benign approach to the preparation of a variety of benzyl derivatives using a triphasic catalyst. The utility of an 18-crown-6 intercalated clay assembly in these nucleophilic substitution reactions provides relatively improved yields.

Experimental

Benzyl halides, other chemicals (Acros Organics) and montmorillonite K10 clay (Aldrich) were used as received. Surfactant pillared clay materials were prepared by stirring the sodium-exchanged clay (6 g) in 0.15 M solution of the corresponding surfactants for 100 h at 53 °C.^{6b} The solution was filtered, washed repeatedly with distilled water and dried overnight in an oven. X-Ray diffraction data show that the spatial distance in the 001 plane increases from 9 to 16 Å and FT-IR spectra show characteristic stretching frequencies of long chain alkyl groups. The crown ether 'doped' clay assembly was prepared by stirring the sodium exchanged clay (6 g) with an aqueous solution of the potassium salt of 18-crown-6 which, in turn, was prepared by mixing equimolar amounts (0.15 M) of 18-crown-6 with KCl. The reaction mixture was stirred for 50 h at 55 °C, the clay solid was filtered, and washed repeatedly with distilled water to remove any surface-adsorbed crown ether.

General procedure

In a typical experiment, benzyl chloride (253 mg, 2 mmol) in 7 ml of hexane and sodium cyanide (98 mg, 2 mmol) in 7 ml of distilled water were placed in a round bottomed flask. To this solution, organo-clay (100 mg) was added with stirring for 0.7–1.5 h at 70–75 °C. After completion of the reaction, followed by TLC using hexane as solvent, the product was extracted into dichloromethane, the organic layer was washed with water and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure to afford benzyl cyanide (90%).

The percentage conversion (entries 9–11 in Table 1) was obtained by analyzing the reaction mixture in a Shimadzu LC-8A modular HPLC system (reversed phase column (ODS), UV detector at 258 nm) using 70% aqueous methanol as the mobile phase. The structural integrity of the products was confirmed by comparing the IR spectra (Perkin-Elmer model 577) and NMR spectra (Perkin Elmer 90 MHz) with those of authentic samples.

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