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LETTERS

Surfactant Pillared Clays in Phase Transfer Catalysis: A New Route to Alkyl Azides from Alkyl Bromides and Sodium Azide

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Abstract: A high yield synthesis of alkyl azides is described from readily accessible alkyl bromides and sodium azide using an inexpensive phase transfer catalyst, surfactant pillared clay. © 1998 Elsevier Science Ltd. All rights reserved.

The versatile reactivity and the synthetic usefulness of the azido group is well documented[1] and there are several methods available for the synthesis of azido compounds. The most common method utilizes alkyl halides via the nucleophilic substitution with sodium azide[2] or lithium azide[3] in various solvents. However, these methodologies often suffer from either complex procedures, long reaction times and low yields. In addition, there are usual purification problems associated with distillation[4] of products from the incomplete reactions since some alkyl azides decomposes rapidly with danger of explosion.[5] Consequently, we decided to initiate a systematic study of the versatility of the nucleophilic substitution of halides using sodium azide, NaN_3, under milder phase-transfer catalysis conditions.[6]

In view of the drawbacks associated with conventional phase transfer catalysts such as low thermal stability, hygroscopicity, separation problems and reusability prompted us to explore the synthesis of immobilized onium cations pillared clays. Herein, we present a novel approach to the synthesis of azides that involves triphase catalyst system for nucleophilic displacement consisting of a dispersed solid phase and two immiscible liquid phases containing the electrophilic and nucleophilic reagents[7a] where the reagents get transferred from the liquid phase to the solid phase. The usual triphase catalysts employed are functionalized organic polymers[6-11] or more popular mineral supports[12-15] that contain immobilized organocations, such as quaternary ammonium ions analogues to those used for conventional liquid-liquid phase transfer catalysts.[16]

Although triphase catalysis greatly simplifies the recovery of the catalyst and provides opportunities for selective chemical conversions based on substrate size or polarity, the technique also has some limitations.[17-19] The polymer-supported triphase catalysts have yet to find industrial applications, in part, because of their diffusion limitations, high cost, tendency to swell and mechanical/chemical instability.[19] Several inorganic supports, involving metal oxides,[12] clays[13,14] and zeolites[15] have been substituted for polymers, but they generally suffer similar disadvantages of low reactivity or structural instability under sustained reaction conditions. Thus, development of new materials for improved triphasic catalysis are desirable.

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We have obtained some interesting results using exchanged clay systems containing basic groups such as 3-aminopropyltriethoxysilane (3-APTES) and much smaller and symmetrical surfactants namely, tetramethyl– , tetraethyl– and tetrabutylammonium bromide into the clay interlayer.[20] This Letter reports a high yield preparation of various alkyl azides in excellent purity utilizing surfactant pillared clays that circumvents the hazards associated with purification of alkyl azides.

In a typical example, the alkyl bromide in hexane and NaN_3 in water are admixed in the molar ratio, 1:1.2, and the reaction mixture is refluxed with continuous stirring (Eqn.).

$$\underset{\text{(hexane)}}{RX} + \underset{\text{(water)}}{NaN_3} \xrightarrow[\text{Reflux with stirring}]{\text{Surfactant pillared clay}} RN_3 + NaX \qquad \textbf{(Eqn.)}$$

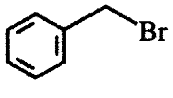
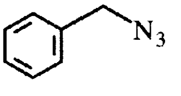
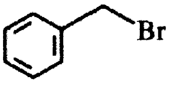
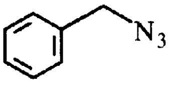
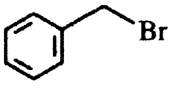
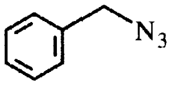
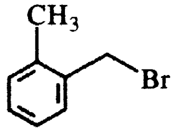
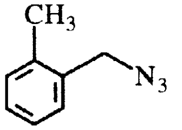
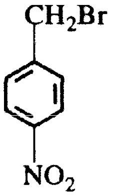
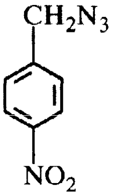
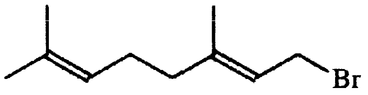
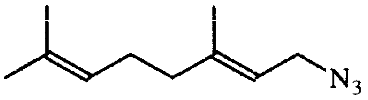
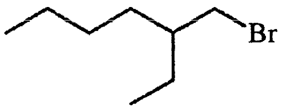
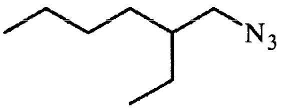
$X = Br$; $R = C_6H_5CH_2$–, $4\text{-}NO_2C_6H_4CH_2$–, $2\text{-}MeC_6H_4CH_2$–, $C_{10}H_{17}$–, C_8H_{17}–

Our results for a variety of azides are summarized in the Table and are exemplified by substrates such as benzyl bromide, substituted benzyl bromides and long chain alkyl bromides. Benzyl bromide bearing an electron withdrawing substituent (entry 5) undergoes the reaction at a much faster rates as compared to the parent or benzyl bromide derivatives with electron releasing group appended. In the case of long chain alkyl halides e.g. geranyl bromide (entry 6) and 2-ethylhexyl bromide (entry 7), the reaction rate is much slower and needs comparatively longer time for completion. This may be due to the increase in the electron releasing capacity with increasing chain length and also due to restricted entry of the hydrophobic long chain alkyl halides into the surfactant pillared clay interlayer. In general, long chain alkyl halides require more time to react. The reaction is found to be very slow at room temperature and does not occur in the absence of the catalyst. Instead, benzyl bromide is found to produce a white polymeric material when natural montmorillonite K 10 clay is used. The reaction is also unaffected by increasing (two-fold) or decreasing (one-half) the amount of the organo-clay composite confirming its catalytic role. Interestingly, the catalyst can be reused without loss in activity; we have reused the recovered clay two to three times with reproducible results (entries 2 and 3).

For all the substrates depicted in the Table, the organo-clay assembly formed a thin membrane-like film at the interface of a hexane-in-water emulsion. The emulsion formation or the catalytic activity was not observed for the natural montmorillonite K 10 clay. The experiments performed in biphasic catalytic conditions with onium salts produce the efficient conversion. This trend is corroborated by earlier work[21-22] and it appears that the decrease in catalytic efficiency upon immobilization of onium ion is a general feature of the triphasic catalysis. We have also analyzed the role of surfactant size in this reaction by varying the alkyl group (tetramethyl–, tetraethyl– and tetra-n-butylammonium bromide) and found that the conversion rate remains essentially unchanged indicating the relative insensitivity of the reaction towards the surfactant size.

Materials: Montmorillonite K 10 clay, tetraethylammonium bromide, tetra-n-butylammonium bromide, 2-ethylhexyl bromide and geranyl bromide are purchased from Aldrich Chemical Co. and rest of the chemicals or reagents are purchased from Lancaster Synthesis Inc. and used as received without further purification. Surfactant pillared clays are prepared by stirring sodium-exchanged clay[13] (6 g) in 0.2 molar solution of the corresponding surfactants for 100 h at 60-70 °C. The solution was filtered, washed repeatedly with distilled water and dried overnight in an oven (at 100-110 °C). X-ray diffraction data shows that the spatial distance in the 001 plane increases from 9 to 16 Å and FT-IR spectra displays characteristic stretching frequencies of alkyl group.[20]

Table: Synthesis of Alkyl Azides from Alkyl Bromides and Sodium Azide Catalyzed by Tetramethylammonium Bromide Pillared Clays

Entry	Substrates	Product	Time (h)	Yield(%)[a]	IR (Neat) cm^{-1}
1			6	84	2094
2			6	82	2094
3			6	82	2094
4			6	83	2095
5			5	91	2100
6			12	93	2095
7			20	85	2095

[a] Yields refers to pure isolated products obtained; the entries 2 and 3 refer to the use of surfactant pillared clay that is recycled second and third time, respectively, under identical conditions.

General procedure for the synthesis of alkyl azides. In a typical experiment, benzyl bromide (360 mg, 2.1 mmol) in petroleum ether (3 mL) and sodium azide (180 mg, 2.76 mmol) in water (3 mL) are admixed in a round-bottomed flask. To this stirred solution, pillared clay (100 mg) is added and the reaction mixture is refluxed with constant stirring at 90-100 °C until all the starting material is consumed, as observed by thin layer chromatography using pure hexane as solvent. The reaction is quenched with water and the product extracted into ether. The ether extracts are washed with water and the organic layer dried over sodium sulfate. The removal of solvent under reduced pressure affords the pure alkyl azides as confirmed by the spectral analysis. The IR spectra displaying the typical absorption bands for azido group (Table) are recorded on a Perkin-Elmer 1310 spectrophotometer.

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