Surfactant pillared clays as phase-transfer catalysts: a facile synthesis of α-azidoketones from α-tosyloxyketones and sodium azide

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The use of inexpensive and recyclable phase-transfer catalysts, surfactant pillared clays, is demonstrated in a simple and highly efficient synthesis of α-azidoketones from readily accessible α-tosyloxyketones and sodium azide.

Keywords: surfactant pillared clay, montmorillonite K 10 clay, phase-transfer catalysis, α-azidoketone, α-tosyloxyketone

1. Introduction

Applications of cation-exchanged montmorillonites, pillared clays and clay-supported reagents have been extensively studied in organic synthesis [1–6] under milder reaction conditions. Several functionalized organic polymers [7–12] and mineral supports [13–16] have been used as triphase catalysts that contain immobilized organocations, such as quaternary ammonium ions analogues to those used for conventional liquid–liquid phase-transfer catalysts [17]. Although triphase catalysis greatly simplifies the recovery of the catalyst and provides opportunities for selective chemical conversions based on substrate size or polarity, the system also has some limitations [18–20]. The industrial applications of polymer-supported triphase catalysts have not materialized yet, partly due to their higher cost, diffusion limitations, swelling tendency and mechanical/chemical instability [20]. Several inorganic supports, e.g., metal oxides [13], clays [14,15] and zeolites [16], have been substituted for polymers, but they generally suffer from similar disadvantages of low reactivity or structural instability. The typical drawbacks associated with phase-transfer catalysts such as low thermal stability, hygroscopicity, separation problems and reusability, etc. need to be addressed in the development of new materials for improved triphasic catalysis. This prompted us to explore the use of immobilized onium cations pillared clays as catalysts in a nucleophilic substitution reaction.

α-azidocarbonyl compounds are useful starting materials for the synthesis of a wide variety of organic molecules [21], including heterocyclic compounds [21e,f], and there are several methods available for the synthesis of α-azidoketones [22]. However, these methodologies often suffer from circuitous procedures, long reaction times and low yields. In addition, there are usual purification problems associated with distillation [23] of products from the incomplete reactions, since some azido compounds decompose rapidly with the danger of explosion [24]. In view of the easy accessibility of α-tosyloxyketones from readily available ketones and common reagent, (hydroxytosyloxy) iodobenzene [25], we decided to conduct a systematic study of the nucleophilic substitution of α-tosyloxyketones using sodium azide, NaN_3, under milder phase-transfer catalysis conditions (scheme 1).

2. Experimental

2.1. Reagents and catalysts

Montmorillonite K 10 clay, tetraethylammonium bromide, tetra-n-butyl-ammonium bromide were purchased from Aldrich Chemical Co. and were used as received without further purification. The α-tosyloxyketones were prepared by refluxing the appropriate ketone with [hydroxy(tosyloxy)iodo]benzene in acetonitrile for 2–3 h [25]. Surfactant pillared clays were prepared by stirring sodium-exchanged clay (6 g) in 0.2 M solution of the corresponding surfactants for 100 h at 60–70 °C [14]. 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 display characteristic stretching frequencies of alkyl group [6]. TLC was performed on silica gel plates obtained from Analtech using hexane : EtOAc (4 : 1, v/v) as the solvent system. Melting points were determined on a Mel-Temp II hot stage apparatus using a Fluke 51 K/J digital thermometer and are uncorrected. IR spectra were recorded on a Perkin-Elmer 1310 spectrophotometer. ^{1}H NMR spectra were recorded

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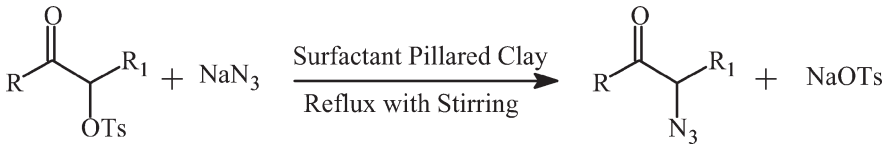
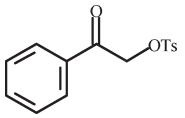
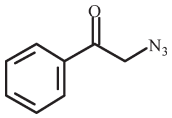
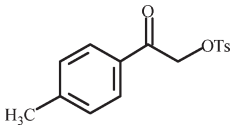
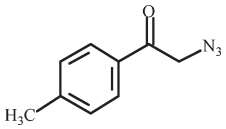
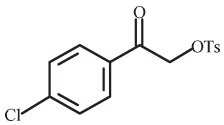
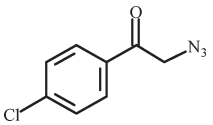
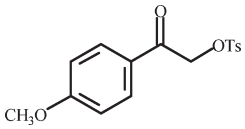
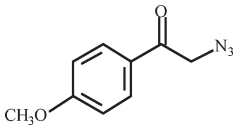
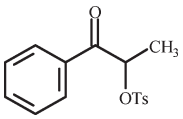
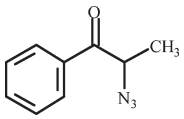
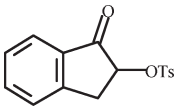
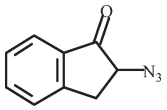
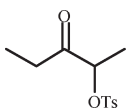
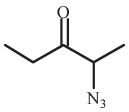
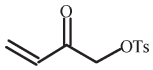
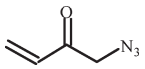


Scheme 1.

Table 1
Synthesis of α-azidoketones from α-tosyloxyketones and sodium azide catalyzed by tetramethylammonium bromide pillared clays.

Entry	Substrates	Products	Time (h)	Yield[a] (%)	IR, ν (cm^{-1})
1			1.5	95	2100
2			1.5	97	2110
3			1.5	93	2105
4			1.5	95	2120
5			2.0	89	2110
6			2.5	92	2100
7			2.5	88	2110
8			3.0	91	2100

[a] Yields refer to pure isolated products which were identified by the comparison of their m.p., TLC, IR and NMR spectral data with those of the known compounds.

in $CDCl_3$ on Jeol 300 MHz spectrometers using TMS as an internal standard.

2.2. Synthetic procedure

The α-tosyloxyacetophenone (260 mg, 1 mmol) in chloroform (5 ml) and sodium azide (78 mg, 1.2 mmol) in water (5 ml) were admixed in a round-bottomed flask. To this stirred solution, pillared clay (100 mg) was added and the reaction mixture was refluxed with constant stirring at 90–100 °C until all the starting material was consumed, as followed by thin-layer chromatography using hexane : EtOAc (4 : 1, v/v) as solvent. The reaction was quenched with water and the product extracted into chloroform (2 × 10 ml). The combined extracts were washed with water and the organic layer dried over sodium sulfate. The solvent was removed under reduced pressure to afford the pure α-azidoacetophenone as an oil (0.135 g, 95%), ν_{max}(neat) = 2100 cm^{-1}. The IR spectra displaying the typical absorption bands for azido derivatives are depicted in table 1.

3. Results and discussion

The synthesis of α-azidoketones involves a triphase catalyst system for nucleophilic displacement that consists of a dispersed solid phase and two immiscible liquid phases containing the electrophilic and nucleophilic reagents [7], where the reagents get transferred from the liquid phase to the solid phase. We conducted this reaction in a variety of

organic solvents and found that chloroform is ideally suited for this nucleophilic substitution in terms of yield and time required for the completion of reactions.

Our results for the preparation of several α-azidoketones are summarized in table 1 and are exemplified by various α-tosyloxy substrates, namely aryl, cyclic and allylic ketone derivatives. There is essentially no difference in the reaction rate for α-tosyloxyketones bearing electron withdrawing or donating substituents. However, in the case of cyclic and allylic ketone derivatives (entries 6–8), the reaction rate is slower and requires comparatively longer time for completion, presumably due to the steric or electronic reasons. The reaction is found to be very slow at room temperature and does not occur in the absence of catalyst. Instead, α-tosyloxyketone produces only a white suspension with natural montmorillonite K 10 clay. The reaction is also unaffected by increasing (two-fold) or decreasing (one-half) the amount of the organo-clay composite, thus confirming its catalytic role. Interestingly, the catalyst can be reused without any loss in activity; we have reused the recovered clay two to three times with reproducible results in the case of α-tosyloxyacetophenone (entry 1).

For all the examples described in table 1, the organo-clay assembly formed a thin membrane-like film at the interface of a chloroform-in-water emulsion. The emulsion formation or the catalytic activity is not observed for the unmodified montmorillonite K 10 clay. The experiments performed in biphasic catalytic conditions with onium salts produce the efficient conversion, a trend confirmed by others [26,27]. 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.

4. Conclusion

The present work describes an efficient synthetic route to α-azidoketones from easily available α-tosyloxyketone using organo-clay assembly as a phase-transfer catalyst which is inexpensive and can be recycled. This protocol affords, useful α-azidoketones, in high yields and excellent purity.

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