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A Heterogeneous approach to Sulfide Oxidation using TBHP-Functionalized Polystyrene Resin

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Abstract

Polymer supported reagent based synthetic strategies have been attracted the attention of chemists due to the providence of a heterogeneous reaction environment which eases the work up procedures and the recovered support can be reused. Owing to such advantages, the attempt has been made to develop heterogeneous oxidation method for sulfides under conventional and microwave conditions using resin bounded t-butyl hydroperoxide. The method succeeded to provide excellent yields in a short reaction time compared to conventional reports. The t-butyl hydroperoxide functionalized resin has been prepared and used as a heterogeneous reagent for the oxidation of sulfides. The recovered heterogeneous polymer support was reused for several times after re-functionalization using t-butyl hydroperoxide without loss in activity. The sulfoxides were prepared under the both conventional as well as microwave conditions from sulfides using supported oxidizing reagent.

Keywords: t-butyl hydroperoxide; microwave; oxidation; supported reagent.

Introduction

Oxidation of sulfides to sulfoxides is essential in pharmaceuticals and agrochemicals. The reported conventional oxidants for the oxidation of sulfide are $NaBO_3$,[1] NaClO,[2] $Ca(ClO)_2$,[3] $H_5IO_6/[MnIV\text{-}MnIV\text{-}(\mu\text{-}O)_3L_2](PF_6)_2$,[4] $KHSO_5$,[5,6] HNO_3,[7] $(NH_4)_2Ce(NO_3)_6$,[8] $NaIO_4$,[9-11] MnO_2,[12] $KMnO_4$,[13] RuO_4,[14] CF_3CO_3H,[15] dimethyldioxirane,[16] $t\text{-}C_4H_9O_2H$,[17] 4-methyl morpholine oxide with OsO_4,[18] $3\text{-}ClC_6H_4CO_3H$,[19] and $[(n\text{-}C_4H_9)_4N]\text{-}HSO_5$[20,21]. but most of these reagents are not satisfactory for oxidation on account of less effective oxygen, producing environmentally undesired by products, may cause over oxidation of sulfide to sulfone and much expensive.

In recent days polymer bounded organic synthesis has provided a large scope as an efficient methodology for designing of numerous useful compounds. Number of methods has been reported to utilize functionalized resins in solid-phase synthesis; specifically, the supports were used according to chemical nature and physical properties that required. During recent years sulfide oxidations has been impacted as a useful tool in multidisciplinary fields, including the pharmaceutical industries and the petroleum industries[22-24]. Developments for selective oxidation are continuing to overcome the challenge of selective oxygenation where sulfides can be oxidized to sulfone/sufoxides which are valuable intermediates in organic synthesis[25,26]. The sulfoxides play a vital role in therapeutic uses such as anti-ulcer,[27] antibacterial, antifungal, anti-atherosclerotic,[28] antihypertensive,[29] and cardiotonic agents,[30] as well as psychotics[31] and vasodilators[32]. Great variety of resin anchored reagents has been arrived for the oxidation of sulfide. Polymer bounded t-butyl hydroperoxide has been prepared as a heterogeneous reagent to convert aryl and alkyl sulfides to sulfoxides with high efficiency. The nature of the polymer backbone strongly influences functionalization of resin for specific reactivity. The present work describes sulfide oxidation to sulfoxides using cross-linked polystyrene supported t-butyl hydroperoxide under both conventional as well as microwave conditions.

Materials and Methods

All chemicals and solvents were analytical grade and used without additional purification. Styrene and divinylbenzene were purchased from Sigma-Aldrich. Anhydrous aluminum chloride, hydrogen peroxide (30%), camphor sulfonic acid (CSA), bromoacetone, and tert-butyl magnesium chloride (1.0 M solution in THF) purchased from commercial vendors. Thin-layer chromatography (TLC) employing silica gel plates with UV visualization was used to trackthe reactions. IR spectra were captured using a Fourier-transform infrared (FTIR) spectrometer. The uncorrected melting points of the products were measured in open capillaries.

Synthesis of cross-linked polystyrene supported t-butyl hydroperoxide: The t-butyl hydroperoxide functionalized resin was synthesized by a multi-step procedure as follows:

Synthesis of oxopropyl resin: The 2% cross-linked styrene-DVB copolymer (10g) (Scheme-1) prepared by reported method[33] was suspended in 4:1 v/v mixture of CS_2 and CH_2C_{12}, for 12 hrs. The round bottom flask containing bromoacetone (20ml) in the DCM was added anhydrous $AlCl_3$ (20g) in portion with constant stirring at 0°C. To the same round bottom flask, the pre-swollen polymer beads were added, then stirred at room temperature and refluxed for 6 hrs. An aqueous ethanol was then used to disintegrate the Lewis acid complex.

The 2-oxopropyl resin **2** (Scheme-1) was obtained through filtration, washed with different solvents, and dried in vacuum. The loading CH_3-CO-CH_2 function of corresponding resin **2** was determined by the iodoform test; the loading capacity of the resin found 4.0 meq/g. The I.R. spectrum of resin **2** showed strong absorption band at 1715 cm^{-1} of the carbonyl group (Figure-1).

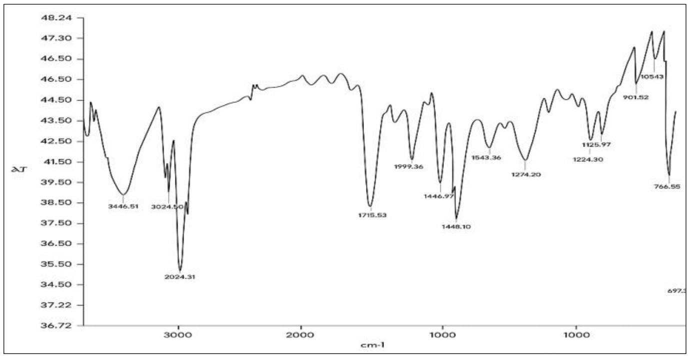


Figure-1: IR spectra of oxopropyl resin.

Synthesis of resin bounded t-butyl alcohol resin: The 5g of oxopropyl resin 2 was first pre-swollen in dry tetrahydrofuran (THF) for 12 hours. Then, under a nitrogen atmosphere and constant stirring, 10 mL of 1.0 M tert-butylmagnesium chloride in THF was added drop wise at 0°C. The mixture was allowed to stir and refluxed gently for 6 hours to ensure complete Grignard addition. Upon completion, the reaction was cooled and quenched by slow addition of dilute sulfuric acid to decompose the excess Grignard reagent. The resin 3 was then filtered, thoroughly washed with distilled water, dilute acid, THF, ethanol, and acetone, and finally dried under reduced pressure. The FT-IR spectrum (Figure-2) confirmed the successful conversion by the disappearance of the carbonyl peak at 1715 cm^{-1} and the appearance of a broad hydroxyl stretch around 3448 cm^{-1}

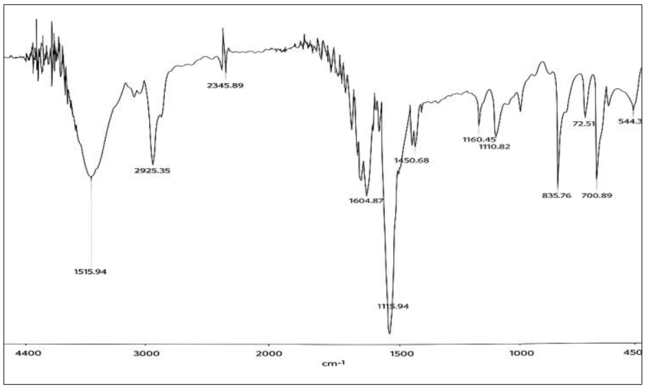


Figure-2: IR spectra of t-butyl alcohol resin.

Synthesis of t- butyl hydroperoxide resin: The prepared resin **3** (Scheme-1) was allowed to swell in T.H.F. for 12 hrs. To the cooled suspension, 70 % H_2SO_4 (10 ml) was added dropwise with gentle stirring and then the 30 vol. H_2O_2 (10 ml) was added to it. Afterwards, the suspension was stirred at room temperature for 10 hrs. The corresponding resin 4 (Scheme-1) was separated from mixture by filtration and subjected to aqueous and solvent washing. The resin 4 was then vacuum dried. The resin 4 showed absorption bands at 757 cm^{-1} and 3400 cm^{-1} in the I.R. spectrum. The loading of hydroperoxide onto resin 4 was evaluated iodimetrically, shown the capacity of 3.11 meq/g (Figure-3).

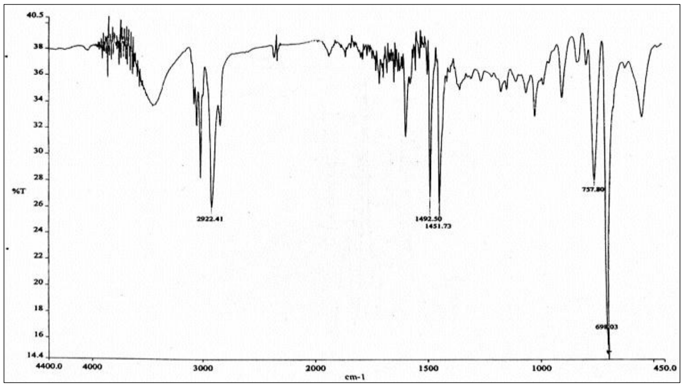
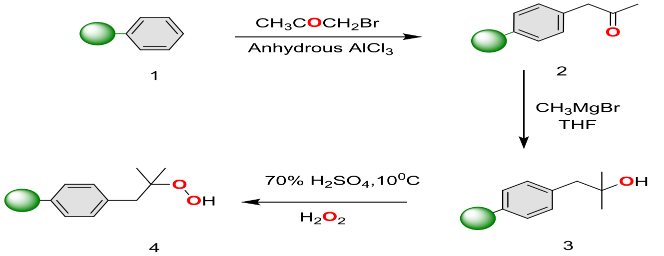


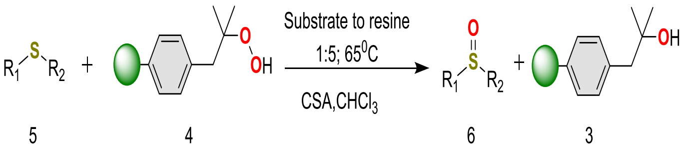
Figure-3: IR spectra of t- butyl hydroperoxide resin.

Synthesis of sulfoxides using polymer-supported reagent: The sulfide (1 mmoles) was stirred with a fivefold excess of t-butyl hydroperoxide resin 4 (Scheme 1) and (0.3 mm) camphor sulfonic acid (C.S.A.) in $CHCl_3$ (20 ml) at reflux temperature. The completion of reaction was confirmed with T.L.C. then content was filtered to dispense residue, washed with n-hexane and ethyl acetate; afforded the oxidized product after vacuum evaporation.

Synthesis of sulfoxides using Microwave technique: A mixture of sulfide **5** (Scheme 2) (1 mmoles), t-butyl hydroperoxide resin (fivefold), and camphor sulfonic acid (C.S.A., 0.3 mmoles) in $CHCl_3$ (20 ml) was irradiated under microwave at 200 W with 30s-time intervals (Table-2). The completion of reaction was confirmed with T.L.C.; then the content was filtered to separate polymer residue, washed with n-hexane and ethyl acetate. The oxidized product was obtained from filtrate after vacuum evaporation.



Scheme-1: Synthesis of t-butyl hydroperoxide functionalized resin.



Scheme-2: Synthesis of sulfoxides using polymer-supported reagent.

Table-1: Effect of molar ratio**.**

Molar Ratio	Reaction Time (Hrs)	Yield (%)
1:1	32	53
1:2	28	60
1:3	22	69
1:4	16	76
1:5	12	89

Results and Discussion

In step-1, acylation of resin 1 was achieved using bromoacetone to afford oxopropyl resin. The resin 2 was converted to alcohol functionalized resin 3 by Grignard reaction. The I.R. absorption band noted for carbonyl resin at 1715 cm^{-1}disappeared, and the absorption band at 3440 cm^{-1} to 3500 cm^{-1} was observed. The resin 3 was then modified to t-butyl hydroperoxide resin 4 using H_2O_2 (Scheme-1).

The study of different molar ratios of sulfide to resin 4 on the oxidation of sulfides to sulfoxides was performed. The increasing molar concentration of the heterogeneous reagent increases the oxidation to a greater extent. The comparative effect of the molar ratio on the oxidation is given in Table-1. When the oxidation is carried out using one-fold molar excess of the reagent, the yield of the product is low, and it takes more time for oxidation, about 32 hrs. As the molar ratio increases, the yield of the product increases, and reaction time decrease. The maximum yield of sulfoxides was obtained with the fivefold molar excess of the reagent. Further increase in a molar ratio, did not able to improve the economy of the oxidation.

The oxidation of sulfide to sulfoxides was noted more efficient in the microwave technique than the conventional method. The traditional reaction required comparatively more time than the microwave method. The yield is slightly more in the microwave method than in the conventional method. The results are given in Table-2. The polymeric by-product, t-butyl alcohol resin, can be recycling and regenerated without loss in activity, as shown in Scheme-2. Substrate size controls the reaction rate. Substrates with larger sizes required a more extended period as compared to a smaller substrate. In the case of biphenyl, sulfide required 22 hrs for oxidation, while butyl methyl sulfide only needed 12 hrs to produce a yield of around 90 %. But the microwave method seems more efficient than the conventional method with notably short time and excellent yield of a product, as given in Table-2.

Thus, resin bound oxidizing reagent was used successfully for the oxidation of sulfide with efficiency under microwave conditions. Since all these compounds are reported; characterized by melting points comparing with those reported in literature.

Table-2: Heterogeneous oxidation of sulfides.

Substituent		Conventional Polymer Supported Synthesis		Microwave-Assisted Polymer Supported Synthesis		Physical Constant	
R1	R2	Reaction Time (hrs)	Yield (%)	Reaction Time (Min)	Yield (%)	Observed MP/BP (°C)	Reported MP / B.P. (°C)
n-Bu	n-Bu	12	87	5	89	30.2-32.4	32.6[34]
Et	Et	12	88	7	89	103-105	104-105[35]
Me	Ph	16	86	10	90	32-33	33-34[35]
Et	Ph	17	87	11	90	145-147	146-147[35]
Ph	CH_2-Ph	19	89	11	89	120-121	121-122[35]
Ph	Ph	22	85	13	87	68-70	69-70[35]
CH_2-Ph	CH_2-Ph	12	90	5	90	132-134	133-135[35]

Conclusion

In this paper we presented a convenient protocol for the oxidation of sulfides to sulfoxides by a solid-supported tert-butyl hydroperoxide reagent anchor to a cross-linked polystyrene support. The method was successful under both thermal and microwave-assisted heating and microwave irradiation provide high yields in shorter time. Reusability of the polymeric reagent is an important advantage of this approach. The resin could be regenerated after each use, retaining its catalytic activity without serious loss of catalytic activity, which was very economical, non-polluting. The experimental procedure was simple and the workup was facile, providing a clean and efficient way to variety of sulfoxides. By reducing waste and avoiding the drawbacks of traditional oxidants, this method offers a valuable alternative for researchers and industry professionals working with sulfur-containing compounds.

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