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## Synthesis of Thiiranes From Oxiranes Under Mild and Nonaqueous Conditions Using Polymer Supported Thiocyanate

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# SYNTHESIS OF THIIRANES FROM OXIRANES UNDER MILD AND NONAQUEOUS CONDITIONS USING POLYMER SUPPORTED THIOCYANATE

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**ABSTRACT:** Oxiranes are efficiently converted to their corresponding thiiranes under mild and nonaqueous condition using polymer supported thiocyanate. The polymeric reagent is regenerable.

Polymer supported reagents, especially the various anionic forms of anion exchange resins, have been widely applied in organic synthesis<sup>1</sup>. These polymeric reagents are generally used in single step reactions. Their main

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advantage over monomeric reagents is their insolubility in the reaction medium and consequently the easier separation of products from the reaction mixtures, in most cases by a simple filtration. The reactions can often be driven to completion by using excess of these reagents without the fear of separating the unspent reagents from the desired reaction products. The spent polymeric reagents can usually be removed quantitatively and regenerated. In addition, anions bound to the macroporous resins have the advantage that they often react successfully in non-polar solvents.

There are many methods reported in the literature for preparation of thiiranes<sup>2,3</sup> and the most general one has been the conversion of oxiranes to thiiranes. For this purpose several sulfured agents such as inorganic thiocyanates<sup>2-5</sup>, thiourea<sup>6</sup>, phosphin sulfides<sup>7</sup>, 3- methylbenzothiazol-2thione<sup>8</sup>, and dimethylthioformamide<sup>9</sup> have been used in hydroorganic homogeneous medium. Potasium thiocyanate, however, has been the most widely reagent used. In general each of these reagents suffer from at least one of the following drawbacks; 1) Aqueous and/or alcoholic medium has to be used; 2) low yield; 3) rapid increase of pH during the reaction; 4) reaction to be carried out in the presence of trifluroacetic acid; 5) difficulty in separation of the product from the original reactant, and 6) formation of the polymeric by-products. Attractive modification procedures different from the classical synthesis of thiiranes from oxiranes using KSCN have also been reported recently. These are the use of silica gel-supported KSCN<sup>10</sup> and low hydrated KSCN-liquid heterogeneous mediums<sup>11</sup>. But as it is reported even in these systems presence of traces of water is necessary. Very recently an efficient conversion of epoxides to thiiranes with ammonium thiocyanate using Ce(IV) as catalyst has also been reported<sup>12</sup>.

Now we report an improved, efficient and easy synthesis of thiiranes from oxiranes under mild nonaqueous condition in high yields using a polymer supported thioyanate.

Amberlit IRA-400 supported thiocyanate was prepared by exchange reaction between the chloride form of the resin with a slight excess of pottassium thiocyanate in water. Using this heterogeneous reagent several epoxides were converted to their corresponding episulfides in cyclohexane which proved to be the solvent of choice among other non-polar organic solvents (Table I).

The advantages of this method of thiirane synthesis are as follows; 1) The reaction can be performed in non-aqueous medium and therefore ideal for epoxides containing water sensetive groups, 2) exess of the reagent can be used, 3) the product can be obtained by simple filtration and evaporation of the solvent, 4) no polymeric by-product is observed, 5) OCN anion moeity remains tighty bound to the polymer support, and 6) the polymeric reagent is easily regenerable.

In conclusion simple work up procedure and the advantages mentioned above makes this polymeric reagent useful in the field of organic synthesis.

### **EXPERIMENTAL**

#### Preparation of Polymer Supported Thiocyanate [P-SCN]

Amberlite IRA-400 (Cl<sup>-</sup>),(10.0g) was added to an aqueous solution of potassium thiocyanate (6.0g in 50 ml) and stirred for 12 hrs. at room temperature. The resin was filtered off and washed repeatedly with distilled water until the filtrate gave negative test for SCN<sup>-</sup>. It was then washed with

Table I. Conversion of epoxides to episulfides using polymer supported thiocyanate, [P-SCN]<sup>a</sup>.

Substrate	Product <sup>b</sup>	Time (hr) rea	Molar ratio gent/sub	Yield % strate
О-Сн-Сн <sub>2</sub>	CH-CH <sub>2</sub>	4.5	5	93
CI-CH-CH <sub>2</sub>		14	8	83
O-OCH <sub>2</sub> -CH-CH <sub>2</sub>	O-och <sub>2</sub> -ch-ch <sub>2</sub>	15	8	85
$\bigcirc \circ$	$\bigcirc$ s	14	8	82
	~~~^\$	18	8	80

- a) Reactions performed in cyclohexane under reflux condition.
- b) Products were G.C. pure and were identified by comparison of their IR and <sup>1</sup>HNMR spectra with those of the authentic samples.

#### THIIRANES FROM OXIRANES

ether and dried under vacuum in presence of  $P_2O_5$  at 40°C. The activity of this polymer supported thiocyanate determined by <sup>1</sup>HNMR spectroscopy<sup>13</sup> was 1.71 mmol/g of the polymer.

#### General Procedure for Conversion of Epoxides to Thiranes.

To a solution of epoxide (1 mmol.) in cyclohexane (15 ml), the polymeric reagent (2.93-4.68 g.) was added and the mixture stirred under reflux condition. Progress of the reaction was followed by TLC (eluent:  $CCl_4$ /ether) or GLC. On completion of reaction the mixture was cooled to room temperature, filtered and washed with cyclohexane and ether. The combined filtrates were evaporated to obtain the pure products in 80-93% yield. The spent polymeric reagent was regenerated by repeated washing with NaCl solution and subsequent treatment with potassium thiocyanate solution. The regenerated reagent has the same capacity as the original form.

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