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2,4,6-Trichloro-1,3,5-triazine catalyzed synthesis of thiiranes from oxiranes under solvent-free and mild conditions

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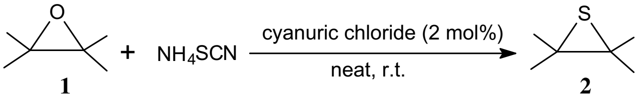
Abstract—A simple, mild and efficient method has been developed for the synthesis of thiiranes from epoxides using a catalytic amount of 2,4,6-trichloro-1,3,5-triazine under solvent-free conditions.

1. Introduction

Synthetic chemists continue to explore new methods to carry out chemical transformations. One of these new methods is to run reactions on the surface of solids. Surfaces have properties that are not duplicated in the solution or gas phase, hence entirely new chemistry may occur. Even in the absence of new chemistry, a surface reaction may be more desirable than a solution counterpart, because the reaction can be more convenient to run or a higher yield of the product is attained. For these reasons, surface synthetic organic chemistry is a rapidly growing field of study.

Organic sulfur compounds are important and useful building blocks in organic synthesis. Due to the importance of thiiranes in the synthesis of polymers, pharmaceuticals, pesticides and herbicides,[1] various methods have been developed for their synthesis. The most common and important method is the transformation of oxiranes into thiiranes with thiourea, thioamides, phosphine sulfide or dimethyl-thioformamide in the presence of trifluoroacetic acid or using inorganic thiocyanates, polymer-supported thiocyanates, silica-supported KSCN or other related compounds.[2] Usually, with these sulfurated agents, Lewis acids such as ceric ammonium nitrate (CAN),[3] $RuCl_3$,[4] $BiCl_3$,[5] $TiO(CF_3CO_2)_2$[6] and $TiCl_3(CF_3SO_3)$[7] have been used as catalysts. Polymer-supported Lewis acid catalysts such as poly-(4-vinylpyridine)-$Ce(OTf)_4$[8] and polymer supported $AlCl_3$[9] as well as polymeric co-solvents[10] have been used for this important transformation. More recently the $[bmim]PF_6$–H_2O solvent system[11] and MW[12] irradiation have been used for the conversion of oxiranes to thiiranes. However, long reaction times, high temperatures, low yields of the products, use of organic solvents, the use of acidic catalysts, difficulties in separation of the product from the original reactant, formation of polymeric by-products, high catalyst loading and in most of the cases, the use of expensive and unrecoverable catalysts are all limitations.

Over the last few years, there has been a considerable growth in interest in the use of 2,4,6-trichloro-1,3,5-triazine or its derivatives in organic synthesis.[13] Recent results from our laboratory showed that readily available 2,4,6-trichloro-1,3,5-triazine (cyanuric chloride) can assist some important organic reactions.[13n–p] This prompted us to explore the catalytic activity of cyanuric chloride for the synthesis of thiiranes. In this letter, we report that thiiranes can be conveniently and efficiently synthesized in high yields from the corresponding oxiranes with ammonium thiocyanate in the presence of cyanuric chloride (2 mol %) at room temperature under solvent-free conditions (Scheme 1).



Scheme 1.

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2. Proposed mechanism

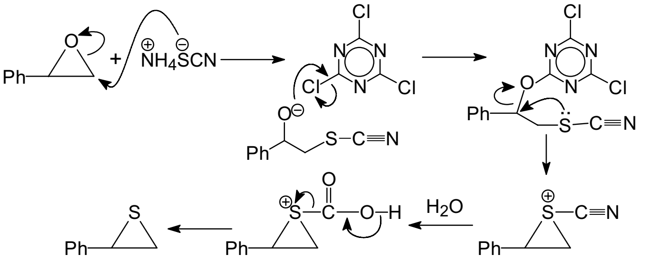


Table 1. Reaction of styrene oxide with ammonium thiocyanate under various conditions

Entry	Solvent	Catalyst (mol %) (cyanuric chloride)	Time, min/[h]	Yield (%)
1	Neat	—	[20]	10
2	CH_2Cl_2	2	50	60
3	THF	2	55	65
4	CH_3CN	2	45	55
5	$CHCl_3$	2	40	60
6	Neat	0.5	10	65
7	Neat	1.0	25	80
8	Neat	1.5	15	88
9	Neat	2	5	98
10	Neat	2.5	5	97
11	Neat	3.3	5	97

The likely role of cyanuric chloride is to act as a catalyst for the activation of epoxide. Initially, a systematic study was carried out for evaluation of cyanuric chloride as a catalyst for the reaction of styrene oxide with ammonium thiocyanate under various conditions (Table 1). The reaction was slow in the absence of catalyst (Table 1, entry 1) and inferior results were obtained in the presence of solvents (Table 1, entries 2–5). Next, we optimized the quantity of catalyst at room temperature under solvent-free conditions (Table 1, entries 6–11) and it was observed that the use of just 2 mol % was sufficient to produce an excellent yield of the product (Table 1, entry 9), whereas more than 2 mol % of the catalyst did not improve the results (Table 1, entries 10–11).

A variety of epoxides reacted smoothly with ammonium thiocyanate in the presence of 2 mol % of cyanuric chloride at room temperature under solvent-free conditions to furnish the corresponding thiiranes in high yields. The reactions were rapid and in most cases thiirane formation was complete in 5–20 min with excellent yields due to the high concentration of substrate in the solid state. The results shown in Table 2 clearly indicate the scope and generality of this protocol as a variety of aliphatic, aromatic and allylic epoxides, including those with electron-withdrawing and -donating substituents, underwent smooth conversion into thiiranes. The present procedure was efficient for the synthesis of thiiranes from styrene oxide (Table 2, entry a), cyclohexene oxide

Table 2. 2,4,6-Trichloro-1,3,5-triazine catalyzed conversion of epoxides to thiiranes at room temperature

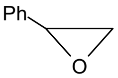
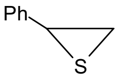
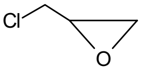
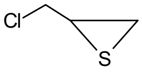
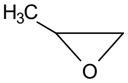
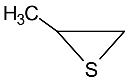
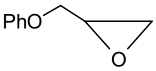
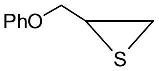
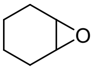
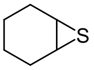
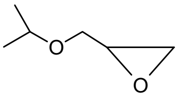
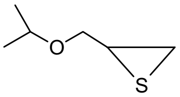
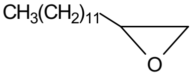
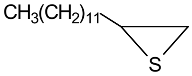
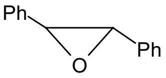
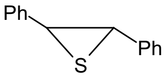
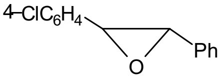
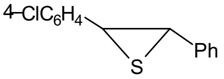
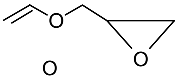
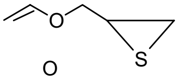
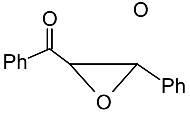
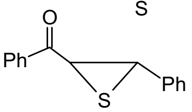
Entry	Epoxide	Product	Time (min)	Yield[a,b] (%)
a			5	98[15]
b			5	94[3]
c			5	92[3]
d			20	90[15]
e			15	90[3]
f			5	95[15]
g			10	92[12]
h			15	98[11]

Table 2 (*continued*)

Entry	Epoxide	Product	Time (min)	Yield[a,b] (%)
i			15	95
j			5	93[15]
k			5	97[11]

[a] All products were identified by comparison of their physical and spectral data with those of authentic samples obtained.[3,15]

[b] Yields refer to isolated pure products.

(Table 2, entry d) and stilbene oxides (Table 2, entries h and i), which are otherwise difficult to prepare.[14]

In conclusion, the present work clearly demonstrates the synthesis of thiiranes from oxiranes using a catalytic amount of cyanuric chloride (2 mol %). It is a valid alternative to the existing methods. The important features of the present method are mild and solvent-free reaction conditions, fast reaction rates, high yields of the products, relatively clean reactions and an inexpensive and easily available catalyst with low loading.

3. General procedure

A mixture of epoxide (5 mmol), ammonium thiocyanate (5 mmol) and cyanuric chloride (2 mol %) was stirred at room temperature for the specified time (Table 2). After completion of the reaction (TLC), the reaction mixture was diluted with water (2 × 10 mL) and extracted with diethyl ether (3 × 15 mL). The combined organic layers were dried over anhydrous Na_2SO_4, concentrated in vacuo and, if required, purified by column chromatography (silica gel Merck; 60–120 mesh, petroleum ether/ethyl acetate 9:1) to afford the pure product.

3.1. Spectroscopic data for novel compound 2i

Liquid bp 75 °C, IR ($CHCl_3$) 710, 1260, 1305, 1450, 1715, 1805, 2920 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 2.35 (d, 1H, $J = 6.7$ Hz), 2.60 (d, 1H, $J = 6.7$ Hz), 7.20 (m, 5H, Ar–H), 7.50 (d, 2H, $J = 8.1$ Ar–H), 7.62 (d, 2H, $J = 8.1$ Hz, Ar–H). Anal. Calcd for $C_{14}H_{11}ClS$ (246.5): C, 68.14; H, 4.49; S, 12.99. Found: C, 68.18; H, 4.51; S, 12.93. EIMS: m/z 246.5 [M^+].

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