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Efficient, Mild, and Regioselective Conversion of Thiiranes to Alkoxy and Acetoxy Disulphides and Dithianes with Ce(IV) Based Oxidants

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Abstract: Alcoholysis of thiiranes with primary and secondary alcohols followed by the formation of their corresponding alkoxy-disulphides is performed efficiently in one step with different Ce(IV) salts, such as ceric ammonium nitrate (CAN), ceric pyridinium nitrate (CPN), ceric triethylammonium nitrate (CTEAN) and ceric sulphate under mild condition and in moderate to excellent yields. Acetolysis of thiiranes with Ce(IV) also produces acetoxy-disulphides in good yields. Dimerization of thiiranes to their corresponding dithianes are also reported.

INTRODUCTION

Considering the multitude of reactions which thiiranes are able to undergo[1], fundamental information is still scarce in this field. The most important reactions from the point of view of organic synthesis are the nucleophilic ring opening of these compounds. This type of reaction has not been investigated extensively and only a few reports are available in the literature[2-5]. Reactions of thiiranes in only primary alcohols and in the presence of highly acidic catalysts such as BF_3, HCl or H_2SO_4[3,6] occured at high temperature and with extensive polymerization[3,7]. β-Alkoxy mercaptans are produced in low yields[3].

Reaction of thiiranes with boiling acetic acid is reported to produce a mixture of monomeric and dimeric acetoxy mercaptans[8]. Formation of dithiane from ethylene sulphide is reported to occure in gas phase by passing a mixture of ethylene sulphide and H_2S through aluminum oxide at 220 °C [9]. Formation of only 15% of 2,5-diphenyl dithiane is also reported from the reaction of styrene sulphide and dimethyl sulphate[10]. Introduction of the new reagents for organic synthesis has always been rewarding to synthetic organic chemists. Recently we have reported that 2,3-dichloro-

5,6-dicyano-p-benzoquinone could be considered as a reagent for alcoholysis of thiiranes[11].

In this paper we wish to report that Ce(IV) salts are suitable reagents for the efficient and regioselective ring opening and dimerization of thiiranes in alcohols and acetic acid. We also report that catalytic amounts of Ce(IV) in carbon tetrachloride convert thiiranes to their corresponding dithianes under mild condition and in good yields.

RESULTS AND DISCUSSION

Ring opening of different classes of thiiranes such as cyclohexene sulphide, styrene sulphide, propene sulphide and thioepichlorohydrine as examples of alicyclic, phenyl, alkyl and polar substituted thiiranes with different Ce(IV) salts were performed in methanol, ethanol, n-propanol, iso-propanol and acetic acid at either room temperature or under refluxing condition. Cyclohexene, styrene and propene sulphide were converted at room temperature to their corresponding alkoxy-disulphides in different alcohols with ceric ammonium nitrate (CAN), ceric triethyl ammonium nitrate (CTEAN), ceric pyridinium nitrate (CPN) and ceric sulphate with moderate to excellent yields. Due to the very low solubility of ceric sulphate in alcohols, its reactions were performed under refluxing condition.

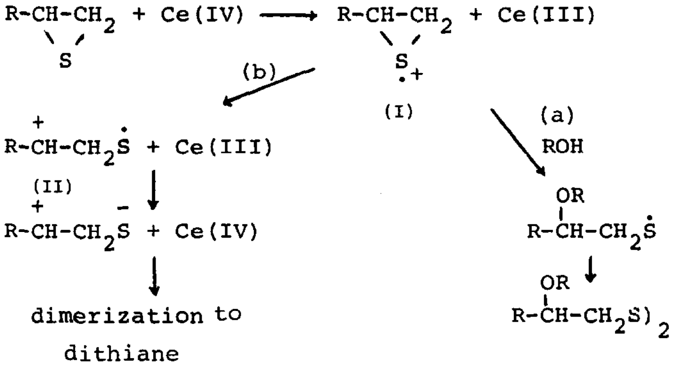
The reactions of thioepichlorohydrine in different alcohols with these Ce(IV) oxidants were occured under refluxing condition and the corresponding bis (2-chloro-2'-alkoxy-isopropyle) disulfides were obtained in 40-70% yield. By comparison of the results obtained from the reactions of thiiranes with Ce(IV) oxidants, the order of reactivity of these reagents were found to be CAN > CTEAN > CPN > ceric sulphate. The results are tabulated in Table 1.

The reactions of these thiiranes in acetic acid with ceric ammonium nitrate (CAN) were performed at 50-60 °C . Their corresponding acetoxy-disulphides were separated in 30-56% yield. The results are tabulated in Table 2.

Dimerization of cyclohexene, styrene and prepene sulphide to their corresponding dithianes were performed with catalytic amounts of CAN in refluxing CCl_4. 2,3,5,6-bis-Tetramethylene dithiane, 2,5-diphenyl and 2,5-dimethyl dithianes were obtained in 27-70% yields. The results are shown in Table 3.

Although the precise mechanism of the reaction is not clear, but on the basis of the results obtained from the reaction of propylene sulphide with Ce(IV) in methanol and in the presence of acrylamide as a radical traping agent[12] or under oxygen atmospher[13], the assumption of the radical cations (I)[14] and (II) as the intermediates may account for the above feature of the reaction (Scheme 1).

Scheme 1



EXPERIMENTAL

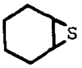
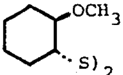
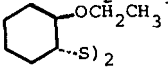
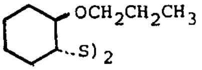
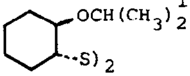
Products were characterized by comparison with authentic sample or with their IR and ^{1}H-NMR spectra. The reactions were monitored by thin layer or gas chromatography. All yields refer to isolated products. Ceric triethyl ammonium nitrate[15] and ceric pyridinium nitrate[16] were prepared according to the procedure discribed.

General procedure for the conversion of thiiranes to alkoxy-disulphides: To 1% solution ($w/_v$) of thiirane (0.01 mole) in the proper alcohol, an equimolar amount of either Ce(IV) reagents was added and stirred at room temperature except the reactions of thioepichlorohydrine which were refluxed. (All the reactions of thiiranes with ceric sulphate were performed under refluxing condition). The completion of the reactions were monitored by gas chromatography and t.l.c. The solvent was evaporated and water was added (60 ml). The organic product was extracted with diethyl ether several times (30 ml). The combined organic extracts were dried over anhydrous sodium sulphate and the solvent was removed. The residue was chromatographed twice on a silica gel column eluting with n-hexane or n-hexene/ ether. Evaporation of the solvent afforded the corresponding alkoxy disulphide in 20-86% yield (Table 1).

General procedure for the conversion of thiiranes to acetoxy disulphides: A 1% solution (w/$_v$) of thiirane (0.01 mole) in acetic acid and equimolar amount of ceric ammonium nitrate was stirred at 50-60 ^{o}C for 30 minutes. The solvent was evaporated and water was added (60 ml). The product was extracted with ether several times (30 ml). The combined extracts were washed with aqueous sodium bicarbonate (2%) and water and dried over anhydrous sodium sulphate. The solvent was evaporated and the resulting crude material was chromatographed twice on silica-gel eluting with n-hexane or n-hexane-benzene. The corresponding acetoxy disulphides were obtained in 30-56% yield.

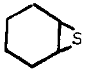
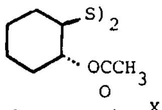
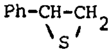
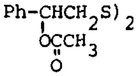
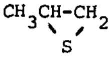
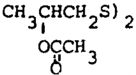
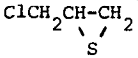
General procedure for the formation of dithianes: A 2% solution (w/$_v$) of thiirane (0.01 mole) in CCl_4 was treated with 0.6 molar equivalent of ceric ammonium nitrate and refluxed for 4.5-6 hrs. The completion of the reaction was followed by gas chromatography. The reaction mixture was cooled and filtered. The filterate was evaporated. The resulting product was purified twice by chromatography on a silica gel column using n-hexane or n-hexane /ether as eluent. The corresponding dithianes were obtained as colourless liquids (27-70%) yields. The products were compared with authentic samples. Some selected ^{1}H-NMR data in CCl_4 are: δ(ppm)(I): 1.1-2.4 (broad, unresolved, 16H), 2.8-3.2 (broad, 4H), 3.3 (singlet, 6H); (II): 1.2 (triplet, 6H), 1.4-2.4 (broad, 16H), 2.9-3.8 (quartet, 4H + broad, 4H); (III): 1.15 (doublet, 12H), 1.4-2.4 (broad, 16H), 3-3.9 (multiplet, 2H + broad, 4H); (IV): 1.15 (6H, triplet), 2.8-30 (doublets of doublet, 4H), 3.3 (quartet, 4H), 4.25-4.45 (doublets of doublet, 2H), 7.2 (singlet, 10H); (V): 0.9 (triplet, 6H), 1.5 (sextet, 4H), 2.7-3.0 (doublets of doublet, 4H), 3.25 (triplet, 4H), 4.2-4.4 (doublets of doublet, 2H), 5.2 (singlet, 10H); (VI): 1.1 (doublet, 12H), 2.7-3.0 (doublets of doublet, 4H), 3.4 (sextet, 2H), 4.25-4.5 (doublets of doublet, 2H), 7.2 (singlet, 10H); (VII): 1.1 (triplet, 6H), 1.4 (doublet, 6H), 2.6-2.8 (doublets of doublet, 4H), 3.1-3.6 (quartet, 4H + sextet, 2H);(VIII): 0.9 (triplet, 6H), 1.4 (doublet, 6H), 2.7-3.0 (doublets of doublet, 4H), 3.2-3.8 (triplet, 4H+ multiplet, 2H); (IX): 1.2 (triplet, 6H), 2.9-3.2 (doublets of doublet, 2H), 3.4-3.7 (triplet, 4H + doublets of doublet, 2H), 3.85 (doublet, 4H), 4.4, (multiplet, 2H); (X): 1.9 (singlet, 6H), 2.2-3.1 (doublets of doublet, 4H), 3.2-4.1 (doublets of doublet, 2H), 7.15 (singlet, 10H); (XI): 1.3 (doublet, 6H), 2.0 (singlet, 6H), 2.8-3.2 (doublets of doublet, 4H), 3.9-4.2 (doublets of doublet, 2H); (XII): 1.1-1.9 (broad complex, 8H), 1.9-2.5 (broad, 8H), 2.7-3.2 (broad, unresolved, 4H); (XIII): 2.2-2.7 (broad, unresolved, 4H), 3.3-3.6 (unresolved multiplet, 2H), 7.15 (singlet, 10H).

Table 1. Reactions of Thiiranes with Equimolar Amount of Ce(IV) Salts in Alcohols.

Thiirane	Solvent	CAN		CTEAN		CPN		Ceric Sulfate[a]		Product
		Time (hr)	Yield %	Time (hr)	Yield %	Time (hr)	Yield %	Time (hr)	Yield %	
	CH_3OH	$\frac{3}{4}$	86	1	80	3	63	$1\frac{1}{2}$	85	 I
"	C_2H_5OH	$2\frac{1}{2}$	85	3	75	5	60	3	82	 II
"	C_3H_7OH	3	80	$3\frac{1}{2}$	70	6	48	3.5	80	
"	$(CH_3)_2CHOH$	$3\frac{1}{4}$	60	4	50	6	25	5	58	 III
$\underset{\diagdown S \diagup}{PhCH\text{-}CH_2}$	CH_3OH	$\frac{1}{3}$	83	$\frac{1}{3}$	70	$\frac{1}{2}$	86	$4\frac{1}{2}$	80	$\mathrm{Ph\underset{\underset{OCH_3}{\mid}}{C}H\text{-}CH_2S)_2}$
"	C_2H_5OH	$\frac{1}{3}$	80	$\frac{1}{2}$	71	$\frac{1}{2}$	65	6	75	IV $\mathrm{Ph\underset{\underset{OC_2H_5}{\mid}}{C}HCH_2S)_2}$
"	C_3H_7OH	$\frac{1}{3}$	75	$\frac{1}{2}$	60	$\frac{2}{3}$	70	6	35	V $\mathrm{Ph\underset{\underset{OC_3H_7}{\mid}}{C}HCH_2S\ )_2}$
"	$(CH_3)_2CHOH$	$\frac{1}{2}$	35	$\frac{2}{3}$	30	$\frac{2}{3}$	25	20	20	VI $\mathrm{Ph\underset{\underset{OCH(CH_3)_3}{\mid}}{C}HCH_2S\ )_2}$
$\underset{\diagdown S \diagup}{CH_3CH\text{-}CH_2}$	CH_3OH	$\frac{1}{3}$	75	$\frac{2}{3}$	50	1	40	—	—	$\mathrm{CH_3\underset{\underset{OCH_3}{\mid}}{C}HCH_2S)_2}$ VII
"	C_2H_5OH	1	75	2	48	$1\frac{1}{2}$	32	—	—	$\mathrm{CH_3\underset{\underset{OC_2H_5}{\mid}}{C}HCH_2S)_2}$ VIII
"	C_3H_7OH	$1\frac{1}{3}$	73	3	40	3	30	—	—	$\mathrm{CH_3\underset{\underset{OC_3H_7}{\mid}}{C}HCH_2S)_2}$
"	$(CH_3)_2CHOH$	6	60	10	35	8	30	—	—	$\mathrm{CH_3\underset{\underset{OCH(CH_3)_2}{\mid}}{C}HCH_2S)_2}$
$\underset{\diagdown S \diagup}{ClCH_2CH\text{-}CH_2}$[a]	CH_3OH	$\frac{2}{3}$	68	1	55	+	50	—	—	$\mathrm{ClCH_2\underset{\underset{CH_2OCH_3}{\mid}}{C}H\text{-}S)_2}$
"	C_2H_5OH	$\frac{2}{3}$	65	$1\frac{1}{3}$	58	$1\frac{1}{2}$	50	—	—	$\mathrm{ClCH_2\underset{\underset{CH_2OC_2H_5}{\mid}}{C}HS)_2}$ IX
"	C_3H_7OH	$\frac{2}{3}$	60	$1\frac{1}{2}$	50	2	48	—	—	$\mathrm{ClCH_2\underset{\underset{CH_2OC_3H_7}{\mid}}{C}HS)_2}$
"	$(CH_3)_2CHOH$	1	40	2	35	3	20	—	—	$\mathrm{ClCH_2\underset{\underset{CH_2OCH(CH_3)_2}{\mid}}{C}HS)_2}$

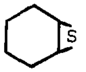
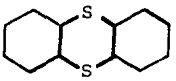
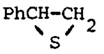
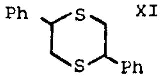
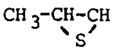
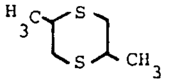
a- The reaction was performed under refluxing condition.

Table 2. Reaction of Thiiranes with Equimolar Amount of CAN in Acetic Acid at Room Temperature.

Thiirane	Solvent	Time(min)	Yield	Product
	CH_3COOH	25	56	
	"	20	30	 X
	"	20	30	XI 
 a	"	35	—	unidentified products

a- The reaction was performed under refluxing condition.

Table 3. Dimerization Reactions of Thiiranes with CAN in Refluxing CCl_4.

Thiirane	Time(hr)	CAN(%mole)	Yield	Product
	5	0.6	70	 XII
	4.5	"	68	 XIII
	6	"	27	

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Refferences and Foot Notes

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