Tetrahedron Letters,Vol.27,No.31,pp 3573-3576,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

STEREOSPECIFIC RHODIUM(I) CATALYZED DESULFURIZATION OF THIIRANES

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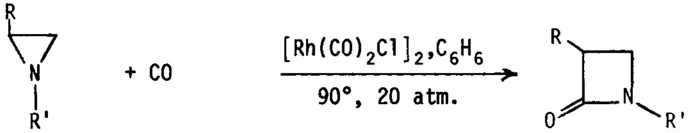
Summary: The first metal catalyzed route for the desulfurization of thiiranes (episulfides) is described.

In 1983, one of us[2] reported the regiospecific, rhodium(I) catalyzed insertion of carbon monoxide into an aziridine to give a β-lactam. This metal catalyzed carbonylation-ring expansion reaction also occurs with α-lactams, affording azetidine-2,4-diones in good yields[3]. To assess the scope of the reaction with respect to the heteroatom, the rhodium(I) catalyzed carbonylation of thiiranes (episulfides) was examined, with thietan-2-ones as the anticipated products. We now describe the interesting results of this investigation.



Starting material was recovered when 2-phenylthiirane [styrene sulfide] was treated with carbon monoxide and a catalytic amount of chlorodicarbonylrhodium(I) dimer in benzene at room temperature and atmospheric pressure for 80 hours. However, after 18 hours at 400 psi and room temperature, styrene was obtained in quantitative yield, with carbonyl sulfide formed as the co-product of the reaction. No reaction occurs in the absence of the metal catalyst. Other rhodium(I) complexes, including the dimer of chloro(1,5-hexadiene)rhodium $[1,5\text{-HDRhCl}]_2$, chloro(1,5-cyclooctadiene)rhodium $[1,5\text{-CODRhCl}]_2$, chlorotris(triphenylphosphine)rhodium, and chlorocarbonylbis(triphenylphosphine)rhodium also catalyze the desulfurization of 2-phenylthiirane but all are inferior to chlorodicarbonylrhodium(I) dimer [see Table 1 for results]. Tetrakis(triphenylphosphine)palladium is rather ineffective and cobalt carbonyl is inert.

The generality of this rhodium(I) catalyzed desulfurization reaction was then examined with a variety of thiiranes using $[Rh(CO)_2Cl]_2$ as the catalyst [50/1 ratio of substrate/catalyst]. As the data in Table 2 indicate, the reaction is applicable to thiiranes bearing alkyl, aryl, alkoxy, and carboethoxy substituents. Furthermore, the process is a stereospecific one with, for example, cis-stilbene being isolated from cis-2,3-diphenylthiirane and trans-stilbene formed from trans-2,3-diphenylthiirane. In some instances [e.g. cyclohexene

Table 1

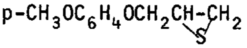
Metal Catalyzed Desulfurization of 2-Phenylthiirane[a]

Catalyst	Reaction time, hr.	Yield of styrene, %
-	90	0
$[Rh(CO)_2Cl]_2$	18	98
$[1,5\text{-}CODRhCl]_2$	18	56
$[1,5\text{-}HDRhCl]_2$	18	42
$(Ph_3P)_3RhCl$	18	50
$(Ph_3P)_2Rh(CO)Cl$	18	33
$Pd(PPh_3)_4$	60	18
$Co_2(CO)_8$	60	0

[a] Reaction conditions: CO/C_6H_6/400 psi/r.t./5 mole % catalyst.

Table 2

$[Rh(CO)_2Cl]_2$ Catalyzed Desulfurization of Thiiranes[a]

Thiirane	Reaction time, hr.	Product[b]	Yield, %
2-phenylthiirane	18	styrene	91
cis-2,3-diphenylthiirane	18	*cis*-stilbene	28
	60	*cis*-stilbene	71
trans-2,3-diphenylthiirane	18	*trans*-stilbene	99
trans-2-methyl-3-phenylthiirane	18	*trans*-β-methylstyrene	27
	60	*trans*-β-methylstyrene	64
cyclohexene sulfide	18	cyclohexene	33[c]
	60	cyclohexene	70[c]
trans-2,3-di-n-butylthiirane	18	*trans*-5-decene	13
	60	*trans*-5-decene	66
ethyl *trans*-2-methylthiirane carboxylate	18	ethyl *trans*-crotonate	97
 $p\text{-}CH_3OC_6H_4OCH_2CH\text{-}CH_2$ (S)	60	$p\text{-}CH_3OC_6H_4OCH_2CH{=}CH_2$	98

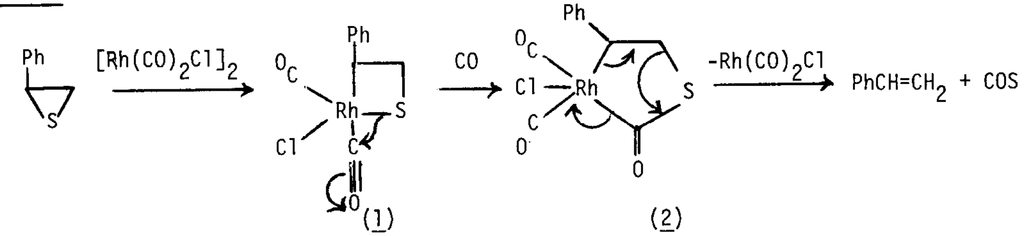
[a] Reaction conditions: CO/C_6H_6/400 psi/r.t./2 mole % $[Rh(CO)_2Cl]_2$

[b] Products were identified by comparison of properties [m.p. or b.p., ir, nmr, ms, gc retention times] with authentic materials. [c] Gas chromatographic yield.

sulfide] a longer reaction time is required in order to realize good yields of products.

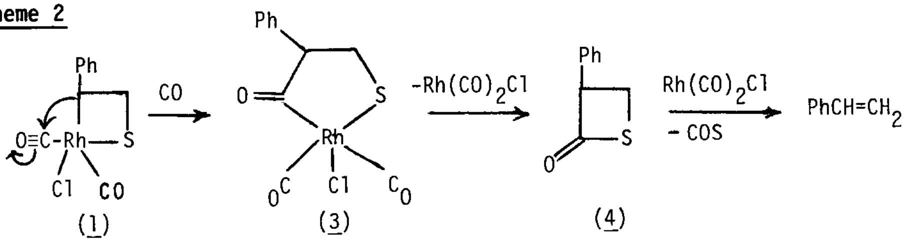
A possible mechanism for the desulfurization reaction is outlined in Scheme 1 [illustrated for 2-phenylthiirane]. Insertion of rhodium into a carbon-sulfur bond of the reactant would give the metallocyclobutane 1. Ligand migration from sulfur-rhodium to carbonyl carbon would form the five-membered ring complex 2. Expulsion of carbonyl sulfide from the latter would generate the olefin and regenerate the rhodium(I) catalyst (as a monomer). It should be noted that carbonyl sulfide is also produced in the cobalt carbonyl catalyzed desulfurization of of mercaptans by carbon monoxide and water[4].

Scheme 1



An alternative pathway (Scheme 2) may involve ligand migration from the carbon-rhodium bond of 1 to carbonyl carbon to give 3. Reductive elimination from 3 would give the thietan-2-one (4). Rhodium(I) can conceivably induce loss of carbonyl sulfide from 4 to form the olefin. While 4 can also arise from 2 by reductive elimination, loss of carbonyl sulfide from 2 should be a favorable pathway. Thietan-2-ones were not detected in any of the thiirane reactions. In addition, thiobutyrolactone is unreactive towards $[Rh(CO)_2Cl]_2$ at 400 psi and room temperature.

Scheme 2



The following general procedure was used: a mixture of the thiirane [1.0 mmol] and $[Rh(CO)_2Cl]_2$ [0.02 mmol] in freshly distilled benzene [30 ml] was stirred overnight (18 hours) at room temperature and 400 psi pressure of carbon monoxide. The solution was filtered through Celite, the solvent was removed from the filtrate by rotary evaporation, and the olefin was then purified by recrystallization [e.g. *trans*-stilbene from ether-pentane] or by thin-layer chromatography or distillation [e.g. *trans*-5-decene].

In conclusion, thiiranes undergo a simple, mild, and stereospecific rhodium(I) catalyzed desulfurization to olefins. There are, of course, other methods [e.g. triphenylphosphine] known for effecting the extrusion of sulfur from thiiranes[5,6]. Several metal complexes [e.g. ruthenium(II), nickel(0), molybdenum(V), tungsten(VI), and iron(0)] have been employed as thiirane desulfurization reagents[5]. However, all of these complexes function as stoichiometric reagents. The method described above is, to our knowledge, the first example of a homogeneous, metal catalyzed desulfurization reaction of thiiranes.

Acknowledgments

We are grateful to the Natural Sciences and Engineering Research Council for support of this research. We are indebted to Johnson Matthey Limited for a loan of hydrated rhodium trichloride.

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(Received in USA 14 April 1986)