Pergamon

Tetrahedron Letters, Vol. 35, No. 26, pp. 4571-4574, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $7.00+0.00

0040-4039(94)00858-2

New Ring-opening Reaction of Thiiranes with Carboxylic Acid Derivatives Catalyzed by Quaternary Onium Salts

Atsushi Kameyama, Masahiro Kiyota, and Tadatomi Nishikubo*

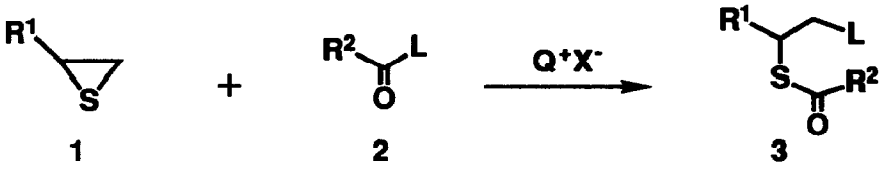
Department of Applied Chemistry, Faculty of Engineering, Kanagawa University
Rokkakubashi, Kanagawa-ku, Yokohama 221

Key Words : Ring-opening Reaction, Thiiranes, Carboxylic Acid Derivatives, Quaternary Onium Salts

Abstract : New ring-opening reaction of thiiranes with carboxylic acid derivatives having good leaving groups was investigated. The reaction of thiiranes with acyl chlorides or *S*-aryl thioesters using quaternary onium salts as neutral catalysts proceeded very smoothly and regioselectively to afford the corresponding *S*-thioesters as addition products.

Although thiiranes are reactive and interesting starting materials similar to oxiranes in synthetic organic chemistry and polymer chemistry, organic reactions of thiiranes have not been developed satisfactorily. Reactions of thiirane compounds with several reagents have been reported, for example, cycloaddition reaction of thiiranes with alkyl or aryl nitriles[1] in the presence of a strong acid yielding thiazoline derivatives have been investigated. Cycloaddition reaction of thiiranes with diethyl malonate[2] and carbon disulfide[3] using bases as catalysts were also reported. Funahashi examined an addition reaction of thiirane with phenyl acetate[4] using a base, however, the reaction did not proceed successfully. In this letter, we wish to report new regioselective ring-opening reactions of thiiranes with various carboxylic acid derivatives using quaternary onium salts as catalysts under neutral conditions.

When the reaction of 3-butoxypropylene sulfide (**1a**, 0.731 g, 5 mmol) with benzoyl chloride (**2a**, 0.703 g, 5 mmol) was carried out without a catalyst in the presence of 1-chloronaphthalene (0.5 g) as the internal standard for gas chromatography (GLC) in a sealed ample tube at 90 °C for 6 h, an addition product



1 2 3

R^1 : $C_4H_9OCH_2$ (1a) : $PhOCH_2$ (1b) Q^+X^- : Quaternary onium salts

Scheme 1

Table 1. Reactions of thiiranes with various carboxylic acid derivatives[a)]

Run	Thiirane 1	Carboxylic acid derv. 2 R^2	L	Cat.	Time / h	Yield of 3[b)] / %
1	**1a**	Ph	Cl (**2a**)	None	6	30 (**3a**)
2				TBAB	6	97 (**3a**)
3				TBAC	6	97 (**3a**)
4				TBPC	6	96 (**3a**)
5	**1a**	CH_3	Cl (**2b**)	TBAB	6	100 (**3b**)
6	**1b**	Ph	Cl (**2a**)	TBAB	6	82 (**3c**)
7	**1a**	CH_3	SPh (**2c**)	None	1	0 (**3d**)
8				TBAC	1	100 (**3d**)
9	**1b**	CH_3	SPh (**2c**)	TBAC	1	97 (**3e**)
10	**1b**	CH_3	SCH_2Ph (**2d**)	TBAC	24	0 (**3f**)
11	**1a**	CH_3	O(*p*-NO_2)Ph (**2e**)	TBAC	96	0 (**3g**)
12	**1a**	CH_3	O(*p*-Cl)Ph (**2f**)	TBAC	96	0 (**3h**)

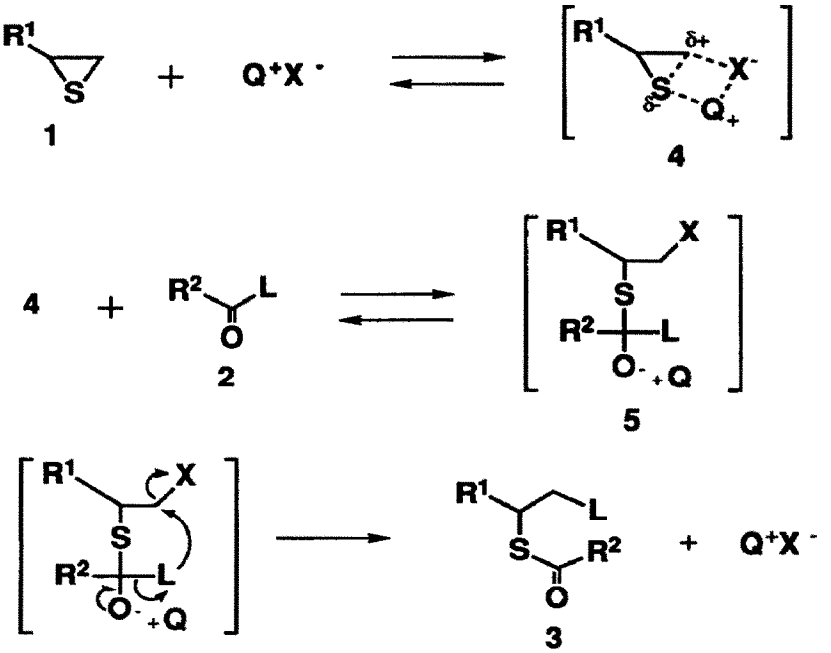
a) The reaction was carried out with 5 mmol of thiirane and carboxylic acid derivative using 0.025 mmol of catalyst at 90 °C in bulk.
b) GLC yield of 3.
c) Reaction temp; 130 °C.

was obtained in 30 % GLC yield. The reaction was catalyzed quantitatively by tetrabutylammonium bromide (TBAB) and chloride (TBAC) to afford the product **3a**. Tetrabutylphosphonium chloride was also effective catalyst on the reaction to give **3a** in 96 % yield. The structure of the product obtained, which was isolated by column chromatography (silica gel, eluent; $CHCl_3$: n-hexane = 1: 2, v/v) in 35 % yield, was ascertained by IR, ^1H NMR spectra, and elemental analysis. In the IR spectrum[5], characteristic peaks due to $\nu C{=}O$ of *S*-thioester group and $\nu C\text{-}O\text{-}C$ were observed at 1666 and 1209 cm^{-1}, respectively. The ^1H NMR[6] in $CDCl_3$ supported the structure as shown in Scheme 1, particularly, a methine proton produced by β-cleavage of the thiirane ring of **1a** was observed at 4.35 ppm with the intensity ratio expected. Furthermore, on the elemental analysis[7], contents of carbon and hydrogen of **3a** agreed well with the calculated values. From these results, it was proved that the reaction of **1a** with **2a** proceeded regioselectively to afford **3a**. The reactions of **1a** with acetyl chloride and of 3-phenoxypropylene sulfide with **2a** also proceeded readily to give **3b**[8] and **3c**[9] in high yields, respectively.

Although the reaction of **1a** with *S*-phenyl thioacetate (**2c**) did not occur at all in the absence of catalysts at 90 °C for 1 h, the reaction using TBAC under the same conditions proceeded very smoothly to give

3d[10] with quantitative yield. The ^{1}H NMR spectral data of **3d** suggested that the ring-opening reaction proceeded regioselectively similar to the reaction of thiiranes with acyl chlorides using quaternary onium salts. On the reaction of **1b** with *S*-alkyl thioesters, *S*-benzyl thioacetate (**2d**) using TBAC catalyst (Run 10), the reaction product was not **3f** but a oligomer[11] with average molecular weight of 1500, which was estimated by intensity ratio of the terminal acetyl and the pendant phenyl groups of the oligomer in the ^{1}H NMR spectrum. The IR spectrum of the oligomer showed a characteristic peak (weak) due to νC=O of the terminal *S*-acetyl group at 1690 cm^{-1}. This result can be understood as follows; at first the addition reaction of **1b** with **2d** proceeded to give a corresponding product *S-alkyl thioester*, and then the reaction of the resulted *S-alkyl thioester* with **1b** took place competitively to afford the oligomer having the terminal *S*-acetyl group. Concerning the reaction of thiiranes with *S*-thioesters, therefore, it was found that the reaction of **1a** with *S*-aryl thioesters using quaternary onium salts proceeded selectively to give the corresponding products.

The reactions of **1a** with *O*-active esters, *p*-nitrophenyl acetate or *p*-chlorophenyl acetate were attempted using TBAC catalyst at 90 °C for 4 days, however, the reaction did not proceed. These results mean that thiiranes have high selectivity for active carboxylic esters. The selectivity on the reaction of thiiranes with carboxylic acid derivatives can be explained considering the ability of leaving groups of the carboxylic acid derivatives as shown in Scheme 2. Thiirane is activated by quaternary onium halide (Q^+X^-) to form a complex (**4**), then **4** reacts with carboxylic acid derivative to form an intermediate (**5**). When the leaving ability of leaving group (L) of **5** is higher than alkyl thiolate, L would be released to replace a halide (X^-) recovering Q^+X^-. In the case of the reaction with *O*-aryl ester, the formed **5** would result in starting compounds due to an equilibrium. When the reaction of thiirane with *S*-alkyl thioester is conducted, reaction of a produced **3** with the starting thiirane proceeds in chain reaction mode to afford a oligomer.

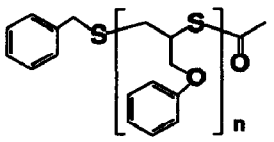


Scheme 2

In summary, the characteristic of the ring-opening reaction of thiiranes with carboxylic acid derivatives using neutral quaternary onium salt catalysts was proved. That is, thiiranes react selectively with carboxylic acid derivatives such as acyl chlorides and *S*-aryl thioesters in the presence of quaternary onium salts to give the corresponding products (*S*-thioesters). Further investigation on the reaction of thiiranes with various carboxylic acid derivatives is now in progress.

REFERENCES AND NOTES

1. G. K. Helmkamp, D. J. Pettitt, J. R. Lowell, Jr., W. R. Mabey, and R. G. Wolcott, *J. Am. Chem. Soc.*, **1966**, 88, 1030.
2. Y. Taguchi and Y. Suhara, *Bull. Chem. Soc. Jpn.*, **1986**, 59, 2321.
3. Y. Taguchi, K. Yanagiya, I. Shibuya, and Y. Suhara, *Bull. Chem. Soc. Jpn.*, **1987**, 60, 727
4. K. Funahashi, *Chem. Lett.*, **1978**, 1043.
5. IR (neat, cm^{-1}) 1666, (νC=O), 1595 (Aromatic νC=C), 1209, 1122 (νC-O-C).
6. ^1H NMR (90 MHz, $CDCl_3$, TMS) δ(ppm) 0.93 ppm (t, J = 6.6 Hz, 3 H,CH_3 of butyl group), 1.16-1.83 (m, 4 H, CH_2 of butyl group), 3.58 (t, J = 6.2 Hz, 2 H, CH_2-O of butyl group), 3.61-3.98 (m, 4H, O-CH_2-CH-CH_2Cl), 4.00-4.35 (m, 1 H, methine), 7.25-7.80 (m, 3 H, Ar), and 7.82-8.27 (m, 2 H, Ar).
7. Found: C,58.72; H, 6.75 %. Calcd. for $C_{14}H_{19}O_2SCl$: C, 58.63; H, 6.68 %.
8. IR (neat, cm^{-1}) 1696, (νC=O), 1129, (νC-O-C). ^1H NMR (90 MHz, $CDCl_3$, TMS) δ(ppm) 0.81-1.03 (m, 3 H, CH_3 of butyl group), 1.22-1.75 (m, 4 H, CH_2 of butyl group), 2.35 (s, 3 H, C(O)-CH_3), 3.07-4.18 (m, 7 H, CH_2-O-CH_2-CH-CH_2Cl).
9. IR (neat, cm^{-1}) 1666, (νC=O), 1595 (Aromatic νC=C), 1208, 1055 (νC-O-C). ^1H NMR (200 MHz, $CDCl_3$, TMS) δ(ppm) 3.56 (dd, J = 5.8 Hz, J = 12.7 Hz, $CH(a)_2$Cl), 3.71 (dd, J = 5.6 Hz, J = 12.7 Hz, 2 H (including *H(a)*), $CH(b)_2$Cl), 3.85-4.09 (m, 1 H, methine), 4.15-4.50 (m, 2 H, O-CH_2-CH), 6.86-8.09 (m, 10 H, Ar).
10. IR (neat, cm^{-1}) 1691, (νC=O), 1116 (νC-O-C). ^1H NMR (90 MHz, $CDCl_3$, TMS), δ(ppm) 0.91 (t, J = 7.3 Hz, 3 H, CH_3), 1.08-1.76 (m, 4 H, CH_2 of butyl group), 2.32 (s, 3 H, C(O)-CH_3),3.12-4.00 (m, 7 H, CH_2-O-CH_2-CH-CH_2Cl), 7.05-7.55 (m, 5 H, Ar).
11. IR (film, cm^{-1}) 1690 (νC=O, week), 1597, 1494 (Aromatic νC=C), 1237 cm^{-1} (νC-O-C). ^1H NMR (60 MHz, $CDCl_3$, TMS) δ(ppm) 2.25 (s, 3 H, CH_3) , 2.55-3.70 (m, 24 H, CH_2-CH-S), 3.65 (s, 2 H, Ph-CH_2-S), 3.70-4.60 (m, 16 H, O-CH_2), 6.60-7.50 (m, 45 H, Ar of the terminal and pendant).



(*Received in Japan* 8 *February* 1994; *accepted* 20 *April* 1994)