SUBSTITUENT EFFECTS ON THE CONTROL OF CATIONIC ISOMERIZATION AND POLYMERIZATION OF FIVE-MEMBERED CYCLIC DITHIOCARBONATES

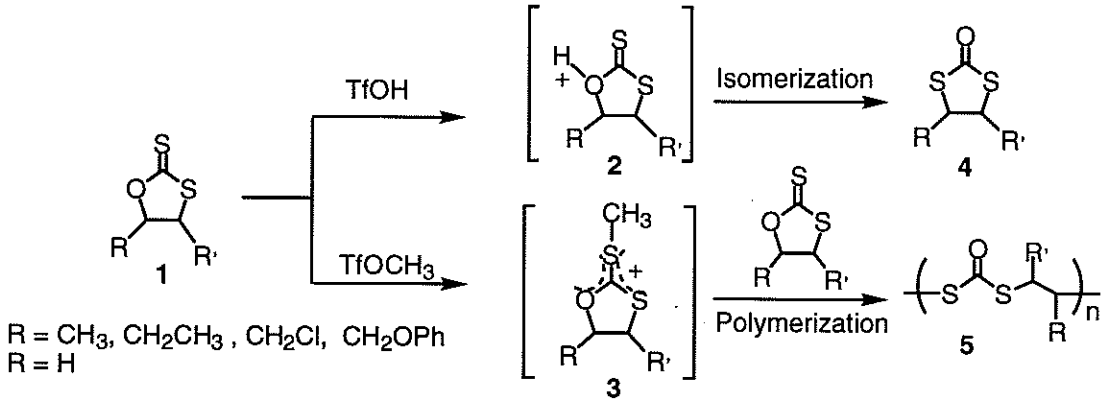
Wonmun Choi, Fumio Sanda, and Takeshi Endo*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology
4259 Nagatsuta-cho, Midori-ku, Yokohama 226-8503, Japan

Abstract- The electrophilic reactions of five-membered cyclic dithiocarbonates were studied. They afforded the isomers and polymers depending on the substituents.

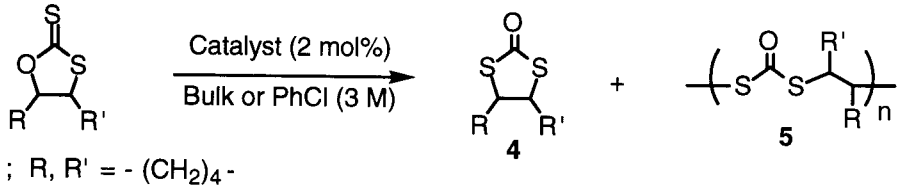
The Chugaev reaction is known as a pyrolytic β-elimination of COS and mercaptan from an *O,S*-dialkyl dithiocarbonate (xanthate ester) to form an olefin.[1] When there is no β-hydrogen at the ether oxygen of the *O,S*-dialkyl dithiocarbonate, a rearrangement takes place to form an *S,S*-dialkyl dithiocarbonate.[2] This rearrangement has been reported to proceed efficiently with a cationic catalyst,[3] whereas the successful rearrangement of a cyclic one has not been reported so far. Recently, we have reported the first example of selective cationic isomerization and ring-opening polymerization of five-membered cyclic dithiocarbonates (**1**) depending on the catalysts. Namely, **1** selectively isomerizes with Lewis acid and protonic acid catalysts, while it selectively polymerizes with CF_3SO_3Me (TfOMe) and CF_3SO_3Et (TfOEt).[4,5] The formations of a cyclic oxonium cation (**2**) and a cyclic carbenium cation (**3**) have been confirmed in the reactions of **1** with CF_3SO_3H (TfOH) and TfOMe, respectively, indicating that the selectivity in the cationic reaction of **1** may be attributable to the different intermediates according to the catalysts (Scheme 1).[5]

Scheme 1



It is important to control the reaction pathways to obtain a target compound selectively in organic chemistry. Electronic and steric factors of compounds as well as catalysts play an important role in the selectivity of the reaction. In this communication, we wish to report the effects of substituents on the control of cationic isomerization and polymerization of five-membered cyclic dithiocarbonates (**1a-c**). The five-membered dithiocarbonates (**1a**; R, R'= -$(CH_2)_4$-, **1b**; R= Ph, R'= H, **1c**; R= $(CH_3)_2$, R'= H) were synthesized by the reactions of the corresponding oxiranes with CS_2 according to the previously reported method.[6] The reactions of **1a-c** were carried out under various cationic conditions to give the isomers (**4a-4c**) and the polymers (**5b**, **5c**) as summarized in Scheme 2 and Table 1.[7]

Scheme 2



1a ; R, R' = - $(CH_2)_4$ -
1b ; R =Ph, R' =H
1c ; R = $(CH_3)_2$, R'=H

Table 1. Cationic Isomerization and Polymerization of **1a~1c**.

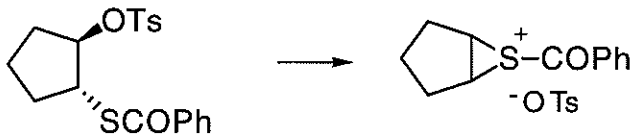
run	compd	cat.	solv.	temp. (°C)	time (min)	conv.[a] (%)	product ratio (%) **4** : **5**
1	**1a**	$ZnCl_2$	PhCl	rt	180	0	
2	**1a**	TfOH	PhCl	rt	30	0	
3	**1a**	TfOH	none	60	60	100	100 : 0
4	**1a**	$TfOCH_3$	PhCl	60	30	100	100 : 0
5	**1a**	$TfOC_2H_5$	PhCl	60	60	100	100 : 0
6	**1a**	$TfOC_2H_5$	none	60	60	100	100 : 0
7	**1b**	$ZnCl_2$	PhCl	rt	120	100	94 : 6
8	**1b**	TfOH	PhCl	rt	30	100	0 : 100
9	**1b**	TfOH	PhCl	60	10	100	0 : 100
10	**1b**	$TfOCH_3$	PhCl	rt	30	100	0 : 100
11	**1b**	$TfOCH_3$	PhCl	60	10	100	0 : 100
12	**1c**	$ZnCl_2$	none	rt	120	0	-
13	**1c**	TfOH	PhCl	rt	120	4	0 : 100
14	**1c**	TfOH	none	60	30	81	19 : 81
15	**1c**	TfOH	PhCl	60	60	73	56 : 44
16	**1c**	$TfOCH_3$	PhCl	60	60	100	37 : 63

Catalyst; 2 mol % vs. **1a~1c**; concentration of **1a~1c** 3 M.

[a] Estimated by ^{1}H-NMR.

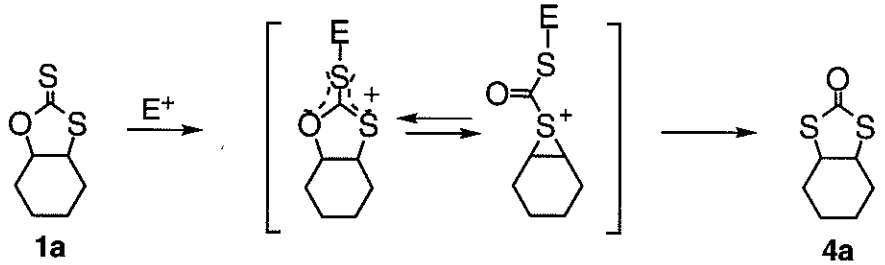
The dithiocarbonate (**1a**) selectively gave the isomer (**4a**) not only with a protonic acid (TfOH), but also with TfOMe. On the contrary, **1b** gave the polymer (**5b**) selectively with TfOH and TfOMe at room temperature and 60 °C, while it selectively afforded the isomer (**4b**) with $ZnCl_2$ at room temperature. Meanwhile, **1c** did not show clear selectivity depending on the catalyst. It was surprising that the product selectivity was completely different according to the substituent, considering the cationic reaction behavior of the previously studied cyclic dithiocarbonates.[4,5] Among several ring-opening reactions involving a C-O bond cleavage, epoxides have been widely studied, where the direction of ring-opening is markedly influenced electronically and sterically by the substituents.[8] In an acidic medium, the C-O bond of cyclohexene oxide cleaves in an S_N 2-like manner, while that of styrene oxide does in an S_N 1-like manner.[8,9] The selective polymerization of **1b** might proceed *via* a carbenium cation stabilized by the phenyl group in an S_N 1-like manner. The selective isomerization of **1b** with $ZnCl_2$ indicates that the catalytic properties such as acidities and counter anions are still important for the selectivity in the reaction. The low reaction selectivity of **1c** may be due to the stabilization effect as well as the steric factor of the tertiary carbon of **1c**. On the other hand, both of the polymerization and isomerization of **1a** may be unfavorable due to the steric factor of the cyclohexene ring. Goodman *et al.* have reported that *trans*-2-(benzoylthio)cyclopentyl tosylate transforms into *S*-benzoylepisulfonium tosylate on long standing at room temperature (Scheme 3).[10]

Scheme 3



In a similar manner, the formation of a benzoylepisulfonium ion may be possible as the intermediate resulted by the sulfur atom participation, followed by the isomerization to yield the isomer selectively (Scheme 4). The polymerization of the isomer (**4**) is negligible, because **4b** does not convert with TfOMe and TfOH at 60 °C. The reactivity of **1a-c** toward cationic catalysts decreased in the order of **4b** > **4a** ≅ **4c**, which might reflect the order of stabilization effect and steric factor of the substituents.

Scheme 4



REFERENCES AND NOTES

1. (a) G. Cernigliano and P. Kocienski, *J. Org. Chem.*, 1977, **42**, 3622; (b) M. Kim and J. D. White, *J. Am. Chem. Soc.*, 1975, **97**, 451; (c) D. J. Cram and F. A. A. Elhafez, *J. Am. Chem. Soc.*, 1952, **74**, 5828; (d) L. S. Mcnamara and C. C. Price, *J. Org. Chem.*, 1962, **27**, 1230.
2. Y. Araki, *Bull. Chem. Soc. Jpn.*, 1970, **43**, 252.
3. (a) T. Kawata, K. Harano, and T. Taguchi, *Chem. Pharm. Bull.*, 1973, **21**. 604; (b) K. Harano and T. Taguchi, *Tetrahedron Lett.*, 1974, 4479. (c) T. Kawata, K. Harano, and T. Taguchi, *Chem. Pharm. Bull.*, 1978, **26**. 3807.
4. W. M. Choi, F. Sanda, N. Kihara, and T. Endo, *J. Polym. Sci., Part A: Polym. Chem.*, 1997, **35**, 3853.
5. W. M. Choi, F. Sanda, and T. Endo, *Macromolecules*, 1998, **31**, 2454.
6. N. Kihara, Y. Nakawaki, and T. Endo, *J. Org. Chem.*, 1995, **60**, 473; 5-Phenyl-1,3-oxathiolane-2-thione (**1f**); white crystal, mp 71.5-73.5 °C, yield 65%, IR 1188 cm^{-1} ($\nu_{c=s}$); ^{1}H-NMR (400 MHz, $CDCl_3$) 3.65~3.70 (m, 1H, one proton of CH_2), 3.82~3.87 (m, 1H, one proton of CH_2), 6.01~6.05 (m, 1H, CH) ppm; 7.37~7.42 (m, 5H, Ph) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$) 40.9, 91.4, 125.6, 128.6, 129.2, 135.1, 211.1 ppm. Anal. Calcd for $C_9H_8OS_2$: C, 55.07; H, 4.11. Found: C, 55.08; H, 4.12.
7. The cationic reactions of **1a**-**c**. Typical procedure: To a glass tube containing **1** (1 mmol) in bulk and chlorobenzene (0.3 mL), an initiator was added at a set temperature under a nitrogen atmosphere. After the reaction mixture was stirred for a set time, it was quenched by the addition of pyridine. The isomer (**4**) was isolated from the reaction mixture by preparative HPLC eluted with $CHCl_3$, and the polymer (**5**) was obtained by precipitation with *n*-hexane. 7,9-Dithiobicyclo[4.3.0]nonan-8-one (**4a**); yellow oil. IR (neat): 1653 cm^{-1} ($\nu_{c=o}$), ^{1}H-NMR (400 MHz, $CDCl_3$) 1.47~2.16 (m, 8H, CH_2), 3.78~3.85 (m, 2H, CH), ^{13}C-NMR (100 MHz, $CDCl_3$) 25.6, 29.5, 58.5, 195.8 ppm. Anal. Calcd for $C_7H_{10}OS_2$: C, 48.24 ; H, 5.78. Found: C, 48.14; H, 5.44. 5-Phenyl-1,3-dithiolan-2-one (**4b**); colorless oil. IR (neat) 1653 cm^{-1} ($\nu_{c=o}$), ^{1}H-NMR (400 MHz, $CDCl_3$) 3.73~3.84 (m, 2H, CH_2), 5.26~5.30 (m, 1H, CH), 7.36~7.49 (m, 5H, Ph), ^{13}C-NMR (100 MHz, $CDCl_3$) 42.8, 56.9, 127.4, 128.9, 129.1, 136.2, 196.7 ppm. Anal. Calcd for $C_9H_8OS_2$: C, 55.07; H, 4.11. Found: C, 55.14; H, 4.08. 5,5-Dimethyl-1,3-dithiolan-2-one (**4c**), colorless oil. IR (neat) 1647 cm^{-1} ($\nu_{c=o}$), ^{1}H-NMR (400 MHz, $CDCl_3$) 1.71 (s, 6H, CH_3), 3.48 (s, 2H, CH_2), ^{13}C-NMR (100 MHz, $CDCl_3$) 28.8, 48.8, 58.3, 197.1, ppm. **5b**; white powder. IR (film) 1641 cm^{-1} ($\nu_{c=o}$), ^{1}H-NMR (400 MHz, $CDCl_3$) 3.49 ~3.55 (m, 2H, CH_2), 4.83 (br, 1H, CH), 7.20~7.34 (m, 5H, Ph), ^{13}C-NMR (100 MHz, $CDCl_3$) 35.7, 49.03, 127.8, 128.3, 128.8, 137.9, 186.8 ppm. Anal. Calcd for $C_9H_8OS_2$: C, 55.07; H, 4.11. Found: C, 55.43; H, 4.54. **5c**; viscous oil. IR (film) 1637 cm^{-1} ($\nu_{c=o}$), ^{1}H-NMR (400 MHz, $CDCl_3$) 1.45 (s, 6H, CH_3), 3.55 (s, 2H, CH_2), ^{13}C-NMR (100 MHz, $CDCl_3$) 26.7, 40.38, 54.0, 187.9, ppm. Anal. Calcd for $C_5H_8OS_2$: C, 40.51; H, 5.44. Found: C, 40.76; H, 5.33.
8. For a review, see: J. G. Smith, *Synthesis*, 1984, 629.
9. N. Miyoshi, K. Kondo, S. Murai, and N. Sonoda, *Chem. Lett.*, 1979, 909.
10. L. Goodman, A. Benitez, and B.R. Baker, *J. Am. Chem. Soc.*, 1958, **80**, 1680.

Received, 20th April, 1999