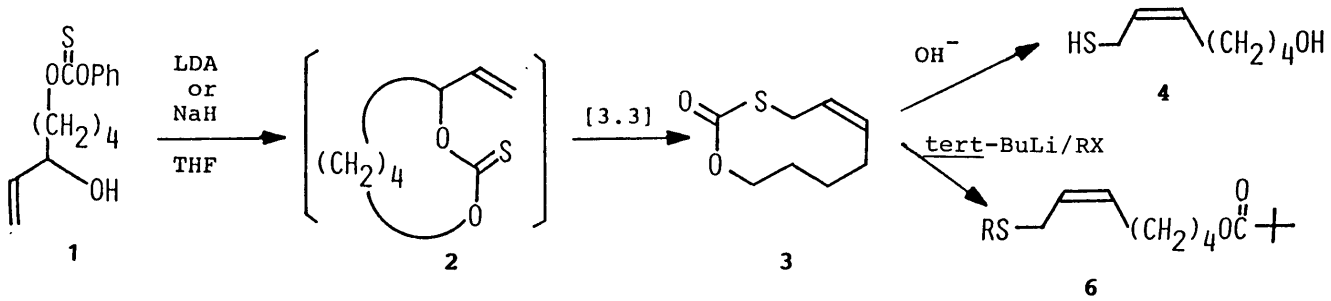
NEW ROUTE TO (Z)-ALLYLIC SULFIDES VIA A 10-MEMBERED THIOLCARBONATE

Shinya HARUSAWA, Toshiko KUROKAWA, Harumi FUJII, Ryuji YONEDA, and Takushi KURIHARA*
Osaka University of Pharmaceutical Sciences, 2-10-65, Kawai, Matsubara, Osaka 580, Japan

A new synthesis of a 10-membered thiolcarbonate containing a (Z)-double bond and its conversion into (Z)-allylic sulfides are described.

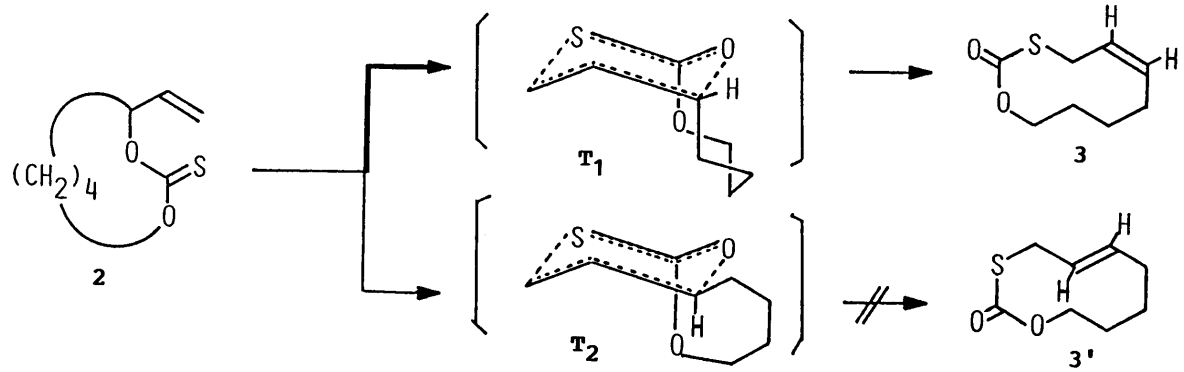
KEYWORDS (Z)-allylic sulfide; 10-membered thiolcarbonate; [3.3]-sigmatropic rearrangement; thionocarbonate

[3.3] Sigmatropic rearrangement of allylic thion-esters have proven to be exceedingly useful for the (E)-selective construction of unsaturated systems.[1,2,3] In our continuing investigation of the formation and synthetic utility of medium- or large-ring thionocarbonates,[4] we have been interested in a [3.3]sigmatropic rearrangement of an 8-membered thionocarbonate **2**. Here, we report the synthesis of a 10-membered thiolcarbonate **3** containing a (Z)-double bond and its conversion to (Z)-allylic sulfides.



1 **2** **3** **4** **6**

Treating of a trifunctional precursor **1** with lithium diisopropylamide (LDA) (or NaH) followed by 1-h refluxing in THF gave a 10-membered thiolcarbonate **3** containing (Z)-double bond in 73% (or 71%) yield *via* [3.3] sigmatropic rearrangement of cyclic thionocarbonate **2** formed *in situ*. The stereochemistry of **3** and its complete isomeric purity, after chromatography on silica gel, were determined by IR, ^{1}H-NMR [$-CH_a=CH_bCH_2S-$: δ 5.37 (H_a) (ddd, J=10.7, 8.4 and 7.4 Hz), 5.57 (H_b) (dt, J=10.7 and 8.2 Hz)] and ^{13}C-NMR data.[5] The corresponding (E)-isomer **3'** was not detected in the crude product. This result is in contrast to the high (E)-selectivity of allyl thiolcarbonate by the rearrangement of a linear allyl thionocarbonate reported by Faulkner and Peterson [96.5% (E)- and 3.5% (Z)-isomer].[3] The formation of (Z)-olefin **3** can be reasonably explained by an assumption of the transition state (T_1) disposing a 1,3-diaxial interaction rather than the more strained transition state (T_2) that would lead to the (E)-olefin **3'**.[6]

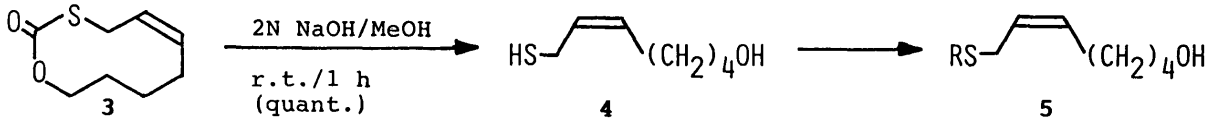


2 **T_1** **3** **T_2** **3'**

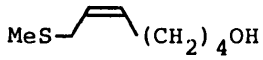
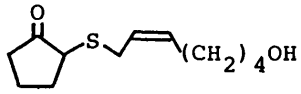
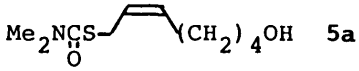
Allylic sulfides have been used widely as intermediates for the formation of carbon-carbon bonds in organic synthesis.[1a] (E)-Allylic sulfides are synthesized by a variety of

methods[7] involving [3.3] sigmatropic rearrangement.[1,2,3] On the other hand, the existing method[8] for the (Z)-allylic sulfides still relies on Lindlar hydrogenation of the corresponding acetylenes.[8a,b] Hydrolysis of **3** with sodium hydroxide in aqueous methanol at room temperature gave (Z)-allylic thiol **4**[9] with liberation of carbon dioxide in quantitative yield. The reaction of the thiol **4** with electrophiles easily led to various kinds of (Z)-allylic sulfides **5** having a versatile alcohol function at the terminal position (Table I). Further, treatment of **3** with tert-butyllithium followed by the addition of electrophile

Table I

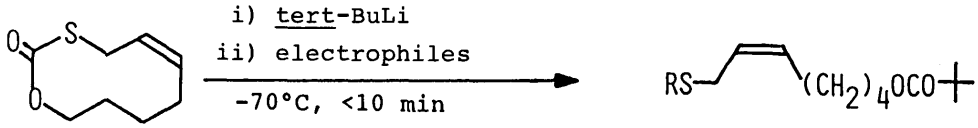


3 **4** **5**

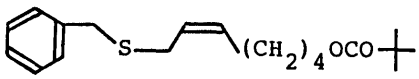
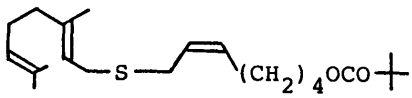
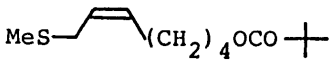
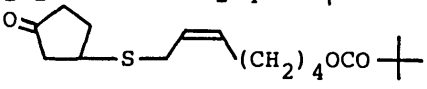
Run	Reaction condition for **4** → **5**	Product	Yield (%)
1	MeI, MeONa, r.t./20 min, MeOH		90
2	2-Bromocyclopentanone MeONa, r.t /1 h, MeOH		58
3	2-Cyclopentenone MeONa, r.t./2 h, MeOH		86
4	Me_2NCOCl, Et_3N, 4-DMAP (cat.) r.t./4.5 h, THF	 **5a**	92
5	Me_2NCSCl, Et_3N, 4-DMAP (cat.) r.t./ 5 h, THF		70

gave unexpected (Z)-allylic sulfides **6** with a pivaloate ester function (Table II).[10] Thus, these conversions of **1** into **5** or **6** provide a new route for (Z)-allylic sulfides.

Table II



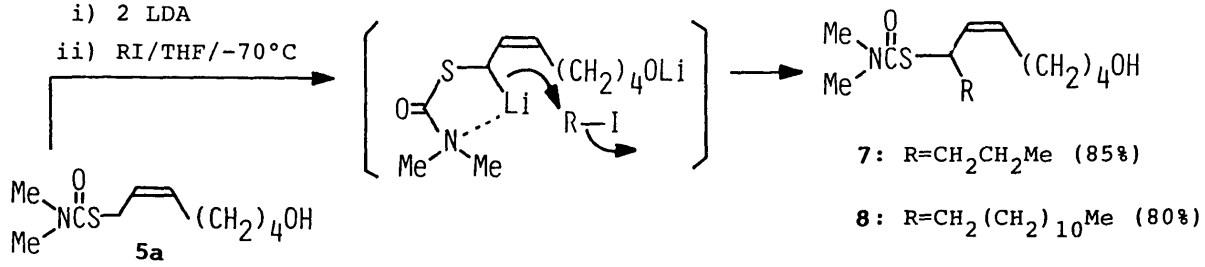
3 **6**

Run	Electrophile	Product **6**	Yield (%)
1	Benzyl bromide		76
2	Geranyl bromide		81
3	MeI	 **6a**	83
4	$Me(CH_2)_2I$		40
5	2-Cyclopentenone		77

In addition, we clarified[2,11] that the (Z)-allylic thiolcarbamate **5a** obtained above underwent α-alkylation in the presence of LDA to give **7** or **8** with complete retention of the double bond position and stereochemistry by the metal chelating effect of the nitrogen

atom. This regioselective alkylation stimulates interest for the stereoselective synthesis of naturally occurring (Z)-alkenol sex pheromones.[12]

We believe that the route described will add flexibility to the existing methodology for (Z)-olefin synthesis.



7: R=CH_2CH_2Me (85%)

8: R=$CH_2(CH_2)_{10}Me$ (80%)

REFERENCES AND NOTES

1) a) For general review; "Reactions of Organosulfur Compounds", Academic Press, New York, 1978; b) T. Nakai and A. Ari-izumi, Tetrahedron Lett., 1976, 2335 and references cited therein.

2) a) T. Hayashi, Tetrahedron Lett., 1974, 339; b) T. Nakai, H. Shiono, and M. Okawara, ibid., 1974, 3625; c) T. Nakai, T. Mimura, and A. Ari-izumi, ibid., 1977, 2425; d) T. Nakai, T. Mimura, and T. Kurokawa, ibid., 1978, 2895.

3) D.J. Faulkner and M.R. Petersen, J. Am. Chem. Soc., 95, 553 (1973).

4) S. Harusawa, N. Shibata, N. Yamasaki, S. Sakanoue, T. Ishida, R. Yoneda, and T. Kurihara, Chem. Pharm. Bull., in press.

5) To a dry THF (400 ml) solution of LDA (4.536 mmol) was added during 25 min a solution of precursor **1** (1.097 g, 4.124 mmol) in THF (30 ml) at 0 °C under argon. The reaction mixture was then refluxed for 1 h. The ordinary workup and purification on silica gel gave the pure cyclic thiolcarbonate **3** (518 mg, 73%) as an oily product which crystallized in a refrigerator. IR (neat) 1690 cm^{-1} (CO); ^{1}H-NMR (δ in $CDCl_3$): 1.5-1.8 (4H, m), 2.37 (2H, bq), 3.40 (2H, bd), 4.39 (2H, bs), 5.37 (1H, ddd, J=10.7, 8.4, and 7.4 Hz), 5.57 (1H, dt, J=10.7 and 8.2 Hz); ^{13}C-NMR (δ in $CDCl_3$): 26.0, 27.2, 27.3, 29.8, 68.7, 126.1, 132.6, 169.8; High MS 172.0566 (calcd. 172.0558) [$C_8H_{12}O_2S$].

6) A related [3.3]sigmatropic rearrangement has been applied to the synthesis of (±)-Phoracantholide J: M. Petrzilka, Helv. Chim. Acta, 61, 3075 (1978).

7) K. Takeda, K. Tsuboyama, K. Torii, M. Murata, and H. Ogura, Tetrahedron Lett., 29, 4105 (1988) and references cited therein.

8) a) T. Hayashi, N. Fujitaka, T. Oishi, and T. Takeshima, Tetrahedron Lett., 21, 303 (1980); b) F. Kido, S.C. Sinha, T. Abiko, and A. Yoshikoshi, ibid., 30, 1575 (1989); c) C. German, A. Alexakis, and J.F. Normant, Synthesis, 1984, 43.

9) ^{1}H-NMR (δ in $CDCl_3$): 1.3-1.65 (6H, m), 2.10 (2H, q, J=7 Hz), 3.16 (2H, t, J=8 Hz), 3.66 (2H, t, J=6 Hz), 5.39 (1H, dt, J=10.7 and 7.2 Hz), 5.56 (1H, dt, J=10.7 and 7.6 Hz).

10) To a solution of **3** (17 mg, 0.1 mM) in THF (4 ml) was added 1.5 M tert-BuLi (0.073 ml, 0.11mM) followed by CH_3I (0.012 ml, 0.2 mM). The ordinary workup and purification on silica gel gave a colorless oil **6a** (20 mg, 83%). ^{1}H-NMR (δ in $CDCl_3$): 1.18 (9H, s), 1.43 (2H, q, J=7.5 Hz), 1.64 (2H, q, J=7.5 Hz,), 2.0 (3H, s), 2.07 (2H, q, J=7.5 Hz), 3.11 (2H, d, J=7.5 Hz), 4.03 (3H, t, J=7.5 Hz), 5.43 (1H, dt, J=10.5 and 6.2 Hz), 5.52 (1H, dt, J=10.5 and 6.8 Hz).

11) Studies on the alkylation of allyl thiolcarbamates have been confined to (E)-isomer: J.F. Biellman and J.B. Ducep, Org. React., 27, 1 (1982).

12) K. Mori, "The Total Synthesis of Natural Products," Vol.4, John Wiley & Sons, New York, 1981, p.1.

(Received July 19, 1989)