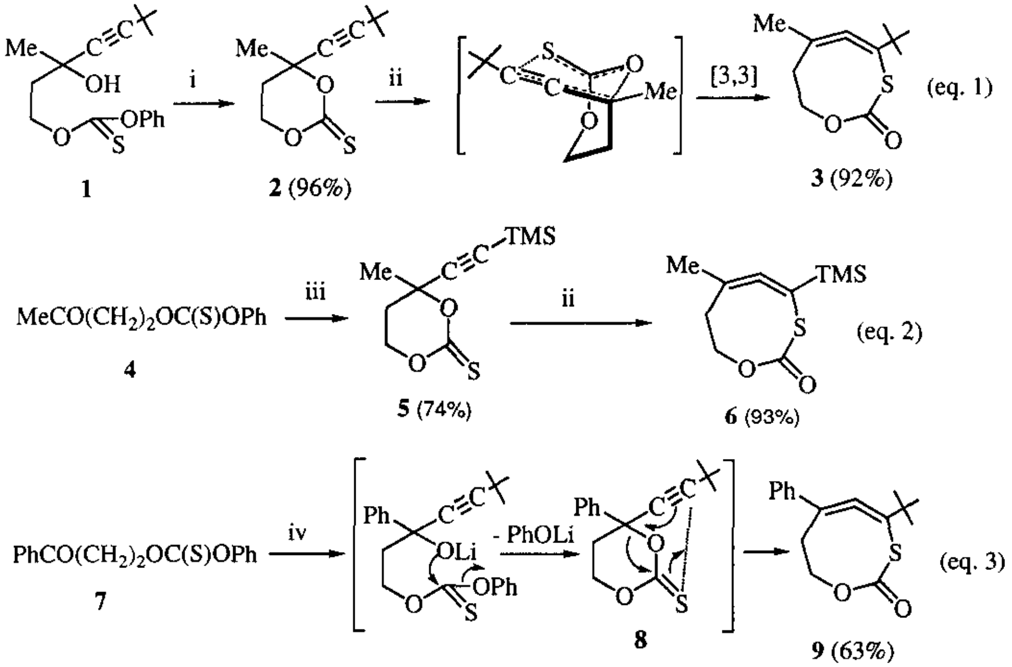
SYNTHESIS OF STRAINED 8-MEMBERED HETEROCYCLIC ALLENES BY [3,3] SIGMATROPIC REARRANGEMENT AND THEIR REACTIVITIES[1]

Shinya Harusawa, Hideki Moriyama, Hirofumi Ohishi, Ryuji Yoneda, and Takushi Kurihara*

Osaka University of Pharmaceutical Sciences, 2-10-65 Kawai, Matsubara, Osaka 580, Japan

Abstract - A new type of 8-membered heterocyclic allenes were synthesized by the [3,3] sigmatropic ring expansion of 6-membered cyclic thionocarbonates. The MNDO optimized structure indicated the allenyl moiety in cyclic allene (**3**) is bent and strained. Reactivities of the heterocyclic allenes were also examined.

Recent interests have focused on attempts to synthesize the highly strained cyclic allenes and to study their properties.[2-5] 1-*tert*-Butyl-1,2-cyclooctadiene[3] has been known as the smallest isolable carbocyclic allene.Two groups[4] independently reported synthesis of 6-membered silacyclic allenes bridged by long Si-Si bonds (2.3-2.4 Å). Recently, we reported[1] a synthesis of medium-membered heterocyclic allenes by the [3,3] sigmatropic ring expansion of cyclic thionocarbonates. In continuation of the study for the synthesis of other cyclic allenes, we report herein the synthesis and reactivities of the 8-membered cyclic allenes containing a thiolcarbonate moiety. Although it has been reported that the strained cyclic allenes easily dimerize ([2+2] cycloaddition),[2] we anticipated that bulky alkyl groups on the allene could make possible to isolate the labile 8-membered molecule. Treatment of diolmonothionocarbonate (**1**) with lithium bis(trimethylsilyl)amide [$(TMS)_2NLi$] in THF at room temperature afforded the 6-membered thionocarbonate (**2**) (96%) (Scheme 1, eq.1). The [3,3] sigmatropic rearrangement of **2** expectedly proceeded in refluxing benzene for 1.5 h and the pure 8-membered heterocylcic allene (**3**)[6] (92%) was obtained. The ^1H- and ^{13}C-nmr spectra of **3** showed the four non-equivalent methylene protons and the characteristic allenic *sp* and sp^2 carbons at 202.9, 117.2, and 102.7 ppm, respectively. This is a new type of isolable 8-membered cyclic allene containing divalent sulfur and oxygen atoms. It should be noted that the sigmatropic rearrangement has been rarely used to generate the strained cyclic allenes.[2] The structure of **3** was estimated from MNDO calculation (Figure 1). The bond angle on the *sp* carbon, C1-C2-C3, is bent from linearity to 170.1°. The dihedral angle, CH_3-C1-C3-^{t}Bu, is strongly twisted (64.3°) from vertical geometry. The bond angle on the *sp* carbon of **3** corresponds to that of carbon skeletal nine-membered cyclic allene estimated from MNDO calculation by Johnson *et al.*[7] Two 8-membered cyclic allenes (**6, 9**) containing a TMS or a phenyl group could be similarly synthesized from ketones (**4,7**) (Scheme 1, eq. 2 and 3). Interestingly, treatment of the ketone (**7**) with lithium acetylide directly afforded **9** (63%) *via* the sigmatropic rearrangement of the 6-membered intermediate (**8**).

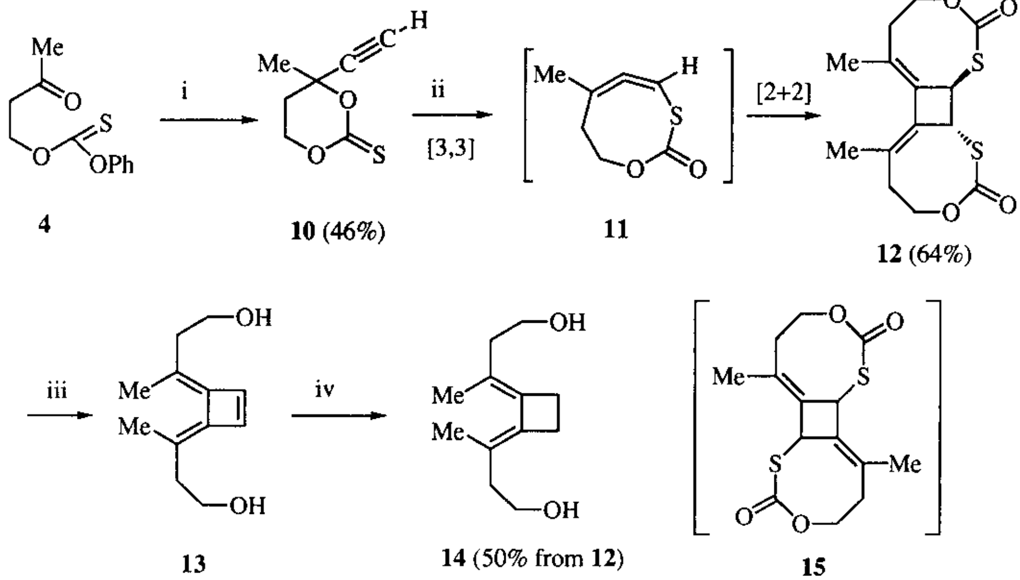


Scheme 1. *Reagent and conditions*: i, $(TMS)_2NLi$ (1.0 eq), THF, room temperature for 1.5 h; ii, benzene, reflux for 1.5 h; iii, TMSC≡CLi, THF, -78°C for 20 min.; iv, ^{t}BuC≡CLi, THF, -78°C → room temperature for 25 min

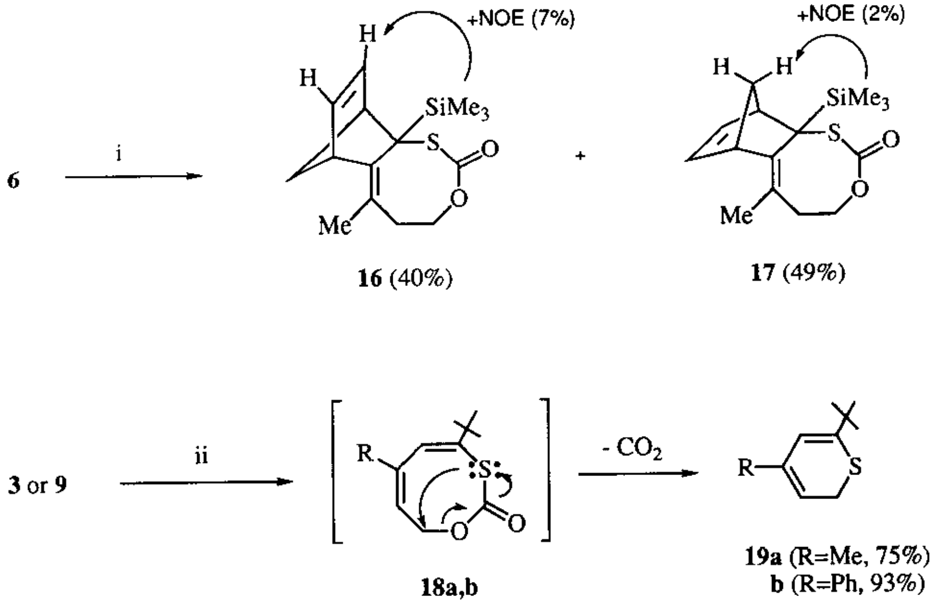
We next investigated a synthesis of the cyclic allene (**11**) lacking a bulky substituent (Scheme 2). Refluxing the cyclic thionocarbonate (**10**), prepared from **4** and ethynylmagnesium bromide, in benzene afforded the [2+2]dimer (**12**) (64%, mp 220-231°C). The formation of **12** is reasonably explained by the dimerization of the intermediate (**11**). We could not initially distinguish between structure (**12**) (head-to-head dimer) and other possible dimerization product (**15**) (head-to-tail dimer). Thus, SmI_2 reduction[1] of **12** followed by catalytic reduction of a cyclobutene derivative (**13**) were carried out to yield a diol (**14**)[8] (50% from **12**). This sequence clearly demonstrates that **12** is a head-to-head dimer. Further, X-ray analysis of **12** confirmed unequivocally the *trans*-configuration of the four-membered ring (Figure 2).

Reactivities of the heterocyclic allenes were also examined (Scheme 3). Diels-Alder cycloaddition of **6** with cyclopentadiene under uncatalyzed thermal conditions afforded two stereoisomeric products (**16**) (40%) and (**17**) (49%), whose structures were determined by ^1H NOE experiments. Intriguing point is the formation of 2*H*-

thiopyran derivatives (**19a**) (75%), (**b**) (93%)[9] by treatments of **3** or **9** with DBU, respectively. Isomerization of the double bond and subsequent CO_2 elimination of the resulting cyclic dienes (**18a**, **b**) may be a plausible mechanism for the formation of **19a**,**b**.



Scheme 2. *Reagents and conditions*: i, CH≡CMgBr, THF, 0°C; ii, benzene, reflux for 2 h; iii, SmI_2 - HMPA, ^{t}BuOH; iv, H_2 / Pd-C, EtOH



Scheme 3. *Reagents and conditions*: i, cyclopentadiene, benzene, 60-70°C for 31 h; ii. DBU (1.0 eq), benzene, room temperature <5 min

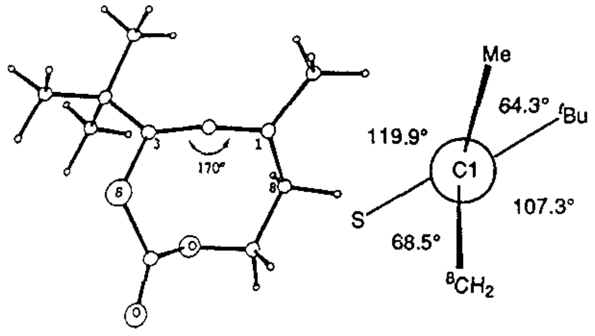


Figure 1. MNDO Estimated Structure of **3** with Dihedral Geometry around the Allenic Moiety

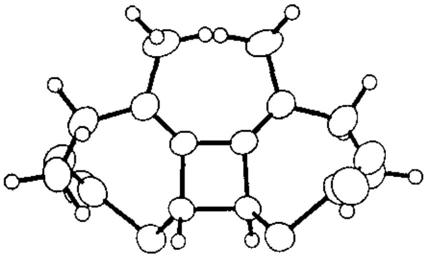


Figure 2. X-Ray Determined Structure of **12**

REFERENCES AND NOTES

1. This is part 11 of the series entitled "[3,3] Sigmatropic Ring Expansion of Cyclic Thionocarbonates". Part 10, see, S. Harusawa, N. Kase, R. Yoneda, and T. Kurihara, *Tetrahedron Lett.*, 1994, **35**, 1255.
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6. **3**, a colorless oil, ir (neat) 1712 cm^{-1} (CO). ^{1}H-Nmr (200 MHz, $CDCl_3$) : 1.16 (9H, s), 1.68 (1H, ddd, *J* = 13.8, 2.6, 2.1 Hz), 1.82 (3H, s), 2.52 (1H, ddd, *J* = 13.8, 10.6, 5.8 Hz), 4.42 (1H, ddd, *J* = 12.0, 5.8, 2.1 Hz), 4.55 (1H, ddd, *J* = 12.0, 10.6, 2.6 Hz). ^{13}C-Nmr ($CDCl_3$) : 19.8 (q), 29.0 (t), 29.5 (q), 35.9 (s), 71.3 (t), 102.7 (s), 117.2 (s), 172.0 (s), 202.9 (s). CI-MS *m/z* : 213 (M^++1), 184 (M^+-CO). HR-ms *m/z* : Calcd for $C_{11}H_{17}O_2S$ 213.0948, Found : 213.0946.
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8. **14**, a colorless oil, ^{1}H-nmr ($CDCl_3$) : 1.82 (6H, s), 2.27 (4H, t, *J* = 6.5 Hz), 2.46 (4H, s), 3.70 (4H, t, *J* = 6.5 Hz). ^{13}C-Nmr ($CDCl_3$) : 19.9 (q), 27.1 (t), 38.2 (t), 60.7 (t), 121.7 (s), 138.2 (s).
9. **19b**, a pale yellow oil, ^{1}H-nmr ($CDCl_3$) : 1.28 (9H, s), 3.37 (2H, d, *J* = 8.3 Hz), 5.71 (1H, td, *J* = 8.3, 1.0 Hz), 6.41 (1H, d, *J* = 1.0 Hz), 7.21-7.43 (5H, m). ^{13}C-Nmr ($CDCl_3$) : 26.7 (t), 29.8 (q), 37.9 (s), 111.1 (d), 117.5 (d), 126.8 (d), 127.8 (d), 128.9 (d), 139.8 (s), 141.5 (s), 151.9 (s).

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