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

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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. Two groups independently reported synthesis of 6-membered silacyclic allenes bridged by long Si-Si bonds (2.3-2.4 Å). Recently, we reported 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), 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 heterocyclic allene (3) (92%) was obtained. The 1H- and 13C-nmr spectra of 3 showed the four non-equivalent methylene protons and the characteristic allenic sp and sp² 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. 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, CH3-C1-C3-²Bu, 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. 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).

\[
\begin{align*}
\text{Me} & \quad \text{C} = \text{C}^- \quad \text{OH} \quad \text{O} \quad \text{S} \quad \text{Ph} \quad \text{Me} \quad \text{C} = \text{C}^- \quad \text{O} \quad \text{S} \quad \text{Ph} \quad \text{Me} \\
& \quad \text{Me} \quad \text{C} = \text{C}^- \quad \text{O} \quad \text{S} \quad \text{Ph} \quad \text{Me} \quad \text{C} = \text{C}^- \quad \text{O} \quad \text{S} \quad \text{Ph} \quad \text{Me} \\
\end{align*}
\]

(eq. 1)

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 \(^1\)H NOE experiments. Intriguing point is the formation of 2H-
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.

\[ \text{Me} \quad \text{O} \quad \text{S} \quad \text{O} \quad \text{Ph} \quad \text{Me} \quad \text{C} \quad \text{C} \quad \text{H} \quad \text{Me} \quad \text{O} \quad \text{S} \quad \text{O} \quad \text{Me} \]

\[ 4 \quad 10 \quad 11 \quad 12 \]

\[ \text{Me} \quad \text{OH} \quad \text{Me} \quad \text{OH} \]

\[ 13 \quad 14 \quad 15 \]

Scheme 2. Reagents and conditions: i, CH=CMgBr, THF, 0°C; ii, benzene, reflux for 2 h; iii, Sml\(_2\) - HMPA, 'BuOH; iv, H\(_2\)/Pd-C, EtOH

\[ \text{Me} \quad \text{H} \quad \text{SiMe}_3 \quad \text{Me} \quad \text{O} \quad \text{S} \quad \text{O} \quad \text{Me} \quad \text{H} \quad \text{SiMe}_3 \]

\[ 6 \quad 16 \quad 17 \]

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

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 (q), 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\(_2\)S 213.0948, Found : 213.0946.
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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