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NEW CYCLIC SULFUR YLIDES, 8-THIAAZULENES. SYNTHESIS AND THERMAL REARRANGEMENTS OF 8-ALKYL-1,3-DIPHENYLDIBENZO[e,h]-8-THIAAZULENES[1)]

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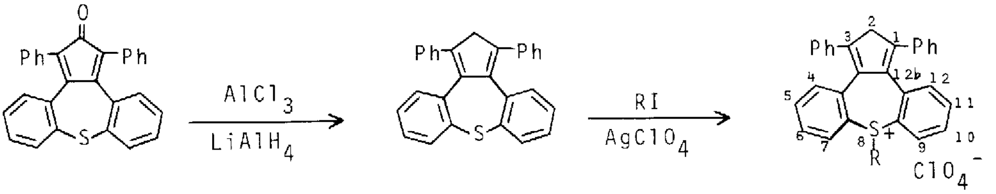
Summary: A new cyclic sulfur ylide, 1,3-diphenyl-8-methyldibenzo[e,h]-8-thiaazulene was synthesized. 8-Alkyl-1,3-diphenyldibenzo[e,h]-8-thiaazulenes were thermally rearranged to give 1,2-rearranged products and 1,4-rearranged products.

In the course of our studies on thiaazulenylium salts,[2)] we have reported cycloaddition reactions of thiaazulenecyclone.[3)] We now wish to report on the synthesis and the rearrangement of new cyclic sulfur ylides, 8-alkyl-1,3-diphenyldibenzo[e,h]-8-thiaazulene derivatives (4a - 4c), which were stabilized by the negatively charged cyclopentadienide moiety.

1,3-Diphenyl-2,8-dihydrodibenzo[e,h]-8-thiaazulene (2), mp 203 - 204°C was obtained by the reduction of thiaazulenecyclone (1)[3)] with $LiAlH_4$-$AlCl_3$ in 36% yield. The structure could be assigned by the NMR spectrum [AB q at δ 3.92, J=24 Hz, $\Delta\nu$=61 Hz, C_2-CH_2 in $CDCl_3$] and the IR spectrum [no CO absorption at 1710 cm^{-1} (KBr disc)]. Thiaazulenium salts (3a - 3c) were readily prepared from 2 with alkyl iodides and $AgClO_4$ in CH_2Cl_2 at room temperature. The NMR data of 3a - 3c are shown in Table I. The S^+-CH_3 signals of 3a at δ 3.70 and 3.83 in the ratio of 1:3 showed that 3a was a mixture of two isomers arising from the pyramidal inversion. However, the configuration of S^+-CH_3 moiety could not be determined. The other sulfonium salts (3b and 3c) had no isomers.

Deprotonation of 3a with NaH in dry THF under N_2 at room temperature yielded 1,3-diphenyl-8-methyldibenzo[e,h]-8-thiaazulene (4a), which is the first example of a stable ylide in the thiaazulene system, as orange plates, mp 135°C in 88% yield: NMR ($CDCl_3$) δ 3.10 (3H, s, S^+-CH_3)



1

2

3a: R=CH_3
b: R=C_2H_5
c: R=n-C_3H_7

Table I. Yields, Melting Points, and NMR Data of 3a - 3c

Compd.	Yield (%)	mp (°C)	N M R (CF_3CO_2H) δ :
3a	87	169-170	3.70, 3.83 (3H, s, S-CH_3), 4.22 (2H, ABq, J=24 Hz, $\Delta\nu$=61 Hz, C_2-H), 7.10-8.20(18H, m, ArH)*
3b	79	216	1.70 (3H, t, J=7.5 Hz, CH_2-CH_3), 4.19 (2H, ABq, J=24 Hz, $\Delta\nu$=63 Hz, C_2-H), 4.32 (2H, q, J=7.5 Hz, CH_2CH_3), 7.10-8.10 (18H, m, ArH)
3c	50	214	1.24 (3H, t, J=7 Hz, CH_3), 2.09 (2H, sex, J=7 Hz, CH_2-CH_2-CH_3), 4.20 (2H, ABq, J=24 Hz, $\Delta\nu$=67 Hz, C_2-H), 4.28 (2H, J=7 Hz, S-CH_2), 7.10-8.15 (18H, m, ArH)

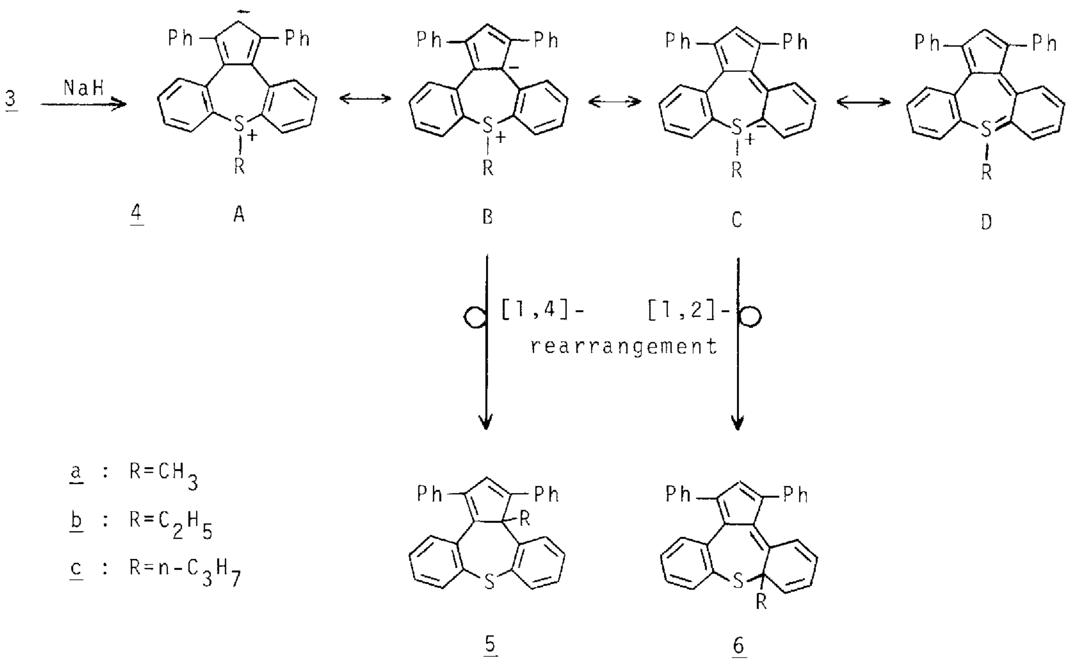
* The ratio of the stereoisomers having the methyl signals at δ 3.70 and 3.83 was 1:3.

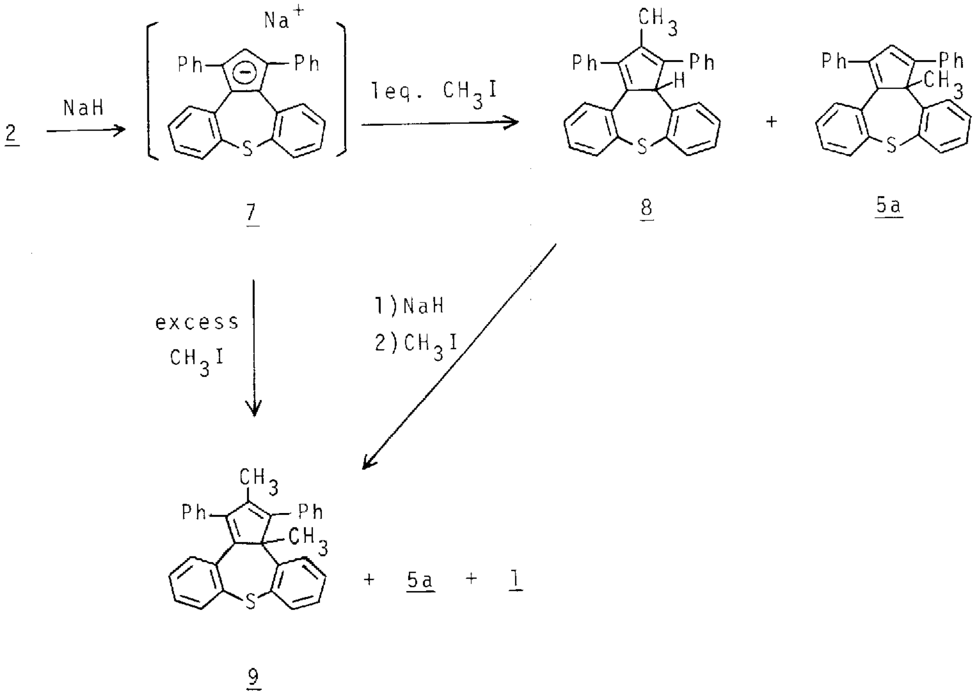
6.57 (1H, s, C_2-H), 6.60 - 7.69 (18H, m, ArH) and (DMSO-d_6) δ 3.30 (3H, s, S^+-CH_3), 6.18 (1H, s, C_2-H), 6.76 - 8.00 (18H, m, ArH). The chemical shift (δ 6.57 in $CDCl_3$) of the cyclopentadiene ring proton is in fair agreement with that (δ 6.20) of dimethylsulfonium cyclopentadienylide[4] and the signal (δ 6.18 in DMSO-d_6) of C_2-H was shifted to the downfield by 0.45 ppm compared to that (δ 5.73) of 1,3-diphenyldibenzo[e,h]-8-thiaazulenide anion (7). This NMR spectral evidence shows that the fulvene structures, C (1,2-ylide) and D (ylene) as well as the canonical structures, A (1,6-ylide) and B (1,4-ylide) contribute to the ylide 4.

Refluxing the ylide 4a in THF gave 1,4-rearranged product 5a (64%, mp 176°C) and 2 (12%). However, 3b and 3c having bulkier group than the methyl group on a sulfur atom were treated with NaH and subsequently heated to give the 1,4-rearranged products, 5b (34%, mp 70 - 71°C) and 5c (14%, mp 60 - 63°C) and the 1,2-rearranged products, 6b (29%, mp 174°C) and 6c (47%, mp 136°C) together with 2 (4% from 3b and 10% from 3c), respectively. It is noteworthy that 6c is more than 5c. The 1,2-rearrangement increased with the bulkiness of the S-alkyl group.

To determine the structure of these rearranged products, 2 was alkylated with CH_3I to give 1,3-diphenyl-2-methyl-8,12b-dihydrodibenzo[e,h]-8-thiaazulene (8) (80.6%, mp 168 - 172°C) and 1,3-diphenyl-12b-methyl-8,12b-dihydrodibenzo[e,h]-8-thiaazulene (5a) (12.8%, mp 176°C), and with excess CH_3I to give 2,12b-dimethyl-1,3-diphenyl-8,12b-dihydrodibenzo[e,h]-8-thiaazulene (9) (62%, mp 195°C) together with 5a (4%) and 1 (3%). Compound 5a was identical with one of the rearranged products of 4a. The NMR data of 8 and 9 in $CDCl_3$ are: 8 δ 1.86 (3H, s, CH_3), 4.78 (1H, s, C_{12b}-H), 6.47 - 7.73 (18H, m, ArH) and 9 δ 1.53 (3H, s, C_{12b}-CH_3), 1.70 (3H, s, C_2-CH_3), 6.33 - 7.61 (18H, m, ArH).

In the NMR spectra, the 1,4-rearranged products (5) showed the singlets of C_2-H at δ 6.50 - 6.42, but the 1,2-rearranged products (6) exhibited the signals of C_2-H which were downfield-shifted to the aromatic region. The UV spectra of the 1,2-rearranged products (6b and 6c) exhibited an absorption at 280 nm assigned to the fulvene structure[5] as shown in Figure 1.


3
NaH
4
A
B
C
D
Ph
R
S
[1,4]-
[1,2]-
rearrangement
a : R=CH3
b : R=C2H5
c : R=n-C3H7
5
6


2
NaH
Na+
Ph
S
7
1eq. CH3I
CH3
H
8
+
5a
excess
CH3I
1)NaH
2)CH3I
9
+ 5a + 1

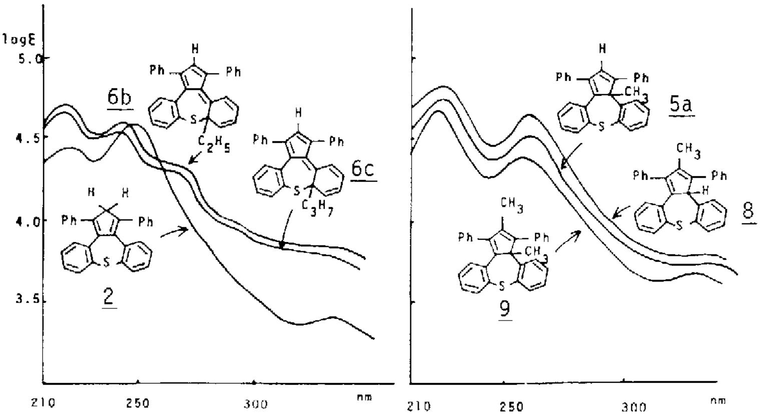


Figure 1. UV Spectra of 1,3-Diphenyldibenzo[e,h]-8-thiaazulenes in EtOH Solution

In our previous reports we described the 1,2- and 1,4-rearrangements of cyclic sulfur ylides.[6] Thermally, the 1,2-rearrangement proceeded via radical mechanism and the 1,4-rearrangement occurred via concerted mechanism. 10-Alkyl-9-duryl(or mesityl)-10-thiaanthracenes underwent exceptionally the radical 1,4-rearrangement.[7] Therefore, in this thiaazulene system the 1,2-rearrangement might proceed via radical pair mechanism and the 1,4-rearrangement might proceed via concerted mechanism.[8] The 1,2-rearrangement in the thiaazulene system is new and very interesting since the cyclopentadienide anion broke the benzenoid stabilization to make the fulvene structure (C) and then S-alkyl group caused the 1,2-migration. The formation of the 1,2-rearranged products elucidates that the canonical structure (C) makes the significant contribution to the structure of 4.

REFERENCES AND FOOTNOTES

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2) M. Hori, T. Kataoka, H. Shimizu, and S. Yoshimura, Yakugaku Zasshi, 94, 1429 (1974).
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4) Z. Yoshida, S. Yoneda, and M. Hazama, J. Org. Chem., 37, 1364 (1972).
5) 6,6-Dimethylfulvene exhibits a $\lambda_{max}^{isooctane}$ 265 nm (log ε 3.9). M. T. Murphy and A. C. Duggan, J. Amer. Chem. Soc., 71, 3347 (1949).
6) M. Hori, T. Kataoka, H. Shimizu, K. Narita, S. Ohno, and H. Aoki, Chemistry Letters, 1974, 1101; M. Hori, T. Kataoka, and H. Shimizu, ibid., 1974, 1117; M. Hori, T. Kataoka, H. Shimizu, S. Ohno, and K. Narita, Tetrahedron Letters, 1978, 251.
7) M. Hori, T. Kataoka, H. Shimizu, and S. Ohno, Tetrahedron Letters, 1978, 255.
8) The ESR signals were observed in the rearrangements. Details will be described elsewhere.

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