REACTIONS OF NEW CYCLIC SULFUR YLIDES, 8-THIAAZULENES WITH ELECTROPHILES[1)]

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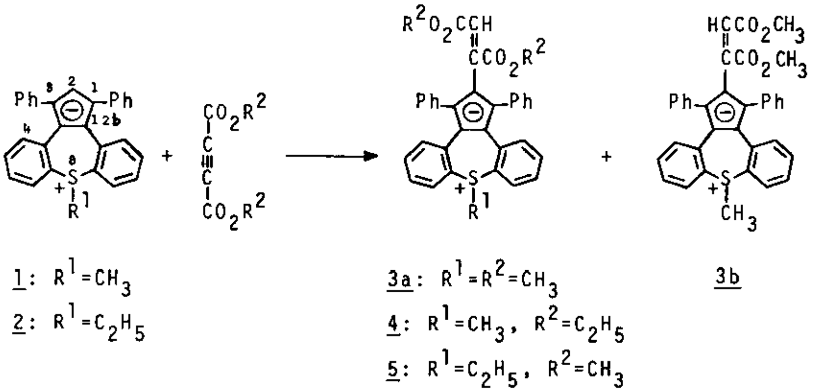
Abstract --- The reactions of 8-alkyl-1,3-diphenyldibenzo[e,h]-8-thiaazulenes with acetylenic electrophiles yielded the considerably stable ylides. The ylides newly formed were not rearranged on refluxing in THF for 1 hr, but caused the intramolecular 1,4-rearrangement at 170 - 200°C. The reaction of 8-methyl-1,3-diphenyldibenzo[e,h]-8-thiaazulene with diphenylcyclopropenethione formed a thiete derivative.

In the preceding paper, we described the synthesis and the rearrangement of the new cyclic sulfur ylides, 1,3-diphenyldibenzo[e,h]-8-thiaazulene derivatives.[2)] We wish to report here the reaction of the thiaazulene ylides with acetylenic electrophiles and the rearrangement of the resulting new ylides.

The ylides 1 and 2 were synthesized in situ from the corresponding sulfonium salts and NaH, and then allowed to react with dimethyl and diethyl acetylenedicarboxylates. The new stable ylides 3 - 6 were formed. Their yields, melting points and NMR data are shown in Table I. The reaction of 1 and dimethyl acetylenedicarboxylate (DMAD) yielded a trans ylide (3a) and a cis isomer (3b), and the other



1: $R^1=CH_3$
2: $R^1=C_2H_5$

3a: $R^1=R^2=CH_3$
4: $R^1=CH_3$, $R^2=C_2H_5$
5: $R^1=C_2H_5$, $R^2=CH_3$
6: $R^1=R^2=C_2H_5$

3b

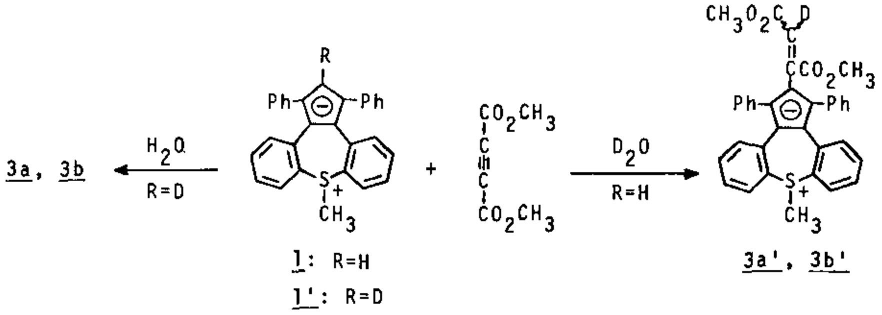
Table I. Yields, Melting Points and NMR Data of Thiaazulenes 3 - 6

Compounds	Yield (%)	mp (°C)	N M R ($CDCl_3$) δ :
3a	52	154-156	3.15 (3H, s, CO_2CH_3), 3.33 (3H, s, S-CH_3), 3.91 (3H, s, CO_2CH_3), 6.35 (1H, s, $C_{2'}$-H), 6.66-7.65 (18H, m, ArH)
3b	12	203	3.09 (3H, s, CO_2CH_3), 3.18 (3H, s, S-CH_3), 3.45 (3H, s, CO_2CH_3), 5.52 (1H, s, $C_{2'}$-H), 6.70-7.65 (18H, m, ArH)
4	70	135-137	0.88 (3H, t, J=7.5 Hz, $CH_2\underline{CH_3}$), 1.47 (3H, t, J=7.5 Hz, $CH_2\underline{CH_3}$), 3.30 (3H, s, S-CH_3), 3.57 (2H, q, J=7.5 Hz, CH_2CH_3), 4.36 (2H, q, J=7.5 Hz, $\underline{CH_2}CH_3$), 6.35 (1H, s, $C_{2'}$-H), 6.10-7.70 (18H, m, ArH)
5	74	153-155	1.32 (3H, t, J=7.5 Hz, CH_2CH_3), 3.16 (3H, s, CO_2CH_3), 3.90 (3H, s, CO_2CH_3), 4.03 (2H, q, J=7.5 Hz, $\underline{CH_2}CH_3$), 6.32 (1H, s, $C_{2'}$-H), 6.60-7.70 (18H, m, ArH)
6	71	116-118	0.91 (3H, t, J=7.5 Hz, $CO_2CH_2\underline{CH_3}$), 1.34 (3H, t, J=7.5 Hz, CO_2-$CH_2\underline{CH_3}$), 1.39 (3H, t, J=7.5 Hz, S-$CH_2\underline{CH_3}$), 3.61 (2H, q, J=7.5 Hz, $CO_2\underline{CH_2}CH_3$), 4.07 (2H, q, J=7.5 Hz, S-CH_2CH_3), 4.39 (2H, q, J=7.5 Hz, $CO_2\underline{CH_2}CH_3$), 6.36 (1H, s, $C_{2'}$-H), 6.70-7.70 (18H, m, ArH)

reactions produced only trans ylides. Steric hindrance prohibited the acetylenic compounds from the electrophilic attack on the C_{12b} position and the reactions occurred at the C_2 position.

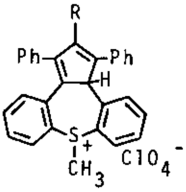
Their stereochemistry was determined by the NMR spectra. Since the vinyl proton signals of fumarates appear in the lower field than those of maleates,[3)] the C_2-H of the trans isomer shifts presumably more to the downfield. Thus 3a is the fumarate and 3b is the maleic product.

To obtain mechanistic information on the ylide formation the following reactions using deuterio compounds were examined further. The ylide 1 was allowed to react with DMAD in the presence of D_2O to form the $C_{2'}$-deuterio products, 3a' and 3b'. On the contrary, C_2-deuterio ylide (1') gave 3a and 3b in the presence of H_2O.



These findings showed that the reaction proceeded via the intermolecular protonation of $C_{2'}$-carbanion and deprotonation of C_2-H.

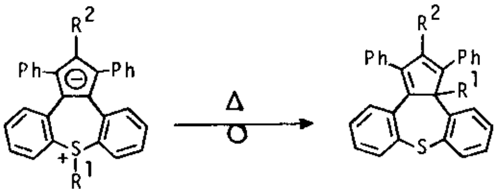
The ylides 3a and 3b were treated with perchloric acid to give the sulfonium salts (7a, mp 228°C and 7b, mp 201 - 202°C), respectively.



7a: R= CH_3O_2CCH $\|$ CCO_2CH_3

7b: R= $HCCO_2CH_3$ $\|$ CCO_2CH_3

The ylides 3 - 6 newly formed were considerably stable and were not rearranged on refluxing in THF for 1 hr. They were heated at 170 - 200°C for 3 - 5 min without solvent to give the 1,4-rearranged products. Reaction conditions and NMR data of the products are summarized in Table II.

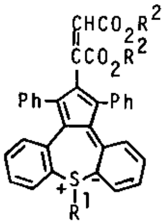


3 - 6 8 - 11

Table II. Reaction Conditions and Products of Rearrangement of Thiaazulenes 3 - 6

Ylides	Reaction Conditions	Compd No.	R^1	Rearranged Products R^2	NMR ($CDCl_3$) δ :
3a	200°C 3 min	8a	CH_3	$CH_3O_2C\text{-}C\text{-}H$ $\|$ $C\text{-}CO_2CH_3$	1.71 (3H, s, C_{12b}-CH_3), 3.52 (3H, s, CO_2CH_3), 3.60 (3H, s, CO_2CH_3), 6.79 (1H, s, $C_{2'}$-H), 6.60-7.55 (18H, m, ArH)
3b	210°C 5 min	8b	CH_3	$H\text{-}C\text{-}CO_2CH_3$ $\|$ $C\text{-}CO_2CH_3$	1.70 (3H, s, C_{12b}-CH_3), 3.22 (3H, s, CO_2CH_3), 3.59 (3H, s, CO_2CH_3), 5.74 (1H, s, $C_{2'}$-H), 6.58-7.60 (18H, m, ArH)
4	170°C 5 min	9	CH_3	$C_2H_5O_2C\text{-}C\text{-}H$ $\|$ $C\text{-}CO_2C_2H_5$	1.09 (6H, t, J=7 Hz, CH_2CH_3), 1.70 (3H, s, C_{12b}-CH_3), 3.95 (2H, q, J=7 Hz, CH_2CH_3), 4.05 (2H, q, J=7 Hz, CH_2CH_3), 6.82 (1H, s, $C_{2'}$-H), 6.50-7.65 (18H, m, ArH)
5	170°C 5 min	10	C_2H_5	$CH_3O_2C\text{-}C\text{-}H$ $\|$ $C\text{-}CO_2CH_3$	0.53 (3H, t, J=7 Hz, CH_2CH_3), 2.20 (2H, q, J=7 Hz, CH_2CH_3), 3.53 (3H, s, CO_2CH_3), 3.59 (3H, s, CO_2CH_3), 6.76 (1H, s, $C_{2'}$-H), 6.50-7.70 (18H, m, ArH)
6	170°C 5 min	11	C_2H_5	$C_2H_5O_2C\text{-}C\text{-}H$ $\|$ $C\text{-}CO_2C_2H_5$	0.52 (3H, t, J=7 Hz, C_{12b}-CH_2CH_3), 1.10 (6H, t, J=7 Hz, $CO_2CH_2CH_3$), 2.18 (2H, q, J=7 Hz, C_{12b}-CH_2CH_3), 3.99 (2H, q, J=7 Hz, $CO_2CH_2CH_3$), 4.05 (2H, q, J=7 Hz, $CO_2CH_2CH_3$), 6.90 (1H, s, $C_{2'}$-H), 6.80-7.70 (18H, m, ArH)

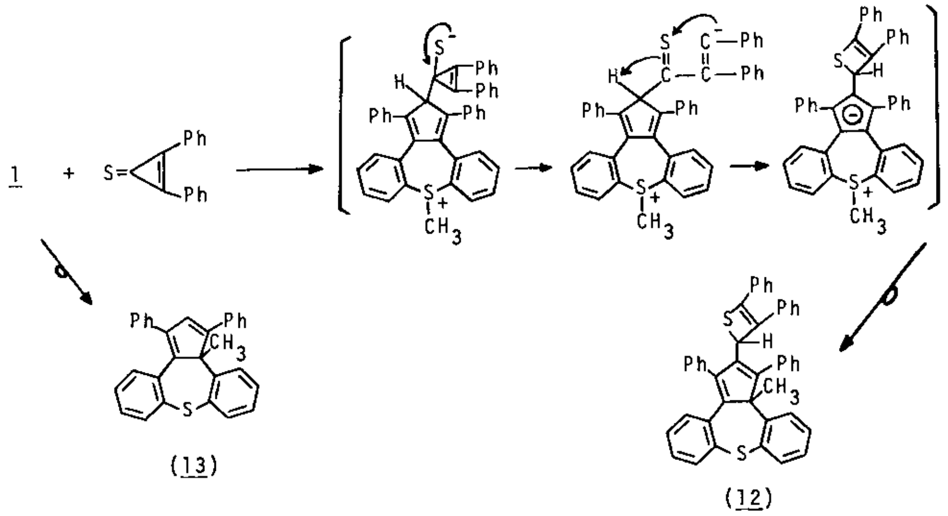
The ylides 3 - 5 quantitatively gave the 1,4-rearranged products 8 - 10, respectively, but 6 yielded the 1,4-rearranged product (11, 25%) together with a mixture of two other products. This result is different from the fact that thiaazulenes without substituent at the C_2 position underwent both the 1,2- and 1,4-rearrangements.2) Electron-withdrawing effect of the fumarate or maleate moiety attracts the electrons towards the substituent and consequently decreased the distribution of the negative charge to the condenced benzene ring i.e. the 1,2-ylidic contribution (A).



(A)

To clarify the mechanism of the thermal rearrangement, a crossover experiment was carried out. The ylides 4 and 5 were mixed well and melted at 170°C. The product was inspected by mass spectrometry and NMR spectroscopy, but it did not contain the crossover products. Consequently, this 1,4-rearrangement proceeded via intramolecular concerted mechanism.

The ylide 1 was allowed to react with diphenylcyclopropenethione at room temperature for 5 days to give 12b-methyl-1,3-diphenyl-2-(2,3-diphenyl-2-thieten-4-yl)-8,12b-dihydrodibenzo[e,h]-8-thiaazulene (12, 8%), mp 182°C as yellow needles together with 1,3-diphenyl-12b-methyl-8,12b-dihydrodibenzo[e,h]-8-thiaazulene (13, 26%).2) The NMR data of 12 are: (CDCl$_3$) δ: 1.55 (3H, s, CH$_3$), 4.30 (1H, s, CH) and 6.40 - 7.70 (28H, m, ArH). The formation of 12 is presumed to proceed through the intermediates shown below.



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