

SYNTHESIS AND CYCLOADDITION REACTIONS OF 1,3-DIPHENYL-2,8-DIHYDRO-DIBENZO[e,h]-8-THIAAZULEN-2-ONE (THIAAZULENOCYCLONE) WITH ACETYLENES, OLEFINS AND BENZYNE<sup>1)</sup>

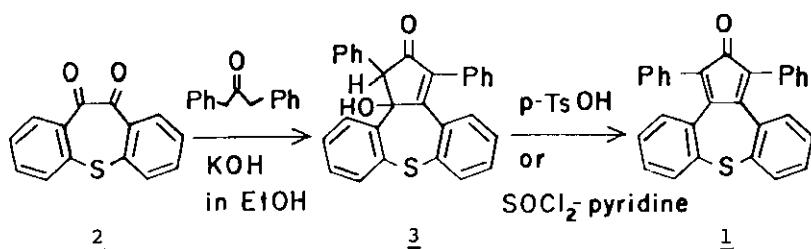
Mikio Hori,\* Tadashi Kataoka, Hiroshi Shimizu, and Mitsuhiro Okitsu  
Gifu College of Pharmacy, 5-6-1 Mitahora-higashi, Gifu 502, Japan

Abstract --- Thiaazulenocyclone was synthesized and its reactions with dienophiles were investigated. Reactions with N-phenylmaleimide, acenaphthylene or norbornene formed the Diels-Alder adducts, but cycloadditions with other dienophiles yielded the decarbonylated products derived from [4+2] adducts.

Some interesting reports on the Diels-Alder reactions of cyclopentadienone and phencyclone<sup>2,3)</sup> prompted us to examine the reaction of 1,3-diphenyl-2,8-dihydro-dibenzo[e,h]-8-thiaazulen-2-one (thiaazulenocyclone)<sup>4)</sup> with dienophiles. We found the new results from the reactions of thiaazulenocyclone derivatives and some nucleophiles. In this communication, we wish to report the synthesis and the cycloaddition reactions of thiaazulenocyclone with acetylenic compounds, electron-deficient olefins, electron-rich olefins and benzyne.

Synthesis of Thiaazulenocyclone (1)

10,11-Dihydrodibenzo[b,f]thiepin-10,11-dione (2)<sup>5)</sup> reacted with dibenzyl ketone in the presence of KOH to give 1,3-diphenyl-1,2,8-trihydro-12b-hydroxydibenzo[e,h]-8-thiaazulen-2-one (3), mp 258°C in 64% yield. Treatment of 3 with p-toluenesulfonic acid or thionyl chloride-pyridine yielded 1 in 27% or 65% yield, respec-



tively. 1: violet needles, mp 246°C. IR (KBr)  $\text{cm}^{-1}$ : 1710 (CO). NMR ( $\text{CDCl}_3$ )  $\delta$ : 7.05 - 7.88 (18H, m, ArH).

#### Cycloaddition Reactions with Acetylenes

Reactions of 1 with acetylenic dienophiles are summarized in Table I.

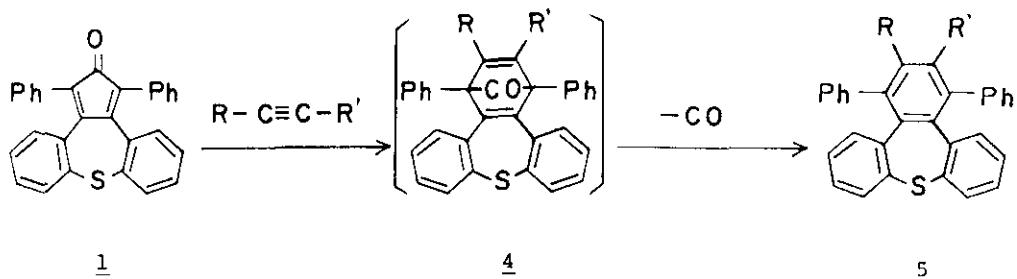


Table I. Reactions of Thiaazulenocyclone (1) and Acetylenes

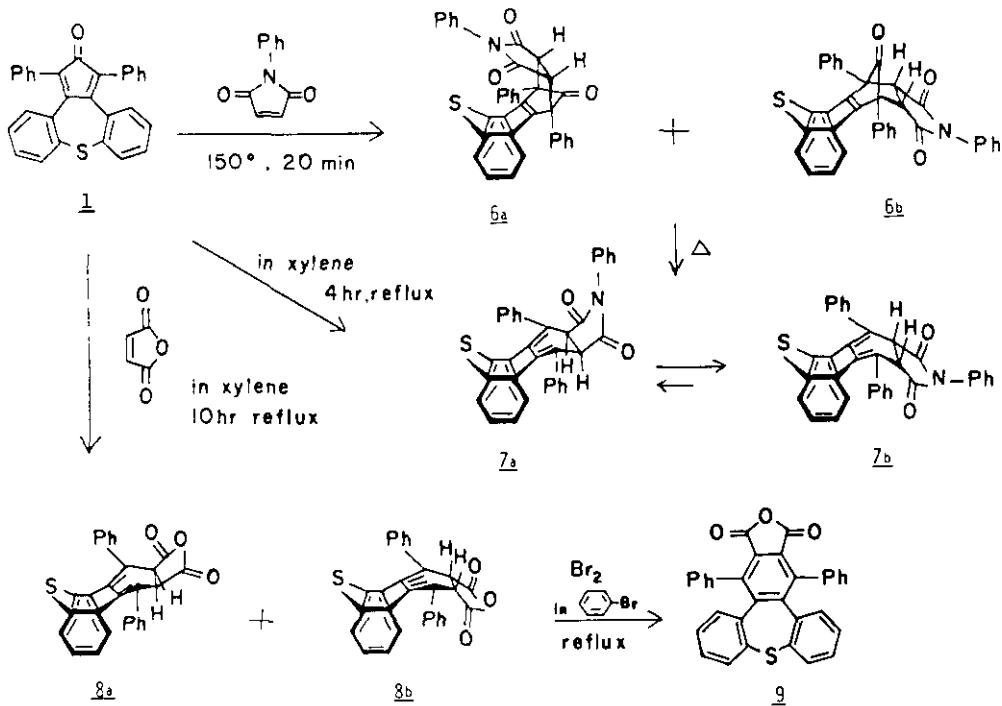
$\text{R}-\text{C}\equiv\text{C}-\text{R}'$		Reaction Conditions		Compd. No.	Products	
$\text{R}$	$\text{R}'$				Yield (%)	mp (°C)
Ph	Ph	200°C	2.5 hr	<u>5a</u>	77	>300
Ph	H	150°C	20 min	<u>5b</u>	70	290
$\text{CO}_2\text{CH}_3$	$\text{CO}_2\text{CH}_3$	reflux in xylene	2 hr	<u>5c</u>	88	245
$\text{CO}_2\text{CH}_3$	H	reflux in xylene	2 hr	<u>5d</u>	76	220

Each reaction proceeded via [4+2] cycloaddition of the cyclopentadienone moiety and acetylenic bond followed by decarbonylation from the adduct 4. Aromatization to tribenzo[*b,d,f*]thiepins (5) accelerates the extrusion of a carbonyl group from the intermediate 4.

#### Cycloaddition Reactions with Electron-Deficient Olefins

A reaction of 1 with N-phenylmaleimide at 150°C for 20 min gave a mixture of endo [4+2] adducts 6 in 73% yield. 6: colorless prisms, mp 218 - 219°C. IR (KBr)  $\text{cm}^{-1}$ : 1800, 1720 (CO). NMR ( $\text{CDCl}_3$ )  $\delta$ : 4.38 (s, methine H of 6b), 4.57 (s, methine H of 6a), 6.85 - 7.92 (23H, m, ArH). The ratio of 6a/6b was 9 on the basis of the intensity of the NMR signals at  $\delta$  4.57 and 4.38. When 6 was refluxed in xylene for 4 hr, a mixture of the decarbonylated products 7 was quantitatively obtained. Compound 7 was also formed directly in 88% yield by refluxing 1 and N-phenyl-

maleimide in xylene for 4.5 hr. 7: colorless prisms, mp 280 - 283°C. IR (KBr)  $\text{cm}^{-1}$ : 1780, 1720 (CONH). NMR ( $\text{CDCl}_3$ )  $\delta$ : 4.31 (s, methine H of 7b), 4.70 (s, methine H of 7a), 6.60 - 7.65 (23H, m, ArH). The NMR spectrum measurement of 7 showed that a main product 7a changed into 7b at room temperature and that they reached equilibrium in the ratio of 1:1.



Thiaazulenocyclone 1 reacted with maleic anhydride in refluxing xylene for 10 hr to give a mixture of the Diels-Alder adducts 8. 8: colorless needles, mp 292 - 295°C. IR (KBr)  $\text{cm}^{-1}$ : 1860, 1785 (CO). NMR ( $\text{DMSO}-d_6$ )  $\delta$ : 4.75 (s, methine H of 8b), 5.23 (s, methine H of 8a), 6.50 - 7.80 (18H, m, ArH). The product ratio (8a/8b = 7/3) was determined by the intensity of the NMR signals at  $\delta$  5.23 and 4.75. Compound 8 was treated with bromine in refluxing bromobenzene to give tribenzol[b,d,f]thiepin derivative 9. This finding suggested that 8a and 8b were stereoisomers.

The structures of the compounds 6 - 8 were determined by comparing their NMR data with those of the products which were formed by the reactions of phenacyclone or azulenocyclone and dienophiles.<sup>3)</sup>

Some other electron-deficient olefins such as p-benzoquinone, 1,4-naphthoquinone,

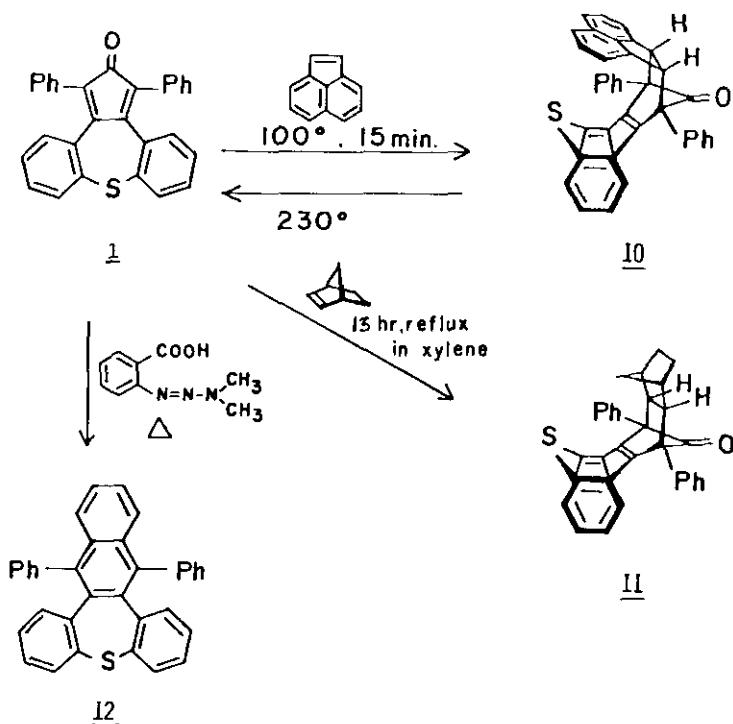
tetracyanoethylene and diphenylcyclopropenone did not react with 1.

#### Cycloaddition Reactions with Electron-Rich Olefins

Acenaphthylene reacted with 1 at 100°C for 5 min to form endo [4+2] adduct 10 in 88% yield. 10: colorless plates, mp 230°C (dec.). IR (KBr)  $\text{cm}^{-1}$ : 1775 (CO). NMR ( $\text{CDCl}_3$ )  $\delta$ : 4.80 (2H, s, methine H), 5.87 - 8.42 (24H, m, ArH). On heating above the melting point, 10 caused the retro Diels-Alder reaction to give 1 and acenaphthylene, quantitatively.

A solution of 1 and norbornene in xylene was refluxed for 13 hr to afford an adduct 11 in 79% yield. 11: colorless prisms, mp 227 - 280°C.

No cycloaddition products were obtained from other olefins such as cyclohexene and cycloheptatriene.



#### Cycloaddition Reaction with Benzyne

Thiaazulenocyclone 1 and 1-(2-carboxyphenyl)-3,3-dimethyltriazene<sup>6)</sup> as a benzyne source was refluxed in chlorobenzene for 6 hr to give 12 in 92% yield. 12: colorless needles, mp > 300°C. IR (KBr) no carbonyl absorption. NMR ( $\text{CDCl}_3$ )  $\delta$ : 6.29 - 8.32 (22H, m, ArH).

Discussion

Thiaazulenocyclone (1) was less reactive to olefinic dienophiles than phencyclone and to p-benzoquinone than azulenocyclone. The facts can be explained by reference to Sasaki's reports:<sup>3)</sup> The energy gap of LUMO (lowest unoccupied molecular orbital) and HOMO (highest occupied molecular orbital) of 1 would be larger than those of phencyclone and azulenocyclone. Therefore, interactions of 1-HOMO and electron-deficient olefin-LUMO, and 1-LUMO and electron-rich olefin-HOMO are weaker than those of phencyclone or azulenocyclone.

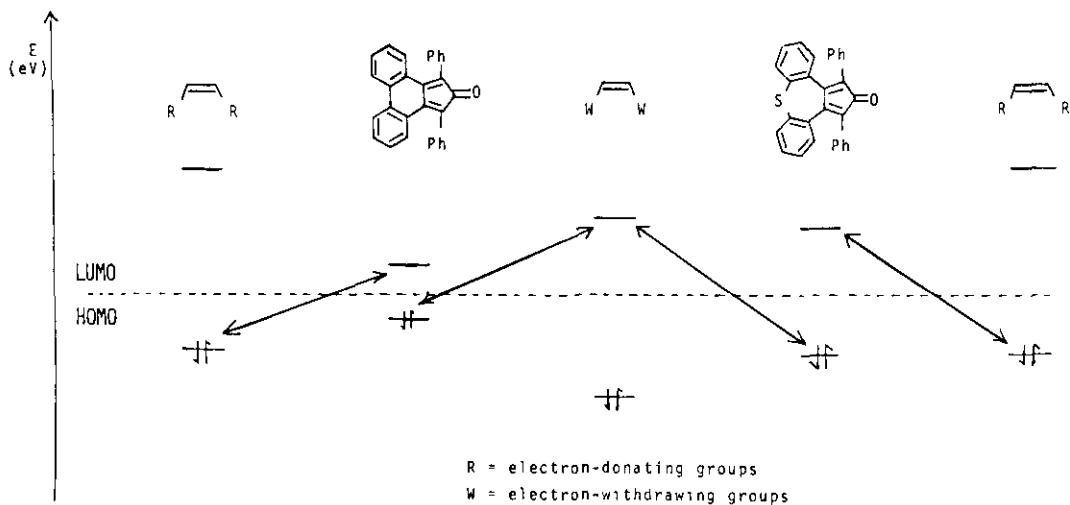


Fig. 1. Frontier Orbital Interactions for Cyclopentadienones and Olefins

Compound 1 reacted with acetylenic compounds, electron-deficient olefins and benzyne to form the decarbonylated products and with electron-rich olefins to give the adducts which caused the retro Diels-Alder reaction. These experimental results were very different from the results that the [4+2] adduct of phencyclone and olefinic dienophiles were stable and did not undergo the decarbonylation and the retro Diels-Alder reaction.<sup>3)</sup> The adducts of phencyclone and dienophiles are stabilized by the phenanthrene moiety, but the adducts derived from 1 does not have such a stabilizing factor. Therefore the latter underwent the decarbonylation or the retrogressive reaction.

In order to account for the formation of stereospecific endo [4+2] isomers in the cycloaddition of 1 and electron deficient olefins, we considered that steric and dipole-dipole interactions controlled mainly the stereospecificity because of the nonplanar structure of 1. As shown in Fig. 2, endo approaches A and C are more

favorable than exo approaches B and D, and the most favorable approach is endo approach A.

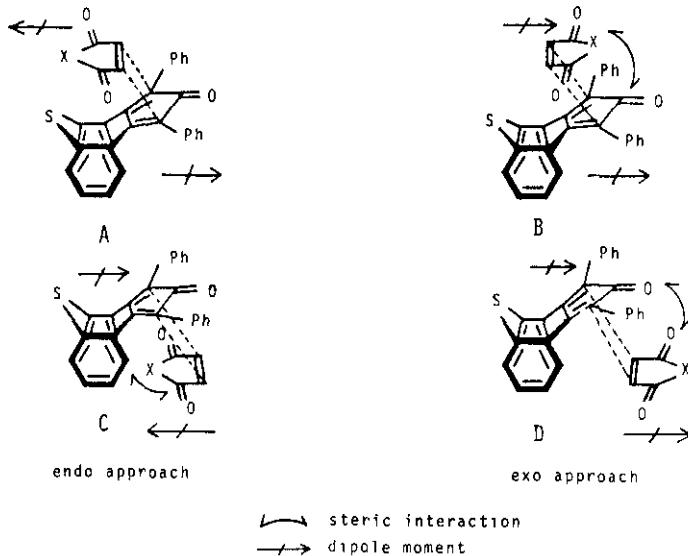


Fig. 2. Possible Approaches in Cycloaddition Reactions of Thiaazulenocyclone with Dienophiles

#### REFERENCES AND NOTES

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