

CYCLOADDITION REACTIONS OF 1,3-DIPHENYLTHIAZOLO[3,4-a]BENZIMIDAZOLE  
WITH FULVENE AND TROPONE SYSTEMS<sup>1)</sup>

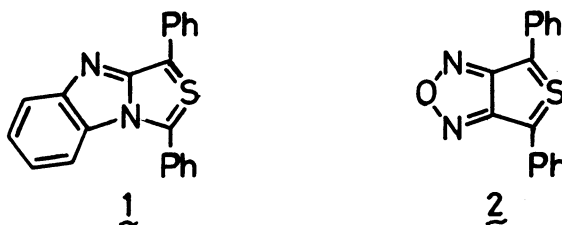
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1,3-Diphenylthiazolo[3,4-a]benzimidazole (1) containing tetravalent sulfur reacts as a thiocarbonyl ylide dipole with 6,6-diphenylfulvene to give a mixture of two regioisomeric exo-[4 + 2] adducts and endo-[4 + 2] adduct. The reaction of 1 with tropone and 8,8-dicyanoheptafulvene proceeds via a [4 + 2] cycloaddition to the C<sub>4</sub>-C<sub>5</sub> and C<sub>1</sub>-C<sub>2</sub> bond of the addend to afford the exo-adduct and desulfurized compound respectively.

Bicyclic 10 $\pi$ -electron heterocycles containing tetravalent sulfur form a group of compounds of considerable theoretical interest and potential practical utility.<sup>2)</sup> We have previously reported a new ring-fused tetravalent sulfur thiazole system, 1,3-diphenylthiazolo[3,4-a]benzimidazole (1), which is a reactive substrate behaving as a thiocarbonyl ylide dipole in cycloaddition reactions with olefinic and acetylenic dipolarophiles.<sup>3)</sup>

It has recently been recognized by several workers that the fulvene<sup>4-6)</sup> and tropone systems<sup>7-9)</sup> can function as either a 2 $\pi$ - or 6 $\pi$ -addend with several 1,3-dipoles. However, the investigation of cycloaddition reaction of thiocarbonyl ylide dipole with the fulvene and tropone systems has not been extended beyond our findings concerning 4,6-diphenylthieno[3,4-c][1,2,5]oxadiazole (2).<sup>10)</sup> Thus, it seemed of interest to compare the reactivity of 1 toward such systems with that of 2. In the present

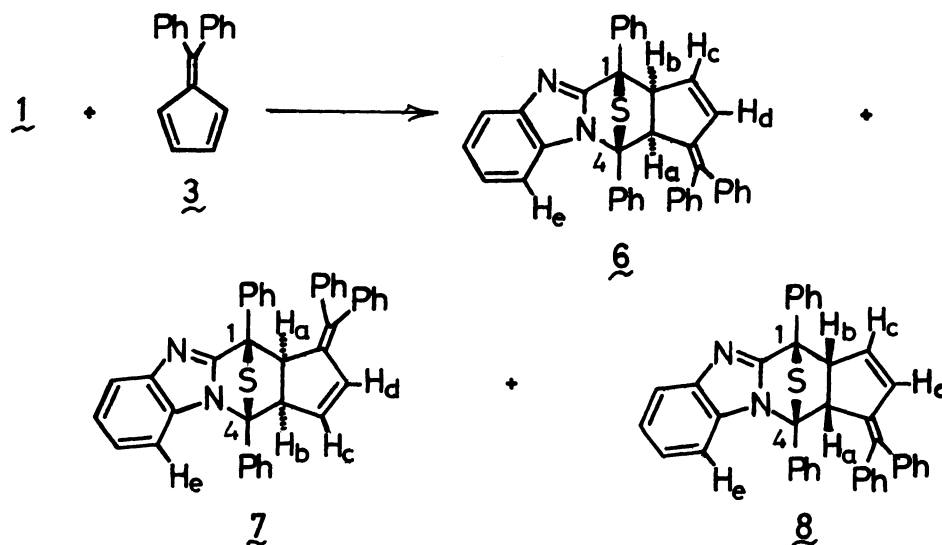


paper we wish to report the cycloaddition reactions of 1 with 6,6-diphenylfulvene (3), tropone (4), and 8,8-dicyanoheptafulvene (5).<sup>11)</sup>

When a solution of equimolar amounts of 1 and 3 in toluene was refluxed, under nitrogen, for 10 h, three isomeric 1:1 adducts, 6, 7, and 8, were obtained in 29, 13, and 5% yields respectively, along with recovery of 3 (28%) (Scheme 1).

The spectral data (Table 1) exclude both [4 + 2] adducts to the exocyclic C=C bond of 3 and [6 + 4] adducts from possible structures for all adducts 6 — 8, and are compatible with [4 + 2] adducts to the C<sub>1</sub>-C<sub>2</sub> bond. On the basis of <sup>1</sup>H NMR spectral data, 6 and 7 were assigned as exo-adducts and 8 as endo-adduct. Thus, the protons H<sub>a</sub> and H<sub>b</sub> in 8 appear at lower fields than those in 6 and 7, because of the deshielding effect of the sulfur bridge. Analogous effects have been noted for other related exo-endo adducts pairs containing a sulfur bridge.<sup>2,10,12)</sup>

The regiochemistry of all adducts 6 — 8 were deduced on the basis of the chemical shift of aromatic proton H<sub>e</sub> in each adduct. An inspection of the Dreiding models indicated that the proton H<sub>e</sub> in



Scheme 1

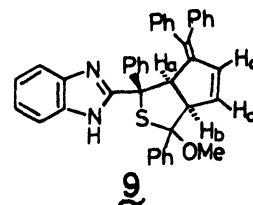
Table 1. Physical and Spectral Data of Adducts 6 — 8.

Adduct	Mp., °C	<sup>1</sup> H NMR(CDCl <sub>3</sub> ) δ (Hz)	M <sup>+</sup> m/e
<u>6</u>	245.5-247 (dec)	4.46(1H, ddd, H <sub>b</sub> , J=6.0, 2.5, 1.5), 4.64(1H, d, H <sub>a</sub> , J=6.0), 5.90-6.07(2H, m, H <sub>c</sub> + H <sub>e</sub> ), 6.38-6.50(2H, m), 6.67(1H, dd, H <sub>d</sub> , J=6.0, 1.5), 6.76-7.14(15H, m), 7.44-7.88(8H, m)	556
<u>7</u>	204-207 (dec)	4.52(1H, ddd, H <sub>b</sub> , J=6.0, 2.5, 1.5), 4.78(1H, d, H <sub>a</sub> , J=6.0), 5.62(1H, dd, H <sub>c</sub> , J=6.0, 2.5), 6.53(1H, dd, H <sub>d</sub> , J=6.0, 1.5), 6.62-6.74(2H, m), 6.84-7.76(22H, m)	556
<u>8</u> <sup>a</sup>	185-186	5.13(1H, dd, H <sub>b</sub> , J=7.0, 1.0), 5.47(1H, d, H <sub>a</sub> , J=7.0), 5.58 (2H, s, H <sub>c</sub> + H <sub>d</sub> ), 6.16(1H, ddd, H <sub>e</sub> , J=8.0, 1.5, 1.0), 6.64- 7.19(15H, m), 7.42-7.40(3H, m), 7.70-7.90(5H, m)	556

<sup>a</sup><sup>1</sup>H NMR(C<sub>6</sub>D<sub>6</sub>) δ 4.87(1H, ddd, H<sub>b</sub>, J=7.0, 2.0, 1.0), 5.34(1H, dd, H<sub>c</sub>, J=6.0, 1.0), 5.41(1H, d, H<sub>a</sub>, J=7.0), 5.61(1H, dd, H<sub>d</sub>, J=6.0, 1.0). <sup>13</sup>C NMR(CDCl<sub>3</sub>) δ 58.82, 63.06(tert. C), 69.68, 82.84 (quat. C), 159.45(C=N).

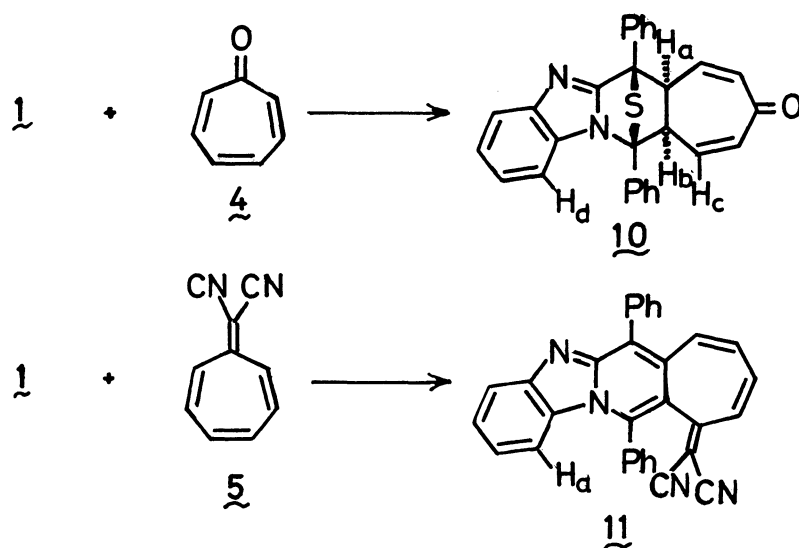
6 and 8 is affected by stronger shielding effect of the 4-phenyl group than that in 7. In fact, the proton H<sub>e</sub> in 6 and 8 appears at higher field than that in 7.

In addition, the following chemical behaviour supports the assigned structures. When a solution of 7 in methanol was refluxed for 20 min, 7 was readily converted into the ring-opening compound 9.<sup>13)</sup> However, 6 and 8 were unchanged even in refluxing methanol for 2 h; the methanolysis would be inhibited owing to their crowded structures.



Next, the reaction of 1 with 4 and 5 was investigated. In the reaction with 4 in refluxing benzene for 24 h, 1 afforded the 1:1 adduct 10 in 14% yield, together with an unidentified 1:1 adduct (10%) and recovery of 4 (67%). On the basis of spectral data,<sup>14)</sup> 10 was deduced to be the *exo*-[4 + 2] adduct to the C<sub>4</sub>-C<sub>5</sub> bond of 4, in contrast to the formation of [4 + 6] adduct from 2 and 4.<sup>10)</sup>

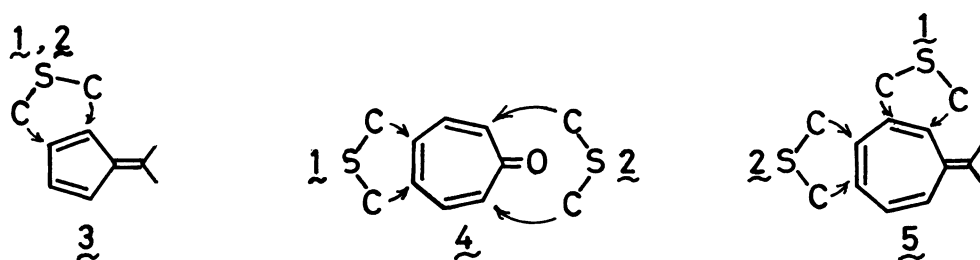
On the other hand, 1 reacted with 5 in refluxing benzene for 21 h to give the desulfurized com-



Scheme 2

compound 11 in 23% yield, along with recovery of 5 (72%). On the basis of spectral data,<sup>15)</sup> 11 was assigned as the pyridobenzimidazole derivative arising from the desulfurization of a [4 + 2] adduct to the C<sub>1</sub>-C<sub>2</sub> bond of 5. This cycloaddition process is also different from that of 2 to 5 giving the desulfurized compound derived from a [4 + 2] adduct to the C<sub>3</sub>-C<sub>4</sub> bond of 5.<sup>16)</sup>

We have summarized the periselectivity results found in the present and previous<sup>10)</sup> works as shown in Scheme 3. It seems reasonable to assume that 1 and 2-LUMO-3-HOMO, 1-LUMO-4-HOMO, 2-HOMO-4-LUMO,



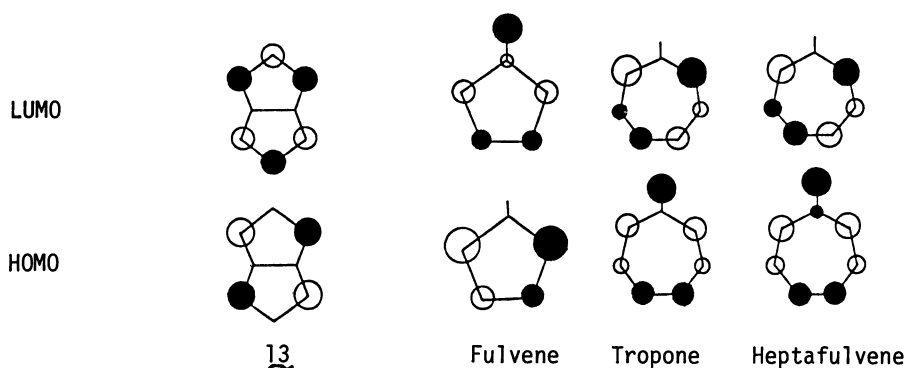
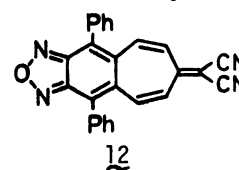
Scheme 3

1-HOMO-5-LUMO, and 2-LUMO-5-HOMO interactions predominate in these reactions.<sup>17)</sup>

#### References and Notes

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- 13) **9**: mp 148–150°C; IR(KBr) 3400  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR( $\text{CDCl}_3$ )  $\delta$  3.47(3H, s), 4.74(1H, d,  $H_a$ ,  $J=5.0$  Hz), 5.32–5.54(2H, m,  $H_b + H_c$ ), 6.11(1H, dd,  $H_d$ ,  $J=5.5, 2.5$  Hz), 6.48–6.60, 6.76–6.88(each 2H, m), 7.00–7.36(18H, m), 7.48–7.60(2H, m), 9.20–9.40(1H, broad, NH); MS  $m/e$  588( $M^+$ ).
- 14) **10**: mp 137–138°C(dec); IR(KBr) 1710  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR( $\text{CDCl}_3$ )  $\delta$  4.10(1H, ddd,  $H_a$ ,  $J=7.0, 2.0, 1.0$  Hz), 4.57(1H, ddd,  $H_b$ ,  $J=7.0, 2.0, 2.0$  Hz), 5.56(1H, m,  $H_c$ ), 6.08–6.20(4H, m,  $=\text{CH} + H_d$ ), 6.87, 7.08(each 1H, ddd,  $J=7.5, 7.5, 1.5$  Hz), 7.40–8.00(11H, m); MS  $m/e$  432( $M^+$ ).
- 15) **11**: mp 232–235°C; IR(KBr) 2200  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR( $\text{CDCl}_3$ )  $\delta$  5.88(1H, ddd,  $H_a$ ,  $J=8.5, 1.0, 1.0$  Hz), 6.57–7.96(17H, m,  $=\text{CH} + \text{ArH}$ ); MS  $m/e$  446( $M^+$ ).
- 16) The reaction of **2** with **5** in refluxing benzene for 48 h afforded the desulfurized compound **12** in 23% yield, along with recovery of **5** (75%). **12**: mp > 300°C; IR(KBr) 2220  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR( $\text{CDCl}_3$ )  $\delta$  6.91, 7.38(each 2H, AA'BB' spin system), 7.40–7.70(10H, m); MS  $m/e$  398( $M^+$ ).
- 17) The HOMO and LUMO coefficients of thieno[3,4-c]thiophene **13**<sup>18)</sup>, fulvene<sup>19)</sup>, tropone<sup>19)</sup>, and heptafulvene systems<sup>19)</sup> are as follows. We assumed that the



HOMO and LUMO coefficients of **1** and **2** are similar to those of **13**.

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