THE CYCLOADDITION REACTION OF 4,6-DIPHENYLTHIENO[3,4-c][1,2,5]OXADIAZOLE WITH NORBORNENE[1]

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Abstract —— 4,6-Diphenylthieno[3,4-c][1,2,5]oxadiazole containing tetravalent sulfur reacted with norbornene to give four stereoisomeric 1:2 adducts, isoxazolinyltetrahydrothiophene derivatives. The reaction proceeds via initial formation of both the endo-exo and exo-exo cycloadducts across the thiocarbonyl ylide dipole. Subsequent ring cleavage of the oxadiazole ring of initial strained cycloadducts generates the nitrile oxide intermediates capable of undergoing cycloaddition to norbornene to afford the 1:2 adducts.

Since tetraphenylthieno[3,4-c]thiophene was first prepared as an isolable nonclassical condensed thiophene[2], syntheses of several stable, nonclassical 10π-electron condensed thiophenes have been reported. These compounds containing tetravalent sulfur are of considerable practical and theoretical interest[3]. Previously, we have reported on the preparation of 4,6-diphenylthieno[3,4-c]-[1,2,5]oxadiazole (1) containing tetravalent sulfur, and its cycloaddition to simple olefins leading to strained oxadiazoles of the thianorbornane system[4]. It has also been found that both the endo- and exo-cycloadducts obtained from 1 and N-phenylmaleimide undergo thermal cleavage of the oxadiazole ring to nitrile and nitrile oxide moieties which can be captured as 1,3-cycloadducts by olefins and acetylenes[5,6].

In this regard, we have investigated the cycloaddition reaction of 1 with norbornene (2), expecting the formation of the highly strained cycloadduct(s), oxadiazole(s) of the highly strained thiatetracyclododecane ring system.

When 1 was allowed to react with an equimolar amount of 2 in refluxing benzene, under nitrogen, for 12 h, four products, 3, 4, 5, and 6, were obtained in low yields, together with recovery of 1. Although the structures of the products, 3 — 6, will be described below, the molecular formulas of all products agreed with that of a 1:2 adduct of 1 to 2. Even when excess of 1 was employed, no 1:1 adduct(s) were formed, whereas the reaction employing excess of 2 resulted in an increase in

yields of 3 — 6 (Table I).

Table I

1/2 mol/mol	Conditions	Yield, % 3	4	5	6	Recovery of 1, %
1/1	in refluxing benzene, 12 h	2	trace	2	trace	79
2/1	in refluxing benzene, 12 h	2	trace	4	trace	85
1/5	in refluxing toluene, 12 h	15	6	22	5	23

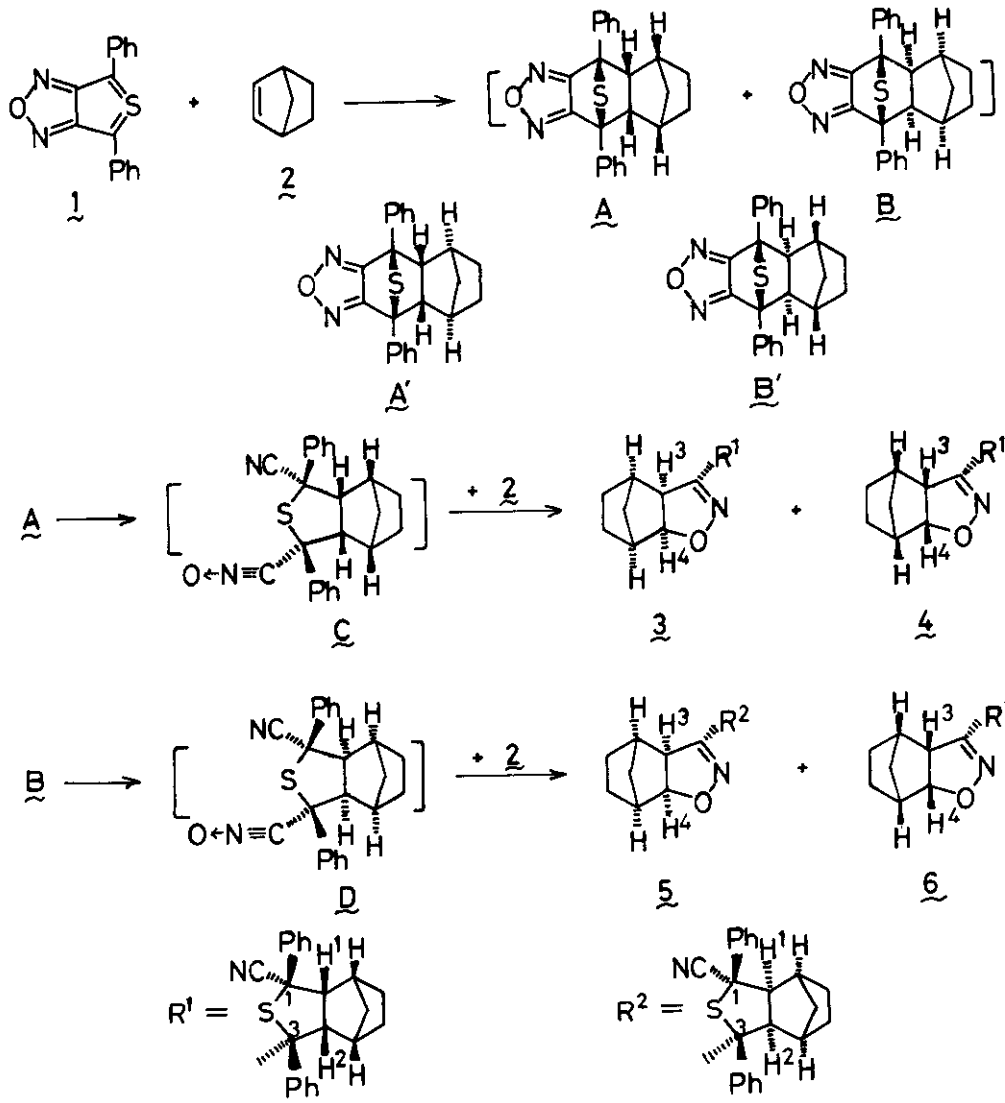
On the basis of spectral data (Table II) as well as the mode of formation, the 1:2 adducts, 3 — 6, were considered to be stereoisomeric isoxazoline derivatives arising from a 1,3-cycloaddition of 2 to nitrile oxide intermediates generated from initial 1:1 cycloadducts. The IR spectra of all 1:2 adducts showed a weak band ascribable to $\nu_{C\equiv N}$ absorption as observed in the 1:2 adducts of 1 to acetylenes[7].

Table II

Adduct[a]	Mp., °C	Appearance	$\nu_{C\equiv N}$[b] cm^{-1}	^1H NMR ($CDCl_3$), δ[c]	M^+ m/e
3	202-203	pale yellow needles	2220	2.84, 2.94 (each 1H, d, J=10.0 Hz, H^1, H^2), 3.60 (1H, d, J=8.0 Hz, H^3), 4.50 (1H, d, J=8.0 Hz, H^4)	466
4	290-291	colorless prisms	2220	2.80 (1H, d, J=8.0 Hz, H^3), 3.14 (2H, s, H^1, H^2), 4.56 (1H, d, J=8.0 Hz, H^4)	466
5	247-248	pale yellow needles	2220	3.03, 3.91 (each 1H, d, J=8.0 Hz, H^1, H^2), 3.81 (1H, d, J=8.0 Hz, H^3), 4.68 (1H, d, J=8.0 Hz, H^4)	466
6	245.5-246.5	pale yellow prisms	2220	2.40 (1H, d, J=8.0 Hz, H^3), 3.15, 3.76 (each 1H, d, J=8.0 Hz, H^1, H^2), 4.45 (1H, d, J=8.0 Hz, H^4)	466

[a]All adducts gave satisfactory elemental analyses. [b]Measured in KBr disks. [c]Norbornane ring protons are as follows. 3: δ 0.7-1.7 (11H, m), 1.96 (1H, s), 2.1-2.5 (3H, m), 3.16 (1H, s). 4: δ 0.7-1.9 (12H, m), 2.32 (1H, s), 2.50 (1H, d, J=4.0 Hz), 2.70 (1H, s), 3.00 (1H, d, J=4.0 Hz). 5: δ 0.6-1.6 (14H, m), 2.12 (1H, d, J=10.0 Hz), 2.48 (1H, d, J=4.0 Hz). 6: δ 0.5-1.6 (12H, m), 1.90, 2.13 (each 1H, d, J=10.0 Hz), 2.58, 2.90 (each 1H, J=4.0 Hz).

Baed on the similarlities of ^1H NMR spectral data with the reported 1:1 adducts, 7 — 10[6], which were obtained from the reaction of olefins with the endo- and exo-cycloadducts of 1 to N-phneyl-maleimide, configurations of the tetrahydrothiophene and isoxazoline moieties in 3 — 6 were as-



Scheme 1

signed as shown in Scheme 1. The methine proton H^3 in 4 or 6 appeared at a higher field than that in 3 or 5, because of anisotropy effect of the respective phenyl group at the 3-position of tetrahydrothiophene ring. Similar phenomena were observed in the ^1H NMR spectra between 9 or 10 and 7 or 8. The differences of values in chemical shifts of methine protons, $\Delta\delta(H^1 \sim H^2)$ and $\Delta\delta(H^3 \sim H^4)$, in 3 — 10 are summarized in Table III. Thus, it is evident that configurations of the tetrahydrothiophene ring in 3 or 4 and 5 or 6 correspond to ϕ_1 in 7 and 9, and ϕ_2 in 8 and 10, whereas the isoxazoline rings in 3 or 5 and 4 or 6 have configurations similar to those in 9 or 10 and 7 or 8, respectively.

Table III

	3	4	5	6	7[6]	8[6]	9[6]	10[6]
$\Delta\delta(H^1 \sim H^2)$	0.1	0	0.88	0.61	0 — 0.41	0.69 — 0.78	0 — 0.29	0.52 — 0.64
$\Delta\delta(H^3 \sim H^4)$	0.9	1.76	0.87	2.05	0.74 — 1.14	0.84 — 0.89	1.26 — 1.56	1.53 — 1.90

It is well known that only exo-protons of bicycloheptane system couple with bridgehead protons, but endo-protons do not couple[8]. The protons, H^1, H^2 and H^3, H^4, in all adducts appeared as sharp signals respectively, indicating that all hydrogens H^1 — H^4 are located at the endo-positions in the respective bicyclohepane rings.

Based on the stereochemistry of 3 — 6, the reaction pathways are illustrated in Scheme 1. The reaction proceeds via favorable formation of two adducts, endo-exo A and exo-exo B, among possible four stereoisomers A, A', B, and B'. Subsequent ring cleavage of the oxadiazole ring of A or B generates the nitrile oxide intermediate C or D capable of undergoing cycloaddition to norbornene to give the final products 3 and 4 or 5 and 6, respectively.

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