HETEROCYCLES, Vol. 62, 2004, pp. 773 - 778
Received, 2nd July, 2001, Accepted, 8th August, 2003,

[2π + 2π] TYPE CYCLOADDITION REACTIONS OF NAPHTHO[*b*]-CYCLOPROPENE WITH TRITHIOCARBONYL COMPOUNDS TO FORM 1,3-DIHYDRONAPHTHO[2,3-*c*]THIOPHENE DERIVATIVES

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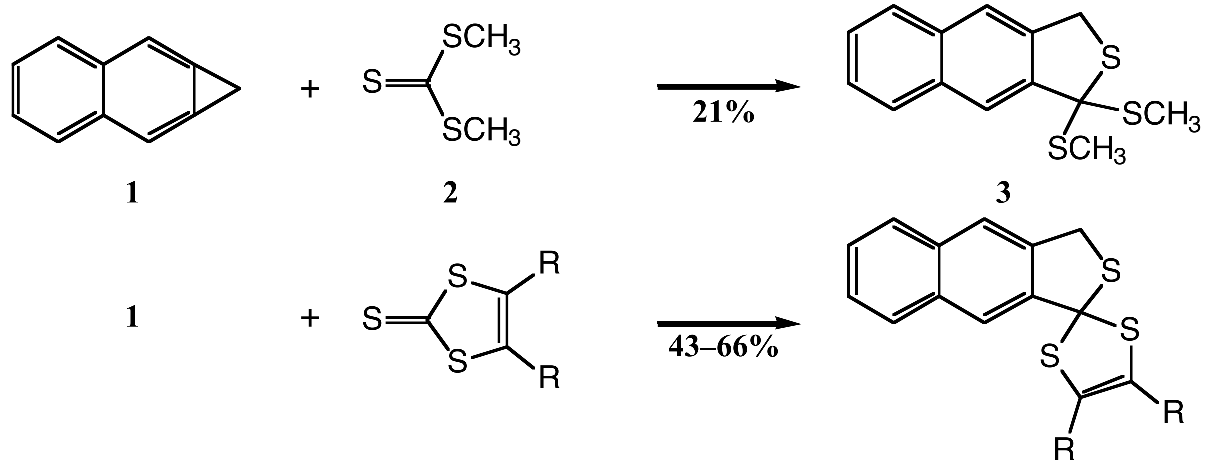
Abstract – Reactions of naphtho[*b*]cyclopropene with trithiocarbonyl derivatives in chloroform afforded 1,3-dihydrobenzo[2,3-*c*]thiophene derivatives in moderate yields through a [2π + 2π] type cycloaddition process. The similar reaction with a dithiocarbonate compound gave a recovery of the starting material. A reaction with thiotropone resulted in a [8π + 2π] type adduct in 5% yield. Solvent effects on the product yields revealed that the reactions proceeded *via* ionic intermediates.

Naphtho[*b*]cyclopropene (**1**) is a stable colorless crystalline material in spite of its large strain energy resulted from the distorted bond angles of the bridge-head sp^2 hybridized carbon atoms. However, it is known that compound **1** is highly reactive as a 2π component in cycloaddition reactions owing to the strained structure and a deficient aromaticity.[1] Recently, the carbenic behavior of **1** was also proposed.[2] The reactivities of cyclopropene derivatives attached to aromatic rings such as benzocyclopropene,[3] 5*H*-cycloprop[*f*]isobenzofuran,[4] or **1** have been researched. Recently, [4π + 2π] and [8π + 2π] types cycloadduct were obtained in reactions of **1** with nitrones and tropones, respectively.[5]

As a series of our research, reactions of **1** with trithiocarbonyl compounds were performed to give 1,3-dihydronaphtho[2,3-*c*]thiophene derivatives. We report here the results of the reactions.

Compound (**1**) and an equimolar amount of dimethyltrithiocarbonate (**2**) in chloroform were refluxed for 3 days. The reaction mixture was separated with column chromatography on silica gel to give a cycloaddition product (**3**) in 21% yield. The analogous reactions of compound (**1**) with 1,3-dithiol-2-thione (**4**) afforded **5** in moderate yields (**5a**: 43%, **5b**: 55%, **5c**: 66%, and **5d**: 63%). The structures of the products were deduced on the basis of their spectral properties. The molecular structures were ultimately determined by an X-ray structural analysis of **5b** as shown in Fig. 1.

As a □-electron system similar to **4**, thiotropone (**6**)[8] was also reacted with **1** to afford a [8□ + 2□] type cycloaddition product (**7**) in low yield (5%).



4a: R = H **4b**: R = SCH$_3$

4c: R = SCOPh **4d**: R-R = S(CH$_2$)$_2$S

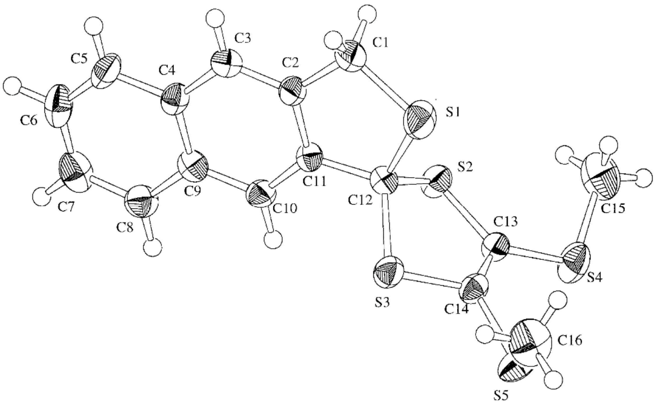
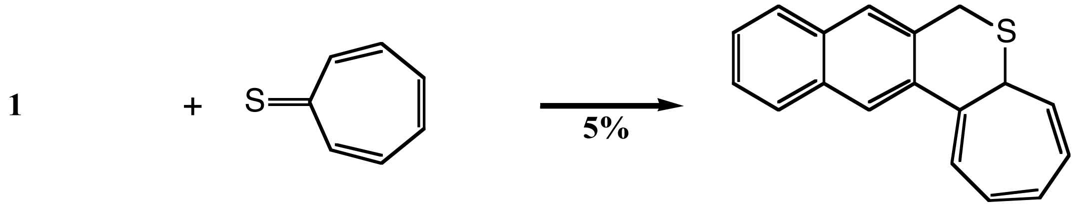


Figure 1. Molecular structure of **5b** (ORTEP).



6 **7**

The reactions of **1** with **4b** in several solvents were examined. The yields of **5b** in the reactions and the solvent parameters[7] are summarized in the following table. The cycloaddition reaction did not proceed in benzene.

Table. Reactions of **1** with **4b** in solvents and the solvent parameters

Solvent	Time (days)	Yield (%)	Relative Permitivity	Swain's Parameter
chloroform	2	43	4.81	1.15
tetrahydrofuran	3	32	7.58	0.84
ethyl acetate	3	21	6.02	0.79
benzene	3	0	2.28	0.73

The table shows that the polarity of the solvents increases the product yields. The electron densities on the carbon atoms of **1** are known to be high at the bridgehead carbon atoms as shown in Figure 2.[5]

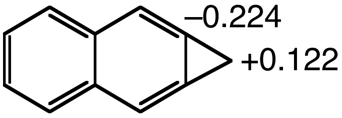
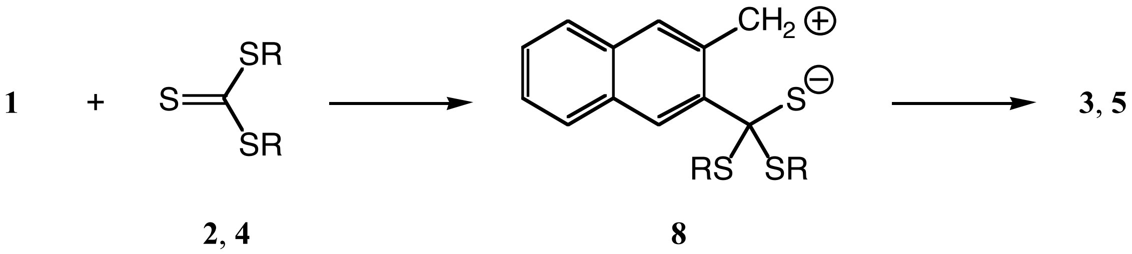
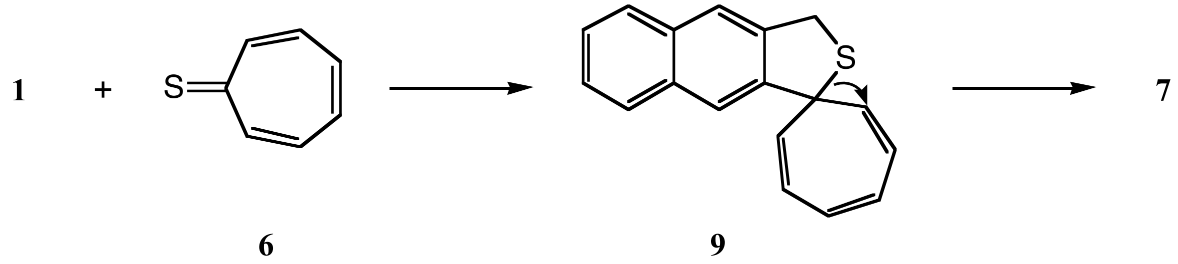


Figure 2. Electron densities of naphtho[*b*]cyclopropene (**1**).

These facts indicate that the reaction of **1** with **2** or **4** proceed through an ionic process as follows. An anionic carbon atom of **1** nucleophilicly attacks to the trithiocarbonyl carbon atom (**2**, **4**) to generate a zwittter ionic intermediate (**8**), which then cyclized to the final product (**3**, **5**).



The reaction of **1** with thiotropone (**6**) may proceed *via* a reaction path similar to those of **2** and **4**. Thus the initial product is supposed to be spiro-type intermediate (**9**), which subsequently isomerizes to the final product (**7**).[5]



EXPERIMENTAL

NMR, MS, and IR spectra were measured with Varian GEMINI 200/300, Hitachi 220A, and JASCO FT/IR-5300 spectrometers, respectively. On the separation of reaction mixture, Wakogel® C-200 (100–200 mesh; 75–150 μm) was used.

Typical reactions are mentioned below.

*Reaction of **1** with **2**.* A mixture of **1** (140 mg, 1 mmol) and **2** (138 mg, 1 mmol) in chloroform (15 mL) was refluxed for 3 days. The solvent was removed in vacuo. The resulted residue was separated with column chromatography on silica gel (eluent: 30 vol% benzene in *n*-hexane) to give **3** (88 mg, 21%).

3: ^{1}H NMR ($CDCl_3$) δ: 2.18 (s, 6H, Me), 4.37 (s, 2H, $–CH_2–$), 7.45–7.58 (m, 2H), 7.71 (s, 1H), 7.79–7.90 (m, 2H), 8.43 (s, 1H). ^{13}C NMR ($CDCl_3$) δ: 12.3, 30.6, 74.3 126.3, 127.4, 128.5, 132.4, 133.4, 137.3, 140.1. IR (KBr): 3056, 2913, 1659 cm^{-1}. MS *m*/*z* (rel. intensity): 278 (M$^+$, 100), 248, 184, 140.

*Reaction of **1** with **4**.* A mixture of **1** (140 mg, 1 mmol) and **4a–d** (1 mmol) in chloroform (15 mL) was refluxed for 3 days. The solvent was removed in vacuo. The resulted residue was separated with column chromatography on silica gel (eluent: 30 vol% benzene in *n*-hexane) to gave **5**.

5a: ^{1}H NMR ($CDCl_3$) δ: 4.47 (s, 2H, $–CH_2–$), 6.13 (s, 2H, CH), 7.45–7.55 (m, 2H), 7.72 (s, 1H), 7.78–7.95 (m, 2H), 8.42 (s, 1H). ^{13}C NMR ($CDCl_3$) δ: 37.2, 86.0, 123.1, 123.2, 126.2, 126.3, 127.3, 128.7, 128.9, 132.7, 133.5, 135.6, 140.1. IR (KBr): 3057, 1522 cm^{-1}. MS *m*/*z* (rel. intensity): 274 (M$^+$, 100), 184, 139.

5b: ^{1}H NMR ($CDCl_3$) δ: 2.46 (s, 6H, Me), 4.46 (s, 2H, $–CH_2–$), 7.49–7.51 (m, 2H), 7.71 (s, 1H), 7.79–7.90 (m, 2H), 8.40 (s, 1H). ^{13}C NMR ($CDCl_3$) δ: 19.4, 36.6, 83.2, 123.4, 124.2, 125.3, 126.4, 126.9, 127.1, 128.5, 132.4, 133.4, 137.3, 140.0. IR (KBr): 3052, 2912 cm^{-1}. MS *m*/*z* (rel. intensity): 366 (M$^+$, 96), 231, 184.0, 150. A crystal data: colorless plate, $C_{16}H_{14}S_5$, M = 366.59, triclinic, space group $P\bar{1}$(#2), a = 7.2598(8)Å, b = 7.791(1) Å, c = 16.714(4) Å, α = 80.07(4)°, β = 79.43(3)°, γ= 63.44(3)°, V = 826.8(3) Å^3, Z = 2, D_{calcd} = 1.472 g cm^{-3}, μ(Mo$K\alpha$) = 6.90 cm^{-1}, F_{000} = 380. A total of

3610 reflections for $2\theta_{max}$ = 55.0° was collected with $I > 2\sigma(I)$ using a Rigaku / MSC Mercury CCD diffractometer (Mo*K*α radiation, λ = 0.71070 Å) at 296 K. The structure was solved using direct method (SIR97) and refined by full-matrix least-squares analysis giving values of R = 0.109, R_w = 0.173, R_1 = 0.075, S = 1.48, $\Delta\rho_{max}$ / $\Delta\rho_{min}$ = 0.51 / –0.48 e Å^{-3}.

5c: ^{1}H NMR ($CDCl_3$) δ: 4.54 (s, 2H, $-CH_2-$), 7.46 (t, *J* = 7.4 Hz, 4H), 7.53 (dd, *J* = 6.2, 3.2 Hz, 2H), 7.60 (tt, *J* = 1.4, 7.4 Hz, 2H), 7.73 (s, 1H), 7.82 (dd, *J* = 5.9, 3.2 Hz, 1H), 7.97 (dd, *J* = 7.1, 1.4 Hz, 4H), 8.03 (dd, *J* = 5.8, 3.6 Hz, 1H), 8.86 (s, 1H). ^{13}C NMR ($CDCl_3$, 300 MHz) δ: 37.2, 86.3, 122.8, 123.1, 123.2, 126.2, 126.3, 126.3, 127.2, 127.4, 127.8, 128.8, 132.7, 133.5, 134.2, 135.6, 136.6, 140.9, 187.2. IR (KBr): 3400, 3055, 1684 cm^{-1}. MS *m*/*z* (rel. intensity): 546 (M$^+$, 1), 216, 184, 139.

5d: ^{1}H NMR ($CDCl_3$) δ: 3.30–3.43 (m, 4H, $-CH_2-$), 4.46 (s, 2H, $-CH_2-$), 7.46–7.55 (m, 2H), 7.71 (s, 1H), 7.78–7.83 (m, 1H), 7.86–7.91 (m, 1H), and 8.40 (s, 1H). ^{13}C NMR ($CDCl_3$) δ: 26.0, 30.7, 36.5, 111.7, 123.3, 123.5, 124.8, 126.3, 127.1, 128.4, 132.2, 133.4, 137.7, 113.8. IR (KBr): 3056, 1530 cm^{-1}. MS *m*/*z* (rel. intensity): 365 (M$^+$, 100), 224, 139.

*Reaction of **1** with **6***. A mixture of **1** (281 mg, 2 mmol), P_2S_5 (3.80 g, 17 mmol), and tropone (1.00 g, 9.5 mmol) in dichloromethane (7 mL) was treated with NEt_3 (1.07 g, 10 mmol) at 0 ˚C under a nitrogen stream. The mixture was stirred for 1 h, then filtrated in the reduced pressure and then the solvent was removed on a rotary evaporator. The resulted residue was separated with column chromatography on silica gel (eluent: 40 vol% benzene in *n*-hexane) to give **7** (28 mg, 5.4%).

7: ^{1}H NMR ($CDCl_3$) δ: 3.15 (d, *J* = 6.0 Hz, 1H), 3.94 (d, *J* = 14.3 Hz, 1H, $-CH_2-$), 4.10 (d, *J* = 14.3 Hz, 1H, $-CH_2-$), 5.28 (dd, *J* = 9.1, 6.3 Hz, 1H), 6.34 (d, *J* = 9.1 Hz, 1H), 6.53 (t, *J* = 3.2 Hz, 1H), 6.72 (t, *J* = 3.2 Hz, 2H), 7.48–7.52 (m, 2H), 7.72 (s, 1H), 7.76–7.86 (m, 4H). ^{13}C NMR ($CDCl_3$) δ: 34.1, 44.5, 122.3, 124.5, 125.0, 125.4, 125.8, 126.0, 127.0, 127.1, 127.2, 127.3, 128.5, 129.7, 130.3, 131.8, 132.9, 136.7. IR (KBr): 3002, 1578, 1501, 914, 874, 758, 721 cm^{-1}. MS *m*/*z* (rel. intensity): 262 (M$^+$, 100), 261, 229, 228, 185.

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