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REACTIONS OF NAPHTHO[*b*]CYCLOPROPENE WITH ISOTHIOCYANATE DERIVATIVES TO GIVE [2 π + 2 σ] TYPE CYCLOADDUCTS USING THE THIOCARBONYL MOIETIES AS 2 π COMPONENTS

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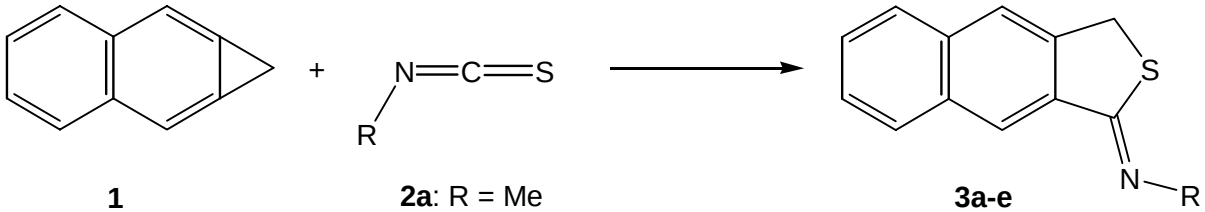
Abstract — Thermal reactions of naphtho[*b*]cyclopropene with isothiocyanate derivatives afforded [2 π + 2 σ] type cycloadducts using the thiocarbonyl moieties as 2 π components in moderate yields. The product yields were promoted by the use of a catalytic amount of $Yb(fod)_3$. The structures of the products were determined by a single crystal X-Ray analysis.

Naphtho[*b*]cyclopropene (**1**) has attracted much attention of chemists owing to the highly strained system. A fusion of the two rings results in a considerable deformation of the naphthalene ring and consequently in a reduction of the aromatic stability.[1] It is known that **1** reacts with olefinic compounds *via* [2 π + 2 π] path, in which the fused π-bond of **1** reacts as a 2 π component.[2] We have investigated the reactivities of **1** with benzocyclopropene to provide the first example of the another type of reaction path, which was a [2 π + 2 σ] path through a σ-bond rupture of the three membered ring.[3] After this finding, the [2 π + 2 σ] type cycloaddition reactions were found in the reactions of various types of olefins.[4] A carbenic reaction was also proposed as a possibility of the third path.[5] We previously reported reactions of benzocyclopropene with a variety of isocyanates affording 2,3-dihydro-1*H*-isoindol-1-ones.[6] In this connection, we investigated reactions of naphtho[*b*]cyclopropene (**1**) with isothiocyanate derivatives (**2**) in order to survey the cyclic compounds arising from the reactivity between C=N and C=S bonds. The results are here reported.

A chloroform solution of **1** and two equimolar amounts of methyl thioisocyanate (**2a**) was

refluxed for 6 days (Scheme 1). The reaction mixture was separated with column chromatography on silica gel to give a [2π + 2σ] type cycloadduct (**3a**) in 36 % yield. The analogous reaction using benzene as a solvent at the refluxing temperature afforded the same product (**3a**) in a low yield (14%). The reactions of **1** with some isothiocyanate derivatives (**2b-2e**) gave the corresponding cycloadducts (**3b-3e**) in the yields summarized in Table 1.



1 **2a**: R = Me; **2b**: R = Ph; **2c**: R = *p*-$MeOC_6H_4$; **2d**: R = *p*-MeC_6H_4; **2e**: R = *p*-ClC_6H_4 **3a-e**

Scheme 1

Table 1. Yields of reaction products of **1** with **2a-e**

Isothiocyanate	Solvent	Reaction time	Yield
2a	chloroform	6 d	**3a**: 36%
	benzene	5 d	**3a**: 14%
2b	chloroform	6 d	**3b**: 49%
	benzene	5 d	**3b**: 20%
2c	chloroform	6 d	**3c**: 26%
2d	chloroform	6 d	**3d**: 39%
2e	chloroform	6 d	**3e**: 35%

Reaction conditions: **1** (1 mmol), **2** (2 mmol), solvent (15 mL), reflux.

It was reported that the cycloaddition reactions of **1** were sometimes improved by the existence of a catalytic amount of ytterbium complex ($Yb(fod)_3$).[4] The influence of the existence of $Yb(fod)_3$ was examined in the case of the reaction of **1** with **2a**. As shown in Table 2, the product yields were clearly improved by the addition of a catalytic amount of $Yb(fod)_3$ and the best result was achieved under the reaction conditions of an

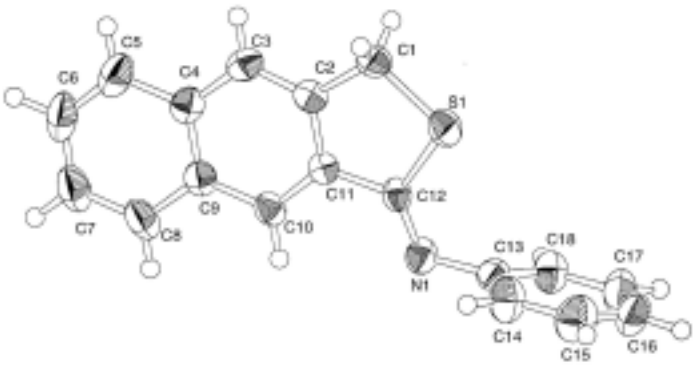
existence of 3 molar % of $Yb(fod)_3$ in chloroform. The structures of the products (**3**) were deduced on the basis of their spectral data and finally decided using a single crystal X-Ray analysis (Figure 1).

Table 2. Yields of **3** in reactions with $Yb(fod)_3$ catalyst

Isothiocyanate	$Yb(fod)_3$ mol %	Reaction time	Yield
2a	1	4 d	**3a**: 38%
	3	4 d	**3a**: 45%
	10	1 d	**3a**: 43%
2b	3	4 d	**3b**: 59%
2c	3	4 d	**3c**: 44%
2d	3	4 d	**3d**: 45%
2e	3	4 d	**3e**: 65%

Reaction conditions: **1** (1 mmol), **2** (2 mmol), reflux, $CHCl_3$ (15 mL).

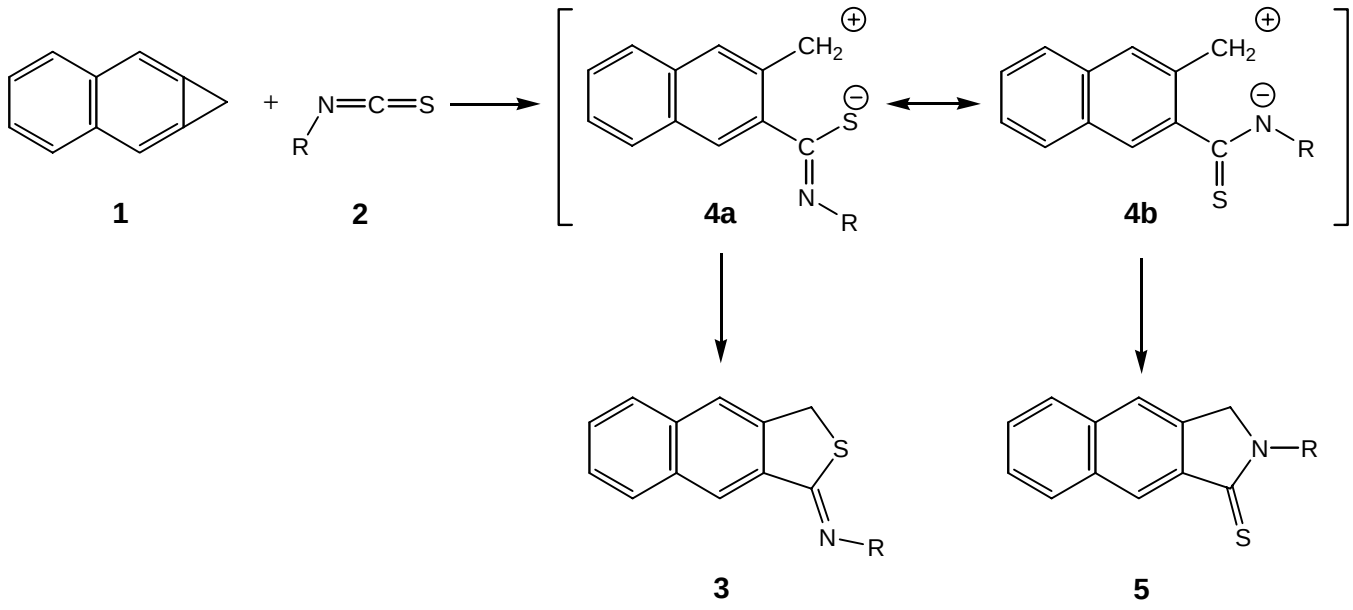
(a)



(b)

Figure 1. Crystal structure of 3b: (a) top view, (b) side view

These reactions are considered to proceed through an ionic process due to the facts that the yield is better in the more polar solvent (chloroform) comparing to benzene and that the cyclopropene moiety of 1 has an ionic character bearing a positive charge at the sp^3-hybridized carbon atom and a negative charge at the fused sp^2-hybridized carbon atom.[5,7] Therefore, the reaction mechanism is proposed as follows. A nucleophilic attack of the negatively charged sp^2-hybridized carbon atom of 1 at the central sp-carbon atom of 2 generates an ionic intermediate (4a), which then cyclizes to form the final product (3) (Scheme 2). It is concluded that the following cyclization reaction of the intermediate (4a) is superior to that of 4b because of the higher nucleophilicity of sulfur atom than that of nitrogen atom.



Scheme 2

ACKNOWLEDGMENT

We would like to thank Dr. M. Tomura (Institute for Molecular Science) for measurement of the X-Ray analysis.

EXPERIMENTAL

Only typical reactions are mentioned below.

Reaction of naphto[b]cyclopropene (1) and isothiocyanate (2a).

Naphto[b]cyclopropene (1) (140 mg, 1.00 mmol) and phenyl isothiocyanate (2a) (270 mg,

2.00 mmol) are stirred in dry $CHCl_3$ (15 mL) at 60˚C for 4 days. After evaporation of the solvent the residue was separated with SiO_2 column chromatography to give **3a** (76 mg, 36%) with an eluent of hexane-ethyl acetate (4 : 1).

3a: MS m/z (rel intensity): 213 (M^+, 100), 198 (24), 183 (24), 154 (16). IR (KBr): 2914, 1637, 1010, 748, 474 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ ppm: 3.46 (s, 3H, Me), 4.57 (s, 2H, CH_2), 7.45-7.55 (m, 2H), 7.81 (d, 1H, J = 8.2 Hz), 7.82 (s, 1H), 7.94 (d, 1H, J = 8.2 Hz), 8.41 (s, 1H).

3b: HRMS m/z: 275.0740. Calcd for $C_{18}H_{13}NS$: 275.0769. MS m/z (rel intensity): 275 (M^+, 100), 243 (6), 198 (4), 154 (4). IR (KBr): 3053, 1693, 1587, 746, 476 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ ppm: 4.58 (s, 2H, CH_2), 7.16-7.21 (m, 3H), 7.39-7.45 (m, 2H), 7.49-7.60 (m, 2H), 7.87 (d, 1H, J = 8.5 Hz), 7.88 (s, 1H), 8.01 (d, 1H, J = 8.5 Hz), 8.63 (s, 1H).

3c: HRMS m/z: 305.0872. Calcd for $C_{19}H_{15}NOS$: 305.0875. MS m/z (rel intensity): 305 (M^+, 100), 290 (100), 205 (88), 184 (42), 141 (35). ^1H NMR ($CDCl_3$, 300 MHz) δ ppm: 3.87 (s, 3H, OMe), 4.59 (s, 2H, CH_2), 6.97 (d, 2H, J = 6.6 Hz), 7.20 (d, 2H, J = 6.6 Hz), 7.52-7.60 (m, 2H), 7.87 (d, 1H, J = 7.7 Hz), 7.89 (s, 1H), 8.01 (d, 1H, J = 8.0 Hz), 8.62 (s, 1H).

3d: HRMS m/z: 289.0898. Calcd for $C_{19}H_{15}NS$: 289.0926. MS m/z (rel intensity): 289 (M^+, 100), 257 (5), 171 (5), 137 (4). ^1H NMR ($CDCl_3$, 300 MHz) δ ppm: 2.39 (s, 3H, Me), 4.57 (s, 2H, CH_2), 7.09 (d, 2H, J = 8.1 Hz), 7.22 (d, 2H, J = 8.1 Hz), 7.52-7.60 (m, 2H), 7.82 (d, 1H, J = 7.3 Hz), 7.99 (s, 1H), 8.01 (d, 1H, J = 7.3 Hz), 8.62 (s, 1H).

3e: HRMS m/z: 309.0364. Calcd for $C_{18}H_{12}ClNS$: 309.0380. MS m/z (rel intensity): 311 (M^++2, 38), 309 (M^+, 100), 274 (6), 196 (7), 154 (5), 137 (9). IR (KBr): 2928, 2363, 1614, 1487, 1091, 744 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ ppm: 4.58 (s, 2H, CH_2), 7.16 (d, 2H, J = 6.6 Hz), 7.39 (d, 2H, J = 6.6 Hz), 7.51-7.62 (m, 2H), 7.88 (d, 1H, J = 8.0 Hz), 7.91 (s, 1H), 8.01 (d, 1H, J = 8.0 Hz), 8.61 (s, 1H). Crystallographic data of **3e** are as follows. $C_{18}H_{13}NS$, M = 275.37, monoclinic, space group $P2_1$, a = 7.577(3) Å, b = 6.539(2) Å, c = 14.137(6) Å, β = 94.747(9)˚, V = 698.0(4) $Å^3$, Z = 4, D_{calc} = 1.310 g cm^{-3}, μ (MoK_α) = 2.20 cm^{-1}, F(000) = 288.00. A Total of 2949 reflection for $2\theta_{max}$ = 55˚ was collected with $I > 2\sigma(I)$ using a Rigaku / MSC Mercury CCD diffract meter (MoK_α radiation, λ = 0.71071 Å) at 296 K. The structure was solved using direct method (SHELEX-97) and refined by Full-matrix least squares analysis giving values of R = 0.095, R_w = 0.148, R_1 = 0.064, S = 1.45, $\Delta\rho_{max}$ / $\Delta\rho_{min}$ = 0.36 / −0.43 e $Å^{-3}$.

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7. Swan's parameters of chloroform and benzene are as follows.

solvent	relative permittivity (ε)	anion solvation ability (A)	cation solvation ability (B)	polarity (A+B)
benzene	2.28	0.15	0.59	0.74
chloroform	4.81	0.42	0.73	1.15