

[2 π + 2 σ] TYPE CYCLOADDITION REACTIONS OF
IMINOTROPONE DERIVATIVES WITH NAPHTHO[*b*]CYCLO-
PROPENE TO FORM CYCLIC AMINE COMPOUNDS

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Abstract-Reactions of iminotropone derivatives with naphtho[*b*]cyclopropene under the presence of a catalytic amount of AgBF₄ afforded cyclic amine derivatives *via* [2 π + 2 σ] type cycloaddition reactions. On the other hand, a reaction using a tropone hydrazone derivative without a catalysis formed a substituted hydrazone *via* a σ -bond rupture of the cyclopropene ring.

While naphtho[*b*]cyclopropene (**1**) has highly distorted three-membered ring, it is a fairly stable colorless crystalline material.¹ The reactivity of **1** toward cycloaddition reactions has been increasingly investigated to find an existence of two types of reaction paths, a π -type path² and a σ -type path.³ In the former reaction path **1** reacts with its π -bond, and in the latter, **1** ruptures the σ -bond in the three-membered ring moiety, respectively. Recently, a carbenic reaction was proposed as a possibility of the third type of reaction path.⁴

Although an enormous amount of papers have been published on the chemistry of tropone, researches on the reactivity of iminotropones⁵ are few in numbers. However, considering the differences in chemical behaviors between tropones and iminotropones, and the possibility to synthesize cyclic amine compounds, the study on iminotropones seems to be worthwhile. Herein, we report on the reactions of **1** with iminotropones.

An anhydrous benzene solution of **1** with two-equimolar amount of *N*-(*p*-methylphenyl)-iminotropone (**2a**) was stirred at 0 °C for 30 min under a nitrogen stream. After evaporation of the solvent, the residue was chromatographed on silica gel to give the recovery of **1** in 92% yield. No obvious addition product was detected. The reaction was fairly improved by an addition of a catalytic amount of AgBF₄.⁶ Thus, a benzene solution of **1** and two equimolar amount of **2a** and 1 mol % of AgBF₄ was reacted under the same reaction conditions as above. The usual treatment of the reaction mixture gave a cyclic amine derivative (**3a**) and an amine derivative (**4a**) in 12% and 15% yields, respectively.⁷

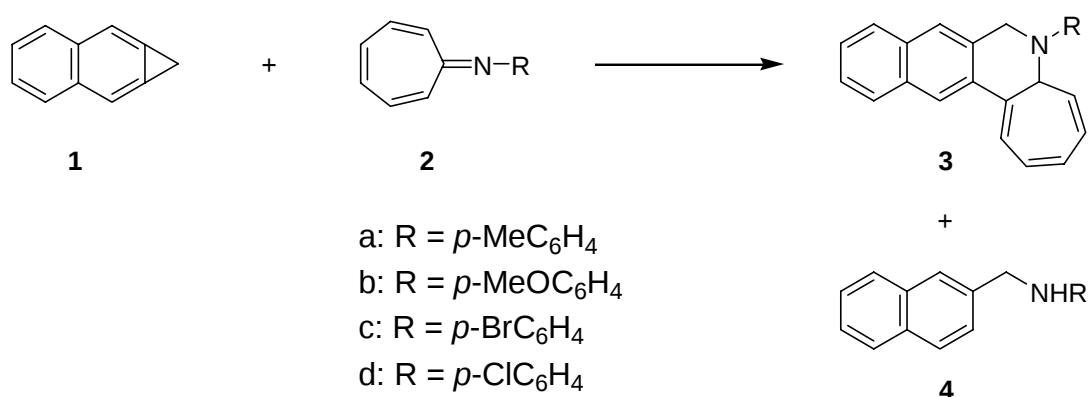


Figure 1

Table 1. Conditions of the cycloaddition reactions at 0 °C

Run	Molar Ratio (1) : (2)	Additive AgBF ₄	Solvent	Reaction Time	Yield (%)	
					(3a)	(4a)
1	1 : 2		benzene	30 min	Recovery of (1) :92	
2	1 : 2	1 mol %	benzene	30 min	12	15
3	1 : 2	1 mol %	CHCl ₃	30 min	×	34
4	1 : 2	1 mol %	toluene	60 min	8	24
5	1 : 2	3 mol %	benzene	30 min	×	45

The amount of AgBF_4 used influenced on the product yields, *i.e.*, the use of 3 mol % of AgBF_4 , in stead of 1 mol %, promoted the yield of **4a** to 45% but on the contrary, that of **3a** was diminished to 0%. The product yields of the reactions with **2a** under various reaction conditions are summarized in Table 1. The best result was achieved under the conditions of the run 2. The product yields of the reactions with several kinds of iminotropones (**2a-d**) under the presence of 1 mol % of AgBF_4 are summarized in Table 2.

Table 2. Yields of products (**3a-d**) and (**4a-d**)

Compounds	a : R = <i>p</i> -MeC ₆ H ₄	b : R = <i>p</i> -MeOC ₆ H ₄	c : R = <i>p</i> -BrC ₆ H ₄	d : R = <i>p</i> -ClC ₆ H ₄
3	12%	5%	0%	0%
4	15%	19%	30%	44%

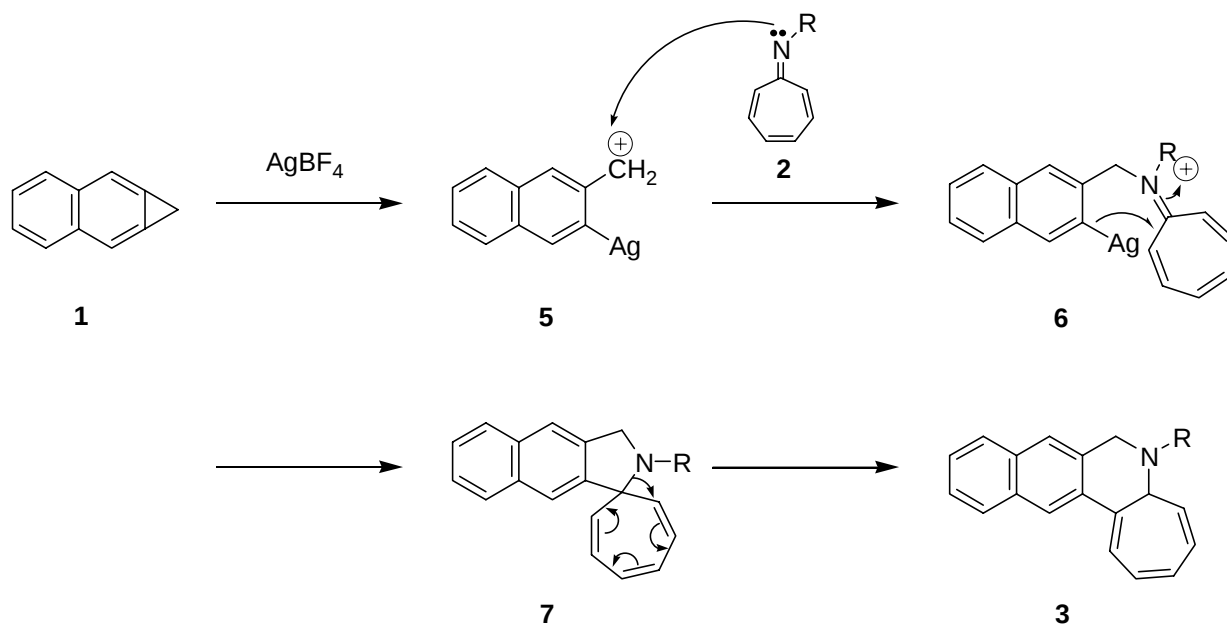


Figure 2

The formation of **3** is considered to proceed as follows according to research reports of benzocyclopropene and **1**.^{1,6} An electrophilic cleavage at the three-membered ring of **1** is carried out by a catalytic amount of Ag(I) ion giving an intermediate (**5**). A nucleophilic attack of iminotropones to the cationic carbon atom of **5** may afford a spiro-type intermediate (**7**) *via* a cyclization process of **6** as well as a reaction of **1** with tropone.⁸ This compound easily provides the final product (**3**) through a 1,2-shift of the nitrogen atom.

When the cyclization process is not performed after the nucleophilic attack of iminotropone to **5**, compound (**6**) may exist as a tropylium ion form in a flask. The intermediate (**6**) is hydrolyzed during working-up to afford compound (**4**).

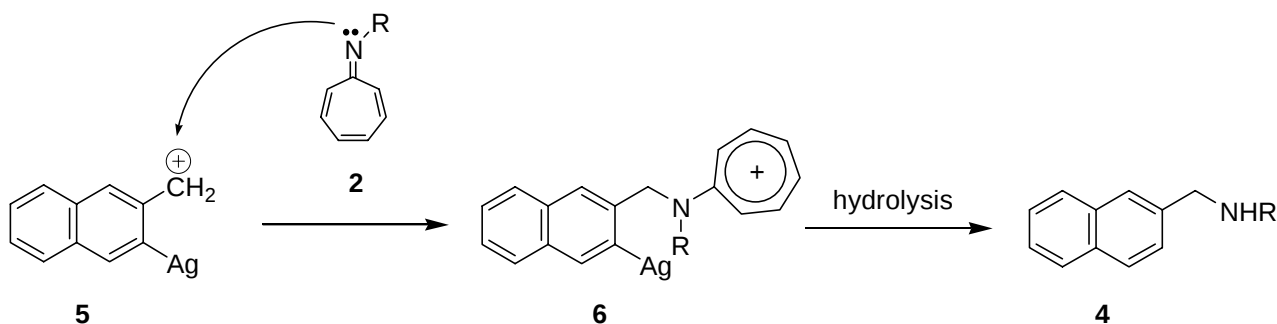


Figure 3

The reaction of **1** with tropone tosylhydrazone (**8**) without any catalyst provided an *N,N*-doubly substituted hydrazone derivative (**9**) in 15% yield.⁹ The reaction is considered to proceed through a nucleophilic attack of the amine nitrogen atom of **8** to the positively charged saturated carbon atom of **1**. Considering the charge densities on the amine nitrogen atom and the imine nitrogen atom of **8** (Figure 5), this reaction mechanism can be considered to be a result of a competition on the nucleophilicity of the nitrogen atoms.

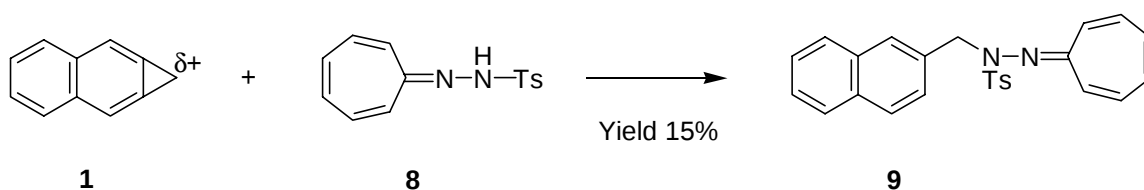
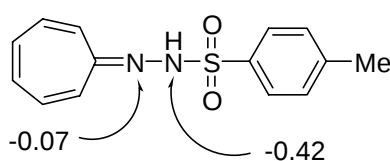


Figure 4



charge densities

Figure 5

In summery, we investigated a nucleophilic reaction of iminotropone (**2**) to **1** with an Ag(I) catalyst and a nucleophilic reaction of **8** to **1** without a catalyst. The former reaction afforded $[2\pi + 2\sigma]$ type cycloadducts (**3**) by the following cyclization.

REFERENCES AND NOTES

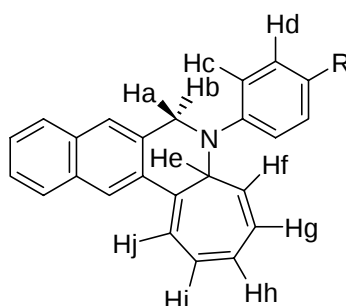
1. B. Halton and M. Banwell, "Cyclopropenes," in "The Chemistry of Functional Groups," ed. by Z. Rapport, Wiley, Chichester, 1978, pp. 1223-1340; B. Halton, *Chem. Rev.*, 1989, **89**, 1161; P. C. Hilberty, G. Ohanessian, and F. Delbecq, *J. Am. Chem. Soc.*, 1985, **107**, 3095; C. Wentrup, C. Mayor, J. Becker, and H. J. Linder, *Tetrahedron*, 1985, **41**, 1601.
2. M. Nitta, S. Sogo, and T. Nakayama, *Chem. Lett.*, **1979**, 1431; H. Kato, S. Toda, Y. Arikawa, M. Maruzawa, M. Hashimoto, K. Ikoma, S. Z. Wang, and A. Miyasaka, *J. Chem. Soc., Perkin Trans. 1*, **1990**, 2035; J. C. Martin and J. M. Muchouski, *J. Org. Chem.*, 1984, **49**, 1040; R. Neidlein and L. Tadessa, *Helv. Chim. Acta*, 1988, **71**, 249.
3. K. Saito, H. Ishihara, and S. Kagabu, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 4141; K. Saito, K. Ito, K. Takahashi, and S. Kagabu, *O. P. P. I. Briefs*, 1991, **23**, 196; S. Kagabu, K. Saito, H. Watanabe, K. Takahashi, and K. Wada, *Bull. Chem. Soc. Jpn.*, 1991, **64**, 106; S. Ando, J. Imamura, A. Hattori, M. Tajits, and K. Saito, *Heterocycles*, 1998, **48**, 1769.
4. W. Pan, M. Jones, Jr., B. Esat, and P. M. Lahti, *Tetrahedron Lett.*, 1998, **39**, 1505.
5. W. E. Truce and J. P. Shepard, *J. Am. Chem. Soc.*, 1977, **99**, 6453; R. T. Guan, S. Sugiyama, A. Mori, and H. Takeshita, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 2393; K. Saito, T. Watanabe, and K. Takahashi, *Chem. Lett.*, **1989**, 2099; G. Mehta and S. R. Kara, *J. Org. Chem.*, 1989, **54**, 2975; K. Saito and K. Takahashi, *Chem. Lett.*, **1989**, 925; K. Ito, Y. Noro, K. Saito, and K. Takahashi, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 2573; K. Saito, C. Kabuto, and K. Takahashi, *ibid.*, 1991, **64**, 2383; K. Ito, K. Saito, and K. Takahashi, *ibid.*, 1992, **65**, 812; K. Ito, K. Saito, and K. Takahashi, *Heterocycles*, 1992, **34**, 2339; *idem*, *ibid.*, 1993, **36**, 21; K. Ito and K. Saito, *ibid.*, 1994, **38**, 2691; K. Ito, Y. Hara, R. Sakakibara, and K. Saito, *ibid.*, 1995, **41**, 1675; K. Ito and K. Saito, *ibid.*, 1995, **41**, 2307; Y. Saito, M. Tomita, H. Taniguchi, H. Okabayashi, and K. Saito, *ibid.*, 1995, **41**, 2181; K. Ito and K. Saito, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 3539; K. Ito and K. Saito, *Recent Res. Devel. Pure & Applied Chem.*, 1999, **3**, 91.

6. W. E. Billups, W. Y. Chow, and C. V. Smith, *J. Am. Chem. Soc.*, 1974, **96**, 1979; W. E. Billups, W. A. Rodin, and M. M. Haley, *Tetrahedron*, 1988, **44**, 1305.

7. ^1H NMR spectral data for the cycloadducts are as follows.

3a: ^1H NMR (CDCl_3), δ : 2.27 (s, 3 H, Me), 3.61 (d, 1 H, $J_{\text{ef}} = 5.4$ Hz, H_e), 4.61 (d, 1 H, $J_{\text{ab}} = 14.8$ Hz, H_a), 4.67 (d, 1 H, $J_{\text{ab}} = 14.8$ Hz, H_b), 5.62 (dd, 1H, $J_{\text{ef}} = 5.4$, $J_{\text{fg}} = 9.4$ Hz, H_f), 6.31 (dd, 1H, $J_{\text{gh}} = 4.9$, $J_{\text{fg}} = 9.4$ Hz, H_g), 6.88 (m, 2 H, $\text{H}_{\text{h,i}}$), 6.93 (d, 2 H, $J_{\text{cd}} = 8.8$ Hz, H_d), 7.00 (d, 2 H, $J_{\text{cd}} = 8.8$ Hz, H_c), 7.02 (d, 1 H, $J_{\text{ij}} = 5.8$ Hz, H_j), 7.39-7.46 (m, 2 H), 7.69 (s, 1 H), 7.76-7.81 (m, 2 H), 8.10 (s, 1 H).

3b: ^1H NMR (CDCl_3), δ : 3.76 (s, 3 H, OMe), 3.55 (d, 1 H, $J_{\text{ef}} = 5.2$ Hz, H_e), 4.46 (d, 1 H, $J_{\text{ab}} = 14.7$ Hz, H_a), 4.61 (d, 1 H $J_{\text{ab}} = 14.7$ Hz, H_b), 5.61 (dd, 1 H, $J_{\text{ef}} = 5.2$ Hz, $J_{\text{fg}} = 9.8$ Hz, H_f), 6.29 (dd, 1 H, $J_{\text{gh}} = 5.5$, $J_{\text{fg}} = 9.8$ Hz, H_g), 6.82-6.86 (m, 2 H, $\text{H}_{\text{h,i}}$), 6.84 (d, 2 H, $J_{\text{cd}} = 9.1$ Hz, H_d), 6.99 (d, 2 H, $J_{\text{cd}} = 9.1$ Hz, H_c), 7.02 (m, 1 H, H_j), 7.41-7.45 (m, 2 H), 7.67 (s, 1 H), 7.76-7.81 (m, 2 H), 8.09 (s, 1 H).



3a : R = Me

3b : R = OMe

8. K. Saito, S. Ando, and Y. Kondo, *Heterocycles*, 2000, **53**, 2601.

9. ^1H NMR spectral data for **9** is as follows.

^1H NMR (CDCl_3), δ : 2.46 (s, 3 H), 4.34 (br s, 2 H), 6.25 (dd, 1 H, $J = 7.7$, 15.3 Hz), 6.28 (d, 1 H, $J = 11.0$ Hz), 6.34 (dd, 1 H, $J = 8.0$, 16.0 Hz), 6.48 (dd, 1 H, $J = 7.6$, 12.2 Hz), 6.55 (dd, 1 H, $J = 2.5$, 12.4 Hz), 7.34-7.44 (m, 5 H), 7.49 (dd, 1H, $J = 1.7$, 8.4 Hz), 7.62 (s, 1 H), 7.68-7.80 (m, 5 H).