HETEROCYCLES, Vol. 53, No. 12, 2000, pp. 2601 – 2606, Received, 28th April, 2000

CYCLOADDITION REACTION OF NAPHTO[*b*]CYCLOPROPENE WITH TROPONE DERIVATIVES UNDER THE PRESENCE OF YTTERBIUM COMPLEX TO FORM CYCLIC ETHERS OR CYCLIC KETONES: SOLVENT EFFECT OF CHLOROFORM AND BENZENE ON THE REACTION PATH

Katsuhiro Saito,* Shinichi Ando, and Yoji Kondo

Department of Applied Chemistry, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan

Abstract -- Reactions of naphtho[*b*]cyclopropene with 2-substituted tropone derivatives in chloroform under the presence of ytterbium complex afforded two types of cyclic ether compounds *via* a [8π+2σ] type cycloaddition reactions. On the other hand, the similar reactions but using benzene as a solvent proceeded through a [6π+2π] type cycloaddition path to form cyclic ketone compounds.

Cyclopropenes fused with aromatic rings such as benzocyclopropene or naphtho[*b*]cyclopropene are known to have high reactivities, which partially depend on highly strained structures caused by the distorted bond angles of the sp^2 hybridization of the bridgehead carbons, and partially on the reductions of the aromaticities, which are proved by considerable bond length alternations.[1] Recently, M. Jones suggested a contribution of a carbenic structure on the reactivity of naphtho[*b*]-cyclopropene.[2]

These types of cyclopropenes are reported to react not only with various types of olefins but also with carbenes[3] to afford adducts. Cycloaddition reactions of these types of cyclopropenes are known to proceed *via* two independent paths, *i.e.*, a path through a π-bond rupture of the cyclopropene site[4] and a path through a σ-bond rupture of the cyclopropene.[5] The authors have published on the first finding for the σ-bond rupture course in cycloadditions of benzocyclopropene with furan derivatives.[5] However, the detailed reaction mechanism of these paths remains unsolved.[6]

The reactivities of these cyclopropenes under the presence of metal complexes also attracted attentions of chemists. It was reported that the electrophilic cleavages of σ-bonds of the cyclopropenes are very effective in the presence of silver complexes to form benzyl derivatives.[7] As a part of our researches on cyclopropenes[8] and troponoid compounds,[9] we investigated reactions of naphtho[*b*]cyclopropene (**1**) with tropone derivatives (**2**). Here the results are discussed.

Naphtho[*b*]cyclopropene (**1**) was heated with two molar equivalents of tropone (**2a**) in chloroform at 60°C for 60 h. The resulting mixture was chromatographed on silica gel to afford a small amount (1 %) of a cyclic ether compound (**3a**). Any recovery of **1** was not detected. An existence of metal complexes promoted the formation of 3a. Thus, the analogous reaction but under the presence of three mol % of ytterbium complex ($Yb(fod)_3$) at 60°C for 90 h gave **3a** in 48 % yield. The same promotion effect was observed with a silver complex ($AgBF_4$), which improved the yield of **3a** to 35 % under the analogous reaction conditions as above.

Analogous reaction but using substituted tropones afforded two types of ether compounds. Reaction of **1** with two molar equivalents of 2-methyltropone (**2b**) in chloroform under the presence of three mol % of the ytterbium complex at 60°C for 47 h gave ether compounds (**3b**) and (**4b**) in 56 and 13 % yields, respectively. The same reaction using 2-phenyltropone (**2c**) gave **4c** in 25 % yield.

On the other hand, reaction of **1** with two equimolar amounts of **2a** in benzene at 80°C for 50 h afforded a cyclic ketone (**5a**) in 18 % yield. In this reaction, both ytterbium and silver complexes had a little effect and reduced the product yields. Analogous reactions using **2b** and **2c** resulted in the corresponding results to form **5b** and **5c** in 35 and 45 % yields, respectively.[10] These results are summarized in Table 1.

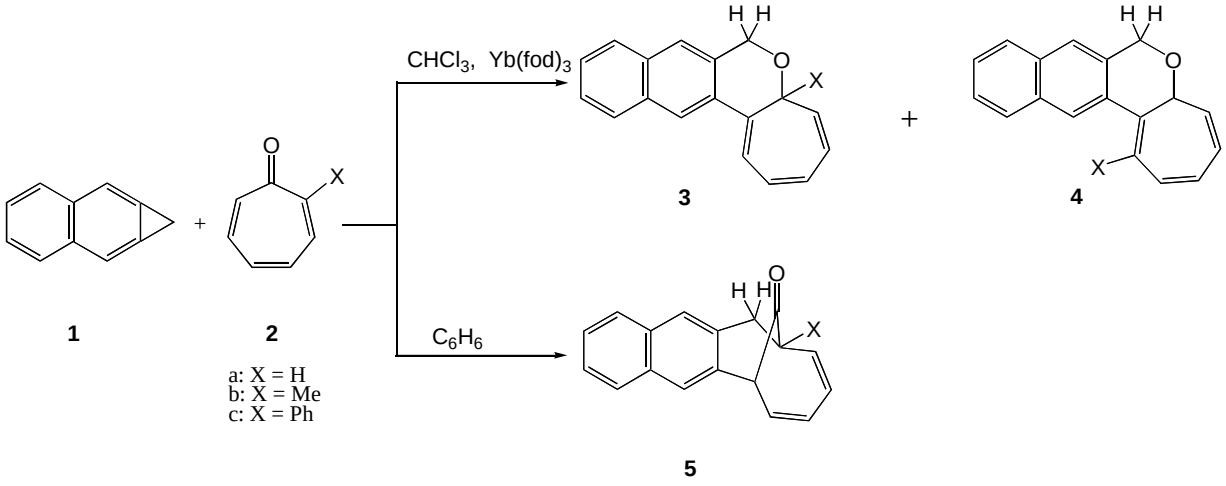


Table 1. Cycloadditions of naphto[*b*]cyclopropene (**1**) with tropone (**2**)

Run	Tropone	Solvent	Additive	Yield (%)		
				(**3**)	(**4**)	(**5**)
1	2a	$CHCl_3$	none	1		0
2	2a	$CHCl_3$	$Yb(fod)_3$	48		0
3	2a	$CHCl_3$	$AgBF_4$	35		0
4	2b	$CHCl_3$	$Yb(fod)_3$	56	13	0
5	2c	$CHCl_3$	$Yb(fod)_3$	0	25	0
6	2a	Bz	none	0		18
7	2b	Bz	none	0	0	35
8	2c	Bz	none	0	0	45

The structures of **3**, **4** and **5** were deduced on the basis of their spectral properties. Elemental analyses showed these products to be 1:1 adducts of **1** and **2**.

An absence of absorptions due to hydroxyl or carbonyl groups in the IR spectra suggested **3** and **4** to be ether compounds, which was supported by the absorption at *ca.* 1100 cm^{-1} (**3a**; 1105 cm^{-1}, **4b**; 1062 cm^{-1}). The ^{1}H NMR spectra showed an existence of a cycloheptatriene moiety. The absorption at *ca.* 77 ppm in the ^{13}C NMR spectra taught an existence of a saturated carbon atom attached by an oxygen atom. The ^{13}C NMR spectra and DEPT spectra confirmed that the saturated carbon atom of **3** (**3b**; 76.8 ppm) was a quaternary carbon atom, on the other hand, that of **4** (**4c**; 76.9 ppm) was a tertiary carbon atom. These facts suggested that the saturated carbon atom of **3** had no hydrogen atom, but that of **4** bared a hydrogen atom. Thus, the structures of **3** and **4** were deduced to be the illustrated ones.

On the other hand, the existence of a saturated carbonyl group in **5** was clearly demonstrated by absorption at 1717 cm^{-1} (**5a**) in its IR spectrum. The ^{1}H NMR spectrum showed an existence of continuos four olefinic hydrogen atoms.

The structures of **3**, **4** and **5** were further supported by good resemblances of their spectral properties with those of the analogous compounds.[11]

Table 2. Solvent effect for the cycloaddition of **1** with **2b** under the presence of 3 mol % $Yb(fod)_3$

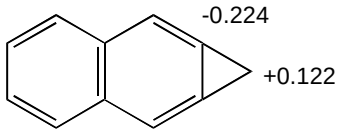
Run	Solvent	Reaction Temp. (°C)	Reaction Time	Yield (%)		
				(**3b**)	(**4b**)	(**5b**)
1	$CHCl_3$	60	47 hr	55.6	12.6	-
2	MeCN	60	5 day	8.3	2.4	7.5
3	THF	60	7 day	3.6	0.6	3.6
4	AcOEt	60	9 day	6.6	1.1	3.9
5	C_6H_6	80	113 h	-	-	5.6

The product distribution of the reaction of **1** and **2** under the presence of $Yb(fod)_3$ was depended on the solvents as shown in Table 2.

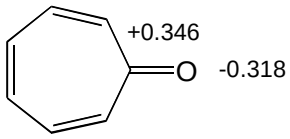
Table 3. The data concerning the polarities of the solvents

Solvent	Relative Permittivity (ε)	Swain's Parameter[12]		
		Anion Solvation Ability (A)	Cation Solvation Ability (B)	Polarity (A+B)
$CHCl_3$	4.81	0.42	0.73	1.15
MeCN	37.50	0.37	0.86	1.22
THF	7.58	0.17	0.67	0.84
AcOEt	6.02	0.21	0.59	0.79
C_6H_6	2.28	0.15	0.59	0.74

Table 3 shows that an ion stabilizing effect of chloroform is bigger than that of benzene. Considering the difference of the ion stabilizing abilities between chloroformandbenzene,wesupposedthereactionsto proceed as follows. In the case of chloroform solvent, which has a larger ion stabilizing capability comparing to benzene, the reaction should proceed through an ionic mechanism.[13] The net atomic charges of **1** and **2a** were calculated to be as follows. The sp^2-carbon atom fused with three-menbered ring of **1** was charged to negative, and the oxygen atom of **2** to positive. These facts suggested that the bridgehead sp^2-carbon atom of **1** attacked the carbonyl carbon atom of **2**.

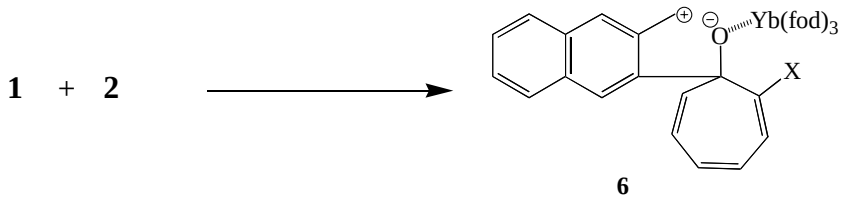


1

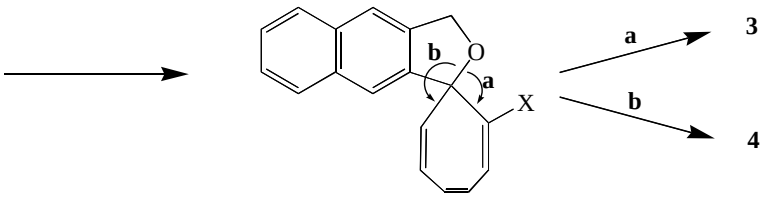


2a

Thus, the carbonyl carbon atom of **2**, which was activated by $Yb(fod)_3$, was attacked by the bridgehead sp^2-carbon atom of **1** to form a zwitter ionic intermediate (**6**), which then cyclized to give a spiro intermediate (**7**). A ring cleavage of **7** *via* path **a** or **b** gave **3** or **4**, respectivity.[14] The regioselectivity between the products **3** and **4** is considered to depend on the steric hindrance of the substituents.[15]

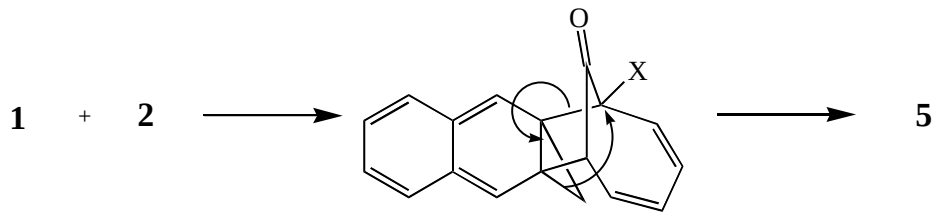


6



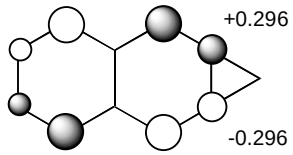
7

On the other hand, the reaction in benzene solvent should proceed through a concerted process. A [6π + 2π]type cycloaddition of **1** with **2** gave an intermediate (**8**),[14] which then isomerized to **5**.

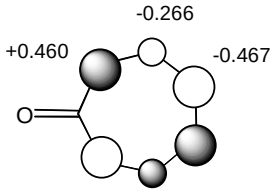


8

The energy gap between the HOMO of **1** and the LUMO of **2** was 8.064 eV, and that between the LUMO of **1** and the HOMO of **2** was 9.070 eV, suggesting that the former interaction controls this reaction. The orbital symmetry of the HOMO of **1** and the LUMO of **2** coincided as follows.



1 (HOMO, -8.989 eV)



2 (LUMO, -0.925 eV)

REFERENCES AND NOTES

1. B. Halton and M. C. Banwell, "Cyclopropenes," in "The Chemistry of Functional Groups," ed. by Z. Rappoport, Wiley, Chichester, 1978, pp. 1223-1340; B. Halton, *Chem. Rev.*, 1989, **89**, 1161; P. C. Hiberty, 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. W. Pan, M. Jones, Jr., B. East, and P. Lahti, *Tetrahedron*, 1998, **39**, 1505.
3. S. Kagabu, S. Sogo and T. Nakayama, *Chem. Lett.*, 1988, **29**, 675.
4. M. Nitta, S. Sogo, and T. Nakayama, *Chem. Lett.*, **1979**, 1431; H. Kato, S. Toda, Y. Arikawa, M. Masuzawa, M. Hasimoto, K. Ikoma, S.-Z. Wang, and A. Miyasaka, *J. Chem. Soc., Perkin Trans.1*, **1990**, 2035; J. C. Martin and J. M. Muchowski, *J. Org. Chem.*, 1984, **49**, 1040; R. Neidlein and L. Tadesse, *Helv. Chim. Acta*, 1988, **71**, 249.
5. 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. Tajitsu, and K. Saito, *Heterocycles*, 1998, **48**, 1769.
6. I. Durucasu, N. Saracoglu, and M. Balci, *Tetrahedron Lett.*, 1991, **32**, 7097.
7. 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.
8. K. Saito, S. Isobe, K. Ito, S. Kagabu, and K. Takahashi, *Chem. Lett.*, **1989**, 1541; K. Saito, K. Ito, and K. Takahashi, *Heterocycles*, 1989, **29**, 2135; K. Saito, K. Ito and K. Takahashi, *ibid.*, 1990, **31**, 1895.
9. K. Saito and K. Takahashi, *Chem. Lett.*, **1989**, 925; K. Saito, T. Watanabe, and K. Takahashi, *ibid.*, **1989**, 2099; K. Ito, Y. Noro, K. Saito, and K. Takahashi, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 2573; K. Saito, S. Suzuki, T. Watanabe, and K. Saito, *ibid.*, 1993, **66**, 2304.
10. Only the physical and spectral properties of typical products are listed below.
3a: Pale yellow needles. mp 130-131°C (ethyl acetate-ethanol). HRMS m/z 246.1037 Calcd for $C_{18}H_{14}O$: 246.041. MS m/z (rel intensity): 246.2 (M^+, 100), 231.2 (12), 218.2 (85), 203.2 (25). IR (KBr): 3056, 1497, 1169, 1105 cm^{-1}. ^1H NMR ($CDCl_3$) δ ppm: 4.00 (dd, 1H, J= 1.8, 3.8 Hz), 4.78 (d, 1H, J= 13.5 Hz), 4.96 (d, 1H, J= 13.8 Hz), 5.51 (dd, 1H, J= 4.2, 9.9 Hz), 6.23 (ddd, 1H, J= 1.8, 4.2, 10.0 Hz), 6.70- 6.84 (m, 3H), 7.41- 7.51 (m, 2H), 7.61 (s, 1H), 7.80 (dd, 1H, J= 6.0, 6.0 Hz), 7.81 (dd, 1H, J= 6.0, 6.0 Hz), 7.96 (s, 1H). ^{13}C NMR ($CDCl_3$) δ ppm: 67.1 (t), 75.8 (d),

118.1 (d), 122.9 (d), 123.3 (d), 124.9 (d), 125.9 (d), 126.5 (d), 126.5 (d), 127.5(d), 128.1(d), 129.4 (s), 130.2 (d), 130.2 (s), 131.3 (d), 132.7 (s), 133.2 (s), 134.9 (s). Anal. Calcd for $C_{18}H_{14}O$: C, 87.78; H, 5.73. Found: C, 87.72, H, 5.67.

3b: colorless needles. mp 163-164°C (ethyl acetate-ethanol). HRMS m/z 260.1191 Calcd for $C_{19}H_{16}O$: 290.1197. MS m/z (rel intensity): 260.2 (M^+,64), 245.2 (44), 217.2(97), 202.1 (43), 27.3(100). IR (KBr): 2973, 2361, 1362, 1321, 1062cm^{-1}. ^{1}H NMR ($CDCl_3$) δ ppm: 1.06 (s, 3H), 4.82 (d, 1H, J= 14.1 Hz), 4.97 (d, 1H, J= 14.1 Hz), 5.79 (d, 1H, J= 10.8 Hz), 6.34 (dd, 1H, J= 6.3, 10.8 Hz), 6.60 (dd, 1H, J= 6.3, 11.1 Hz), 6.72 (dd, 1H, J= 6.9, 11.1 Hz), 7.03 (d, 1H, J= 6.9 Hz), 7.41- 7.48 (m, 2H), 7.58 (s, 1H), 7.76-7.84 (m, 2H), 8.15 (s 1H). ^{13}C NMR ($CDCl_3$) δ ppm: 17.6 (q), 63.9 (t), 76.8 (s), 119.0 (d), 122.5 (d), 123.8 (d), 125.3 (d), 125.8 (d), 126.3(d), 127.3(d), 128.0(d), 129.3 (d), 129.8(s), 131.8(d), 132.0(d), 132.3(s), 133.1(s), 133.8(s), 135.9(s).

4c: Pale yellow needles. mp 169-170°C (ethyl acetate-ethanol). HRMS m/z 322.1360 Calcd for $C_{18}H_{14}O$: 322.1353. MS m/z (rel intensity): 322.4 (M^+,100), 307.1 (9), 294.1(43), 279.1 (21), 265.1 (10), 245.1. IR (KBr): 3019, 2843, 1491, 889cm^{-1}. ^{1}H NMR ($CDCl_3$) δ ppm: 3.94 (dd, 1H, J= 1.8, 4.8 Hz), 4.87 (d, 1H, J= 12.9 Hz), 4.94 (d, 1H, J= 12.9 Hz), 5.51 (dd, 1H, J= 4.2, 9.3 Hz), 6.30 (ddd, 1H, J= 1.8, 5.1, 9.6 Hz), 6.74 (d, 1H, J= 11.4 Hz), 6.91 (dd, 1H, J= 5.1, 11.4 Hz), 7.10- 7.30 (m, 8H), 7.39 (m, 1H), 7.62 (s, 1H), 7.75(d, 1H, J= 7.8 Hz). ^{13}C NMR ($CDCl_3$) δ ppm: 67.8 (t), 76.9 (d), 122.8 (d), 124.7 (d), 125.5 (d), 126.5 (d), 127.0 (d), 127.2 (d), 128.1(d), 128.2(d), 129.1(s), 129.2 (d), 130.8(d), 131.5(d), 132.1(s), 132.2(d), 132.3(s), 132.9(s), 134.3(d), 134.4(d), 137.1(s), 141.4(s).

5a: Orange tar. HRMS m/z 246.1039 Calcd for $C_{18}H_{14}O$: 246.041. MS m/z (rel intensity): 246.1 (M^+, 100), 229.2 (19), 218.2 (55), 203.1 (18). IR (KBr): 3019, 2919, 1717, 1601 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ ppm : 3.34 (dd, 1H, J= 3.3, 15.8 Hz), 3.58 (dd, 1H, J= 3.0, 15.9 Hz), 3.60 (m, 1H), 4.51 (d, 1H, J= 6.9 Hz), 5.71 (dd, 1H, J= 5.7, 10.8 Hz), 5.94 (dd, 1H, J= 6.9, 11.0Hz), 6.01- 6.12 (m, 2H), 7.40- 7.44 (m, 2H), 7.59 (s, 1H), 7.61 (s, 1H), 7.73- 7.70 (m, 2H). ^{13}C NMR ($CDCl_3$) δ ppm : 38.1 (t), 51.4 (d), 55.3 (d), 125.6 (d), 125.8 (d), 125.9 (d), 126.0 (d), 127.0 (d), 127.1 (d), 127.2 (d), 127.3 (d), 128.2 (d), 129.8 (d), 132.0 (s), 132.3 (s), 132.5 (s), 135.4 (s), 203.9 (s, C=O).

11. S. Ito, Y. Fujise, T. Okuda, and Y. Inoue. *Bull. Chem. Soc. Jpn.*, 1966, **39**, 1351; J. H. -Farmer, B. Friedlander, and L. M. Hammond, *J. Org. Chem.*, 1973, **38**, 3145.
12. C.G.Swain, R.B.Moseley, and D.E.Bown, *J. Am. Chem. Soc.*, 1955, **77**, 3721
13. When $CHCl_3$ (dried with $CaCl_2$, pH = 5.0) was used as a solvent, the reaction of **1** with **2a** gave **3a** in 48 % yield. On the other hand, when $CHCl_3$ (dried with CaH_2, pH = 5.5) was used, the reaction gave **3a** in 37 % yield. This fact suggested that the acidic nature of the solvent had a significant influence on the reaction.
14. R. Neidlein and B. Kramer, *Chem. Ber.*, 1991, **124**, 353.
15. In the case of **2b**, which has a relatively smaller substituent, the difference of the charge density of the tropone moiety in the intermediate (**7**) seems to displays a great influence on the regioselectivity.