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Reactivity and π-Facial Selectivity of Nucleophile Addition to the Radical Cations of 7-Benzhydrylidenenorbornene Derivatives

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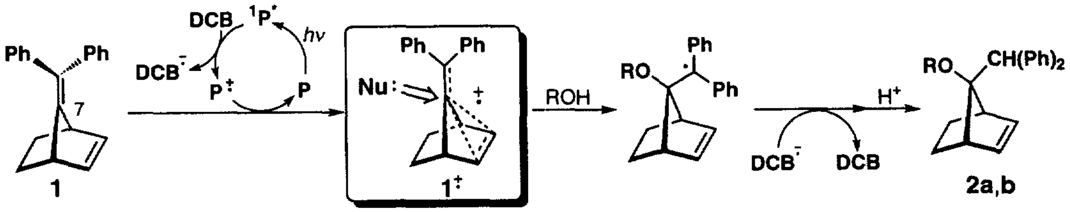
Abstract. For correlating a homoconjugation structure of a radical cation to its reactivity with a nucleophile, the reactivity and π-facial selectivity of CH_3OH and H_2O addition to the radical cations of 7-benzhydrylidenenorbornene derivatives generated by photoinduced electron transfer reactions were investigated.

Keywords: Photochemistry, electron transfer, nucleophilic addition, 7-benzhydrylidenenorbornene

The radical cation of 7-benzhydrylidenenorbornene (**1**), generated by a photoinduced electron transfer reaction using a mediator (phenanthrene) in acetonitrile, undergoes a stereoselective addition of a nucleophile at the C7 position from the *anti* face to the endo olefin (Scheme 1) [1]. This stereoselective reactivity of the radical cation $\mathbf{1}^{+\bullet}$ has been explained by a non-classical cation character caused by the homoconjugative interaction between two double bonds. In the structure of **1**, the 7-benzhydrylidene group works as a good electron donor and a probe for investigating a π-facial selectivity of nucleophilic attack to the radical cation [2]. The reactivity of a radical cation species with a nucleophile has attracted much attention in the viewpoints of organic synthesis [3,4], physical [5], and theoretical chemistry [6]. In this paper, we focus on the relationship between the structure of a homoconjugation system of a radical cation and its reactivity with a nucleophile [7]. Therefore, we designed 7-benzhydrylidenenorbornane **3** and its derivatives **4-8** possessing a various π-system in the norbornane skeleton. This paper reports herein the reactivity and π-facial selectivity of the nucleophile addition to the radical cations of norbornane derivatives **1** and **3-8**.



Scheme 1
(P= phenanthrene, DCB= 1,4-dicyanobenzene, **a**: R = CH_3, **b**: R = H)

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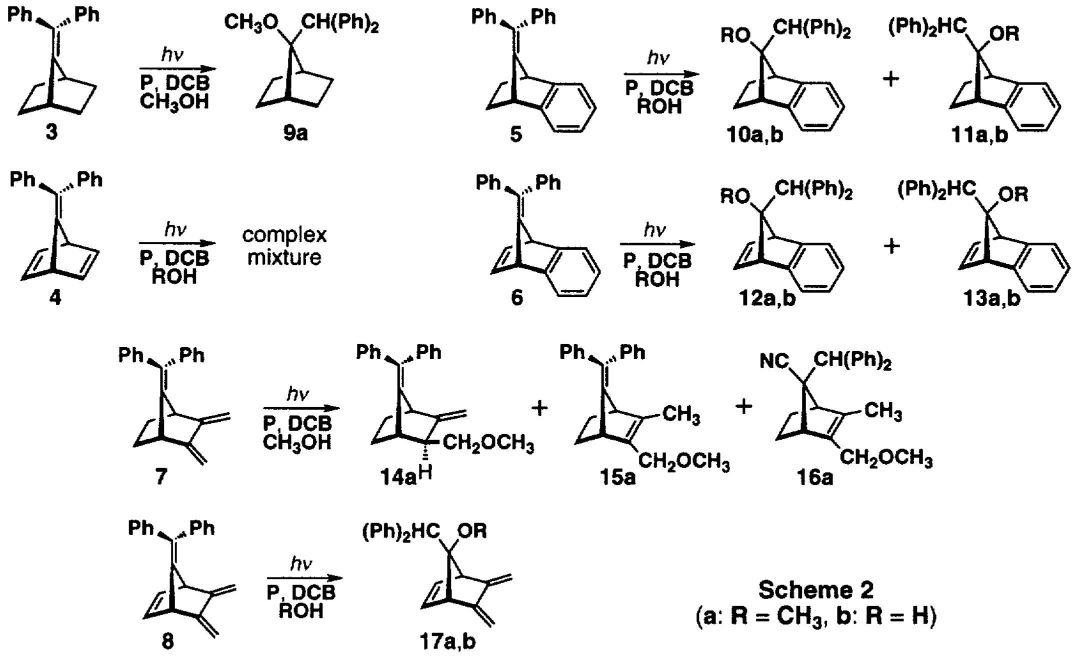


Scheme 2
(a: R = CH_3, b: R = H)

The solutions of 7-benzhydrylidenenorbornene **1** and its derivatives **3-8** (0.02 mol l^{-1}) in the presence of 1,4-dicyanobenzene (**DCB**, 0.05 mol l^{-1}) and phenanthrene (**P**, a mediator, 0.01 mol l^{-1}) in acetonitrile containing 10% v/v ROH (R= CH_3 or H) were irradiated with a high-pressure Hg lamp (100 W, $CuSO_4$ filter, $\lambda > 334$ nm) under Ar. Under these conditions, the radical cations of **1** and **3-8** were generated by indirect electron transfer according to the reported pathway as shown in Scheme 1 [1,8]. The structures of the isolated products from **3-8** were determined by their spectral properties as illustrated in Scheme 2, and the stereochemistry of the ROH adducts was confirmed by NOE or by using a shift reagent [9]. The yields were summarized in Table 1 together with the oxidation potentials of **1** and **3-8**.

Norbornene **1** gave only *anti* adduct **2a,b** with both CH_3OH and H_2O in good yields as reported previously [1]. Norbornane **3** also gave the methanol adduct **9a**, indicating that a steric effect of the norbornane skeleton doesn't inhibit the nucleophilic attack of methanol to the C7 position. Norbornadiene **4**, however, gave no remarkable ROH adduct but a mixture of various products in small amount. It is noteworthy that the conversion of **4** was lower than those of **1** and **3** under the reaction conditions. In the case of benzonorbornene **5**, the *anti* facial selectivity to the benzene moiety was observed. The photoreaction of **6** that has the character of both **1** and **5** resulted in the predominant production of **13a,b** rather than **12a,b**, indicating that the *anti* facial selectivity to the endo olefin prefers to that of the benzene moiety. The capture of the radical cation of 2,3-dimethylene-norbornane **7** by methanol gave **14a** and **15a**, showing that methanol reacted at the 2,3-dimethylene group of $7^{+\bullet}$. Product **16a** may be obtained by a secondary photoreaction [10]. On the other hand, the radical cation of **8** gave methanol adduct **17a,b** indicating that methanol attacked at the benzhydrylidene group with the *anti* selectivity to the endo olefin.

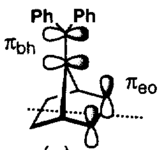
The reactivity and π-facial selectivity of the ROH addition are explained by the structures of radical cations of **1** and **3-8** based on the molecular orbital consideration in a manner similar to that for the 7-norbornenyl cation

Table 1. Yields of CH_3OH and H_2O Adducts in Phenanthrene Mediated Photoinduced Electron Transfer Reactions of **1** and **3-8**, and Their Oxidation Potentials.

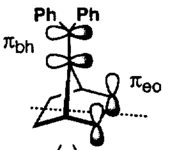
compounds	ROH	time / h	conversion / %	ROH adduct (conversion yield / %)	$E_{p/2}^{ox}$ / V[a] vs Ag / Ag+
1	CH_3OH	2	100	**2a** (85)	1.22
	H_2O	2	100	**2b** (90)	
3	CH_3OH	3	99	**9a** (88)	1.28
4	CH_3OH	3	58	0	1.06
	H_2O	3	41	0	
5	CH_3OH	3	56	**10a** (62), **11a** (8)	1.22
	H_2O	1	99	**10b** (85), **11b** (0)	
6	CH_3OH	3	62	**12a** (2), **13a** (24)	1.12
	H_2O	2	82	**12b** (9), **13b** (32)	
7	CH_3OH	3	85	**14a** (4), **15a** (9), **16a** (12)	1.24
8	CH_3OH	3	84	**17a** (27)	1.18
	H_2O	1.5	87	**17b** (45)	

[a] Measured by cyclic voltammetry in acetonitrile with tetrabutylammonium perchlorate (0.1 M) as electrolyte. The oxidative waves of **1** and **3-8** were not reversible. Their half-wave potentials were estimated by using the 100 mV/s sweep rate.

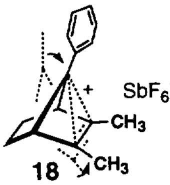
derivatives [11]. In the case of **1**, the interaction between the HOMO of the benzhydrylidene group (π_{bh}) and the HOMO of the endo olefin (π_{eo}) gives the two molecular orbitals, $\pi_1(+)$ with the bonding character and $\pi_1(-)$ with the anti-bonding character [12]. The orbital $\pi_1(-)$ is the HOMO of **1**, and a single electron oxidation of **1** loses one electron from $\pi_1(-)$. Therefore, the bonding interaction of $\pi_1(+)$ would become a dominant character of radical cation $\mathbf{1}^{+\bullet}$ compared to the anti-bonding interaction of $\pi_1(-)$, resulting in a deformed structure of $\mathbf{1}^{+\bullet}$ similar to that of 7-norbornenyl cation **18** [13], which causes the *anti*-selective nucleophilic capture. Similarly, radical cation $\mathbf{4}^{+\bullet}$ is expected to have an efficient interaction between the norbornadiene part and the benzhydrylidene group [12], which leads to a low oxidation potential of **4**, although an isolable product was not obtained [7a,14]. The *anti* selective nucleophilic capture of radical cation $\mathbf{5}^{+\bullet}$ is explained by the molecular orbital interaction between the benzene moiety and the benzhydrylidene group [15], in which the boning interaction of $\pi_5(+)$ would work as a dominant character of radical cation $\mathbf{5}^{+\bullet}$ compared to the corresponding anti-boning interaction. The stereo-selective nucleophilic capture of radical cation $\mathbf{6}^{+\bullet}$ suggests that the interaction ($\mathbf{6}^{+\bullet}$**-A**) between the benzhydrylidene group and the endo olefin stabilizes the radical cation more than the interaction ($\mathbf{6}^{+\bullet}$**-B**) between the benzhydrylidene group and the benzene moiety, because a homoconjugative interaction in $\mathbf{6}^{+\bullet}$**-B** decreases the aromatic character of the benzene moiety. A molecular orbital interaction between the HOMO of the benzhydrylidene group (π_{bh}) and the HOMO of 2,3-dimethylene moiety (π_{dm}) in **7** is shown in π_7. Since



$\pi_1(+)$



$\pi_1(-)$



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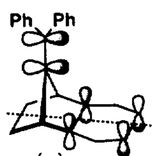
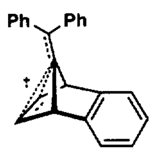
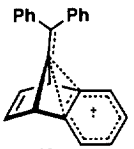


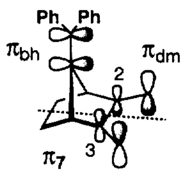
$\pi_5(+)$



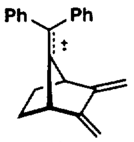
$\mathbf{6}^{+\bullet}$**-A**



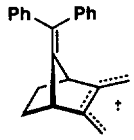
$\mathbf{6}^{+\bullet}$**-B**



π_7



$\mathbf{7}^{+\bullet}$**-A**



$\mathbf{7}^{+\bullet}$**-B**

π_{dm} has a node between C2 and C3, the interaction between π_{bh} and π_{dm} is non-bonding [15]. And it was reported that the value of the first ionization potential of 2,3-dimethylenenorbornane (8.41 eV) [16] is close to that of 1,1-diphenylethylene (8.25 eV) [17]. Therefore, the radical cation of **7** may have dual character of the localized radical cation of benzhydrylidene group (**7**$^{+\bullet}$**-A**) and the localized radical cation of 2,3-dimethylene moiety (**7**$^{+\bullet}$**-B**). Since the 2,3-dimethylene moiety is sterically less hindered than the benzhydrylidene group, a nucleophilic capture of **6**$^{+\bullet}$ takes place at the 2,3-dimethylene moiety in preference to the benzhydrylidene group, to give **14a** and **15a**. In the case of radical cation **8**$^{+\bullet}$, the effective homoconjugative interaction between the benzhydrylidene group and the endo olefin leads to the *anti* selective nucleophilic capture of **8**$^{+\bullet}$ to the endo olefin. In summary, among the π–π interactions in the radical cations of **1** and **4-8**, the interaction between the benzhydrylidene group and the endo olefin induces the efficient nucleophilic capture of a radical cation at the benzhydrylidene group with the *anti* selectivity to the endo olefin.

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[9] All products gave satisfactory spectroscopic data. For example, **12a**: colorless cubes: mp 145-146 °C; IR (KBr) ν 2810, 1600, 1495,1445 cm^{-1}; ^{1}H NMR (270 MHz, acetone-d_6) δ 7.18-7.32 (12 H, m), 7.06 (2 H, dd, J= 2.9, 5.1 Hz), 6.65 (2H, dd, J= 2.2, 2.2 Hz), 3.86 (1 H, s), 3.80 (2 H, dd, J= 2.2, 2.2 Hz), 2.79 (3 H, s); HRMS (EI) Found: *m/z* 338.1663. Calcd for $C_{25}H_{24}O$: M, 338.1671. NOE was observed between the methoxy protons (2.79 ppm) and the endo olefin protons (6.65 ppm). **13a**: colorless cubes: mp 115-115.5 °C; IR (KBr) ν 2830, 1600, 1495,1450 cm^{-1}; ^{1}H NMR (270 MHz, acetone-d_6) δ 7.47-7.50 (4 H, m), 7.22-7.35 (6 H, m), 7.20 (2 H, dd, J= 2.9, 5.1 Hz), 6.91 (2H, dd, J= 2.9, 5.1 Hz), 6.83 (2 H, dd, J= 2.2, 2.2 Hz), 5.27 (1 H, s), 3.85 (2 H, dd, J= 2.2, 2.2 Hz), 2.41 (3 H, s); HRMS (EI) Found: *m/z* 338.1669. Calcd for $C_{25}H_{24}O$: M, 338.1671. NOE was observed between the methoxy protons (2.41 ppm) and the protons (6.91 and 7.20 ppm) of the benzene moiety.

[10] **16a**: colorless oil; IR (KBr) ν 2980, 2230, 1660, 1600, 1495, 1450 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.45 (4 H, m), 7.20-7.34 (6 H, m), 4.44 (1 H, s), 4.00 (1 H, d, J= 11.9 Hz), 3.93 (1 H, d, J= 11.9 Hz), 3.37 (3 H, s), 2.99 (1 H, m), 2.60 (1 H, m), 2.19 (2 H, m), 1.72 (3 H, s), 1.28 (2 H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.21, 140.91, 137.62, 133.52, 129.21, 128.96, 128.51, 128.29, 126.94, 126.88, 122.20, 66.94, 61.46, 58.47, 54.68, 51.67, 49.10, 25.75, 24.59, 12.07; (HRMS (EI) Found: *m/z* 343.1926. Calcd for $C_{24}H_{25}NO$: M, 343.1936. Generation of cyanide ion and nucleophilic capture of a radical cation by cyanide ion were reported: Arnold, D. R.; McManus, K. A.; Chan, M. S. W. *Can J. Chem.*, **1997**, *75*, 1055-1075; McManus, K. A.; Arnold, D. R. *Can J. Chem.*, **1994**, *72*, 2291-2304, and references therein.

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