Photoinduced Electron-transfer Reaction of 7-Benzhydrylidenenorbornene: Chemical Capture of a Radical Cation Intermediate with Nonclassical Cation Character

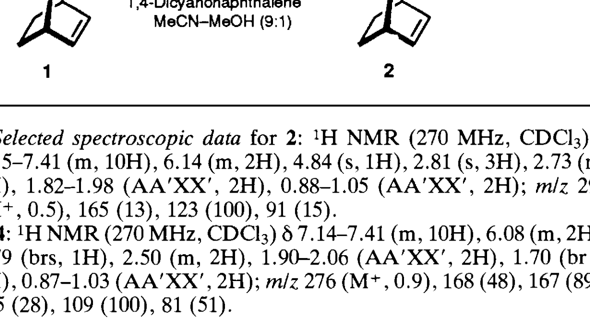
Takashi Hirano, Satoshi Shiina and Mamoru Ohashi*

Department of Applied Physics and Chemistry, The University of Electro-Communications, Chofu, Tokyo 182, Japan

A photoinduced electron-transfer reaction of benzhydrylidenenorbornene **1** as an electron donor gives the radical cation $\mathbf{1}^{+\cdot}$, which could be captured chemically by methanol or by the intramolecular hydroxy group, indicating the existence of a strong homoconjugative interaction between the exocyclic double bond and the C(2)–C(3) double bond.

7-Methylidenenorbornene and its derivatives have been investigated as models of homoconjugative interactions. The orbital splitting due to interaction between the exocyclic double bond and the C(2)–C(3) double bond of 7-isopropylidenenorbornene was confirmed by photoelectron spectroscopy,[1] and this homoconjugation causes the polarization of the exocyclic double bond observed by ^{13}C NMR spectroscopy[2] and the electronic control of stereoselective addition of singlet oxygen.[3] The chemistry of the radical cation of 7-methylidenenorbornene is also expected to be controlled by this homoconjugation.[4] Especially, the cationic nature of this radical ion will be similar to those of 7-norbornenyl cation, which has been widely investigated as the nonclassical ion, experimentally[5] and theoretically.[6] In this paper, we report highly stereoselective nucleophilic addition and intramolecular addition to the novel radical cation of 7-benzhydrylidenenorbornene **1** generated by a photoinduced electron-transfer reaction, indicating the existence of a strong homoconjugative interaction.

Upon 1,4-dicyanonaphthalene (DCN, $E_{1/2}^{red}$ −1.28 V *vs.* SCE) (saturated calomel electrode) sensitized irradiation ($h\nu \geqslant 334$ nm) of **1** (m.p. 68–69 °C, E_p^{ox} 1.50 V *vs.* SCE) in acetonitrile containing 10% of methanol under argon,† the *anti* methanol adduct **2**‡ was obtained accompanied with the diphenylmethane, and we could not obtain any *syn* methanol



1 **2**

---

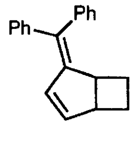
† Oxidation potentials were measured by cyclic voltammetry in acetonitrile with tetraethylammonium perchlorate (0.1 mol l^{-1}) as electrolyte.

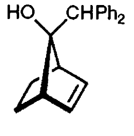
‡ *Selected spectroscopic data* for **2**: ^1H NMR (270 MHz, $CDCl_3$) δ 7.15–7.41 (m, 10H), 6.14 (m, 2H), 4.84 (s, 1H), 2.81 (s, 3H), 2.73 (m, 2H), 1.82–1.98 (AA′XX′, 2H), 0.88–1.05 (AA′XX′, 2H); *m/z* 290 (M^+, 0.5), 165 (13), 123 (100), 91 (15).

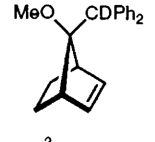
4: ^1H NMR (270 MHz, $CDCl_3$) δ 7.14–7.41 (m, 10H), 6.08 (m, 2H), 4.79 (brs, 1H), 2.50 (m, 2H), 1.90–2.06 (AA′XX′, 2H), 1.70 (br s, 1H), 0.87–1.03 (AA′XX′, 2H); *m/z* 276 (M^+, 0.9), 168 (48), 167 (89), 165 (28), 109 (100), 81 (51).

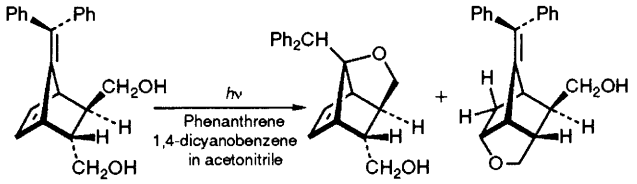
6: ^1H NMR (270 MHz, $CDCl_3$) δ 7.12–7.43 (m, 10H), 6.10 (dd, *J* 5.7, 3.0 Hz, 1H), 6.06 (ddd, *J* 5.7, 3.0, 1.4 Hz, 1H), 4.42 (s, 1H), 4.08 (d, *J* 6.6 Hz, 1H), 3.81 (br d, *J* 6.6 Hz, 1H), 3.41 (dd, *J* 11, 7 Hz, 1H), 3.37 (dd, *J* 11, 8 Hz, 1H), 2.87 (m, 1H), 2.60 (m, 1H), 2.31 (ddd, *J* 8.1, 8.1, 5.1 Hz, 1H), 1.83 (br s, 1H), 1.41 (OH); *m/z* 318 (M^+, 26), 196 (25), 167 (72), 165 (40), 152 (32), 151 (100), 104 (50), 91 (29).

7: ^1H NMR (270 MHz, $CDCl_3$) δ 7.10–7.34 (m, 10H), 4.49 (dd, *J* 7.3, 5.1 Hz, 1H), 3.90 (dd, *J* 8.1, 4.0 Hz, 1H), 3.84 (d, *J* 8.1 Hz, 1H), 3.44–3.58 (m, 2H), 3.11 (br dd, *J* 5, 5 Hz, 1H), 2.61 (d, *J* 3.7 Hz, 1H), 2.22 (m, 1H), 2.00 (ddd, *J* 13.2, 7.3, 3.7 Hz, 1H), 1.71 (td, *J* 7.1, 2.2 Hz, 1H), 1.52 (OH), 1.40 (d, *J* 13.2 Hz, 1H); *m/z* 319 (M^+ + 1, 25), 318 (M^+, 100), 243 (40), 215 (33), 167 (53), 165 (54), 91 (51).

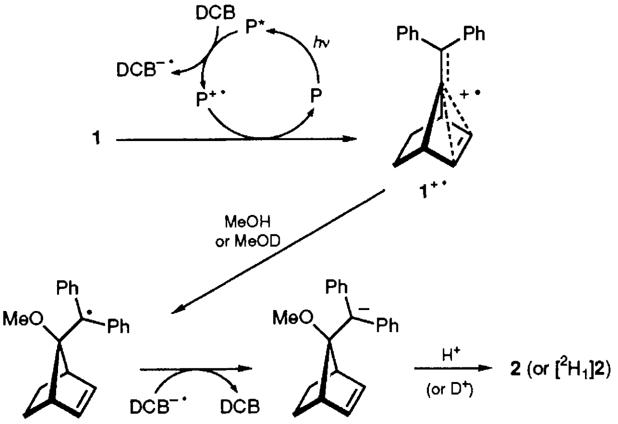

3


4


[$^2H_1$]2



5 **6** **7**



P: Phenanthrene
DCB: 1,4-Dicyanobenzene

Scheme 1

adduct. Prolonged irradiation gave diphenylmethane as the major product along with the consumption of **2**, indicating that diphenylmethane was the secondary product of the photoreaction of **2**. The stereochemistry of the methoxy group of **2** could be confirmed by NMR spectroscopy using the shift reagent [Eu(fod)$_3$]. The fluorescence of DCN was efficiently quenched by **1** at the rate of $k_q = 1.3 \times 10^{10}$ mol^{-1} l s^{-1} in acetonitrile. With direct irradition (*hv* 254 nm) of **1** under the same conditions, however, no methanol addition could be observed and 4-benzhydrylidenebicyclo[3.2.0]hept-2-ene **3** was obtained as the major product. These results suggest that the formation of **2** under DCN-sensitized photoreaction of **1** proceeds *via* the radical cation $\mathbf{1}^{+\bullet}$ generated by an electron-transfer process. Since the ether **2** (E_p^{ox} 1.70 V *vs.* SCE) is also a good electron donor, the secondary electron-transfer reaction of **2** proceeds to give diphenylmethane, which is similar to the photoinduced electron-transfer reaction of 2,2-diphenylethyl ether derivatives reported by Arnold.[7]

The phenanthrene (mediator) sensitized irradiation of **1** in the presence of 1,4-dicyanobenzene (DCB) in similar conditions improved the yield of methanol adduct **2** (85%), although **1** was completely recovered in the absence of methanol, which shows the radical cation $\mathbf{1}^{+\bullet}$ to be the stable intermediate under these conditions. Similar photolysis of **1** in the presence of water gave *anti* alcohol **4**‡ stereoselectivity in 70% yield. The formation of these adducts was not observed in the absence of DCB. To obtain mechanistic information, the same photoreaction of **1** in the presence of MeOD was carried out to give the adduct [^{2}H]**2**, which possessed deuterium at C(8) exclusively, indicating that the hydroxy group of methanol was the proton source. This together with the fact that DCB is the effective quencher of the phenanthrene excited single state and that the oxidation potential of **1** is lower than that of phenanthlene ($E_{\frac{1}{2}}^{ox}$ 1.58 V *vs.* SCE) support the mechanism proposed as shown in Scheme 1. Because product **2** has a higher E^{ox} value than that of phenanthrene, secondary reaction of **2** was suppressed under these conditions.

The anti-Markovnikov formation of the alcohol adduct **2** matches with the known nucleophilic trapping of the 1,1-diarylethylene radical cation with alcohol,[8] and the observed highly stereoselective formation of the *anti* adduct indicates the existence of unequivocal homoconjugative overlap between the 7-benzhydrylidene group and the C(2)–C(3) double bond of $\mathbf{1}^{+\bullet}$. For supporting evidence of this homoconjugation, we investigated the intramolecular hydroxy addition reaction of diol **5**. Under phenanthrene-sensitized irradiation of **5** in the presence of DCB in acetonitrile under argon, two cyclized ethers **6**‡ and **7**‡ were obtained in 42 and 19% yields, respectively. The generation of ether **7** accompanied by the anti-Markovnikov addition product **6** indicated clearly that the cationic nature of radical cation $\mathbf{5}^{+\bullet}$ was delocalized on the C(2)–C(3) double bond.

In conclusion, this work demonstrates the *anti*-stereoselective capture of radical cation of 7-benzhydrylidenenorbornene by methanol as well as its intramolecular hydroxy group addition reaction. The formation of each product provides for the first time the direct confirmation of the existence of homoconjugative interaction between the *exo* methylene double bond and the C(2)–C(3) double bond of the radical cation $\mathbf{1}^{+\bullet}$, possessing a nonclassical cation character.

The authors gratefully acknowledge financial assistance provided by a Grant-in-aid for Cooperative Research by the Ministry of Education, Science and Culture of Japan (No. 03303001).

Received, 27th July 1992; Com. 2/04020D

References

1 E. Heilbronner and H.-D. Martin, *Helv. Chim. Acta*, 1972, **55**, 1490.
2 R. W. Hoffmann and H. Kurz, *Chem. Ber.*, 1975, **108**, 119.
3 K. Okada and T. Mukai, *J. Am. Chem. Soc.*, 1978, **100**, 6509; L. A. Paquette, L. W. Hertel, R. Gleiter and M. Böhm, *J. Am. Chem. Soc.*, 1978, **100**, 6510.
4 Homocojugative interaction of radical cation species of 9-methylenebicyclo[4.2.1]nonatriene derivatives have already been investigated by CIDNP; C. J. Abelt and H. D. Roth, *J. Am. Chem. Soc.*, 1986, **108**, 6734.
5 The pioneering kinetic study; S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, *J. Am. Chem. Soc.*, 1955, **77**, 4183; S. Winstein and M. Shatavsky, *J. Am. Chem. Soc.*, 1956, **78**, 592; W. G. Woods, R. A. Carboni and J. D. Roberts, *J. Am. Chem. Soc.*, 1956, **78**, 5653. NMR investigation; R. K. Lustgarten, M. Brookhart, S. Winstein, P. G. Gassman, D. S. Patton, H. G. Richey, Jr. and J. D. Nichols, *Tetrahedron Lett.*, 1970, 1699; G. A. Olah and G. Liang, *J. Am. Chem. Soc.*, 1975, **97**, 6803; recent X-ray crystal structure analysis; T. Laube, *J. Am. Chem. Soc.*, 1989, **111**, 9224.
6 M. Bremer, K. Schötz, P. v. R. Schleyer, U. Fleischer, M. Schindler, W. Kutzelnigg, W. Koch and P. Pulay, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1042; R. Houriet, T. Schwitzguebel, P.-A. Carrupt and P. Vogel, *Tetrahedron Lett.*, 1986, **27**, 37.
7 D. R. Arnold and A. J. Maroulis, *J. Am. Chem. Soc.*, 1976, **98**, 5931.
8 R. A. Neuteufel and D. R. Arnold, *J. Am. Chem. Soc.*, 1973, **95**, 4080; T. Majima, C. Pac, A. Nakasone and H. Sakurai, *J. Am. Chem. Soc.*, 1981, **103**, 4499; S. L. Mattes and S. Farid, *J. Am. Chem. Soc.*, 1986, **108**, 7356.