Bull. Chem. Soc. Jpn., 72, 1049—1055 (1999)

Study of Reactive Intermediates in Photoinduced Electron Transfer Anti-Markovnikov Addition of Methanol to 1-Phenylcycloalkenes

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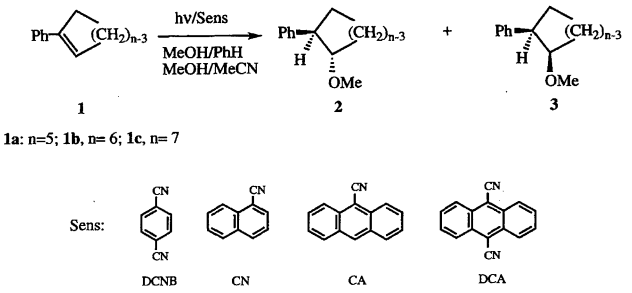
(Received October 19, 1998)

Irradiation of 1-phenylcycloalkenes (**1**) with cyanoaromatics as electron-accepting sensitizers in MeCN and PhH containing 1.0 M MeOH gave *trans*- (**2**) and *cis*-isomers (**3**) of anti-Markovnikov adducts. It was found that the isomer ratio of **2/3** depended on the ring size of **1** and solvent polarity, but not on the sensitizers used. The mechanisms for adduct formation in MeCN and PhH were studied by means of fluorescence spectroscopy, pulse radiolysis, and semiempirical molecular orbital calculation (PM3) and are discussed on the basis of the reactivities of the three kinds of intermediates involved in the reaction [cation radicals of **1** ($\mathbf{1}^{\bullet+}$), free radicals generated by addition of MeOH to $\mathbf{1}^{\bullet+}$, and carbanions produced by reduction of the free radicals by anion radicals of the sensitizers]. On the basis of the results obtained by the calculation, it is concluded that the ratio of **2/3** in MeCN is dependent on the structures and stabilities of the radicals and carbanions, while for PhH the formation of exciplex between **1** and the sensitizers causes *cis* addition of MeOH to **1** due to steric hindrance, finally to yield **2** as the predominant adduct.

Since Neunteufel and Arnold achieved anti-Markovnikov nucleophilic addition of alcohol to aromatic acyclic alkene through photoinduced electron transfer (PET) reaction,[1] addition and cycloaddition reactions through PET have aroused considerable interest among photochemists.[2] The reaction mechanism has been satisfactorily explained by processes involving the three kinds of reactive intermediates: a cation radical of the alkene initially generated by PET reaction, a free radical produced by nucleophilic addition of alcohol to the cation radical, and a carbanion formed by reduction of the free radical by an anion radical of the sensitizer. It has also been found that the nucleophilic addition to aromatic cycloalkenes (**1**) gave *trans*- (**2**) and *cis*-isomers (**3**) of anti-Markovnikov adducts dependent on the ring size of the starting alkenes (Eq. 1).[3] Until recently, however, no attempt has been made to study the factors determining the isomer ratio,[4,5] presumably because of the complexity of the reaction processes described above. We report here the detailed results of the PET addition of MeOH into 1-phenylcycloalkenes (**1a—c**), reinvestigated with several cyanoaromatics as sensitizers. In addition, on the basis of the results obtained by means of product analysis, fluorescence spectroscopy, pulse radiolysis, and semiempirical molecular orbital calculation (the PM3 method),[6] we propose that it is the structures and stabilities of the radical (**4**) and carbanion intermediates (**5**), generated through the PET reaction, which determine the isomer ratio of anti-Markovnikov adducts **2/3** produced in a polar solvent.



(1)

Experimental

Materials. 1-Phenylcycloalkenes (**1**) were prepared by a reaction of the corresponding cycloalkanones with phenylmagnesium bromide, followed by treatment with *p*-toluenesulfonic acid in PhH.[7] The alkenes were distilled before use. All of the solvents employed in the photochemical reactions were guaranteed reagents (Nacalai Tesque, Inc. and Wako Pure Chem. Ind., Ltd.) and distilled over calcium hydride prior to use. 9-Cyanoanthracene (CA), 9,10-dicyanoanthracene (DCA), 1-cyanonaphthalene (CN), and 1,4-dicyanobenzene (DCNB) were purified by recrystallization.

Electrochemical and Spectroscopic Measurements. Oxidation and reduction potentials vs. Ag/AgCl in MeCN were obtained as previously reported.[8] Emission spectra and fluorescence lifetime were measured using a Shimadzu RF-5300PC spectrofluorophotometer and a Horiba NAES-700 time-resolved photolumines-

cence and fluorescence spectrometer, respectively.

Pulse Radiolysis. The L-band linear accelerator at Osaka University was used as the source of electron pulse, with an energy value of 28 MeV, pulse width of 8 ns, and dose of 0.7 kGy per pulse. The diameter of the electron beam spot on the surface of the cell was ca. 3 mm. A 450-W xenon lamp (Osram, XBO-450) was used as the analyzing light source. The light passing through the sample solution was monitored first by using a monochromator (CVI-Laser, DIGIKROM-240) and then by a photomultiplier (Hamamatsu Photonics, R-1477). The light signal was amplified on a transient digitizer (Tektronix, 7912AD).

Molecular Orbital (MO) Calculation. The MO calculations were carried out using MOPAC Ver. 5.0 and Ver. 6.0.[6] The optimum geometries were calculated using the PM3 method from the optimized structures of neutral olefins **1** for cation radical $\mathbf{1}^{\bullet+}$ and from adducts **2** and **3** in the cases of **4** and **5**. The SCF convergence test was carried out on the total energy using the RHF/PM3 method for **1**—**3** and **5**, and the UHF/PM3 method for $\mathbf{1}^{\bullet+}$ and **4**. The convergence criterion was 1×10^{-6} and the RMS gradient was set at 0.01 kcal $Å^{-1}$ mol^{-1} (1 kcal = 4.184 kJ) as terminal condition for the calculation. RHF/PM3 method calculations using optimized structures of **2**—**5** were also performed to give the heat of formation.

Irradiation of 1 with Electron Acceptors in the Presence of MeOH. Cycloalkenes **1** (0.1 M; 1 M = 1 mol dm^{-3}) were irradiated under argon using a 400-W high-pressure mercury lamp (Riko UVL-400HA) in MeCN and PhH containing 1.0 M MeOH in a Pyrex glass tube (≥290 nm bandpass; effective excitation wavelength, 313 nm) with CN (0.05 M) or DCNB (0.01 M), or in a uranium glass tube (≥340 nm bandpass for a 366-nm light) with CA (0.001 M) or DCA (0.001 M). Anti-Markovnikov adducts (**2** and **3**) produced on reaction of MeOH with **1** were isolated by column chromatography on silica gel using hexane and benzene as eluents, and their structures were identified by means of ^{1}H and ^{13}C NMR (Bruker AC-250 spectrometer) and GCMS analysis (Shimadzu GCMS-QP1000 gas chromatograph mass spectrometer).[3] Conversion of **1**, yield of the adducts, and the isomer ratio of **2**/**3** were determined using a Shimadzu GC-8A gas chromatograph equipped with a flame ionization detector and a Chemicals Inspection & Testing Institute G-450 capillary column.

***trans*-1-Methoxy-2-phenylcyclopentane (2a):** Colorless oil; ^{1}H NMR ($CDCl_3$) δ = 1.6—1.9 (4H, m), 1.92—2.05 (1H, m), 2.1—2.23 (1H, m), 3.04 (1H, dt, J = 5.9, 8.2 Hz), 3.26 (3H, s, OCH_3), 3.79 (1H, dt, J = 4.7, 7.0 Hz), 7.15—7.38 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ = 23.2 (CH_2), 31.7 (CH_2), 33.2 (CH_2), 52.0 (CH), 57.2 (OCH_3), 89.3 (CH), 126.0 (CH), 127.3 (CH), 128.4 (CH), 144.8 (C); MS *m*/*z* 176 (M^+; 34%), 144 (77%), 129 (85%), 117 (44%), 91 (48%), 71 (100%).

***cis*-1-Methoxy-2-phenylcyclopentane (3a):** Colorless oil; ^{1}H NMR ($CDCl_3$) δ = 1.62—1.77 (1H, m), 1.80—2.1 (5H, m), 2.93—3.03 (1H, m), 3.05 (3H, s, OCH_3), 3.82 (1H, dt, J = 2.3, 4.7 Hz), 7.15—7.36 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ = 22.1 (CH_2), 29.3 (CH_2), 31.1 (CH_2), 50.7 (CH), 57.0 (OCH_3), 85.0 (CH), 126.0 (CH), 127.9 (CH), 128.8 (CH), 141.1 (C); MS *m*/*z* 176 (M^+; 40%), 144 (85%), 129 (97%), 117 (46%), 91 (52%), 71 (100%).

***trans*-1-Methoxy-2-phenylcyclohexane (2b):** Colorless oil; ^{1}H NMR ($CDCl_3$) δ = 1.15—1.60 (4H, m), 1.67—1.95 (3H, m), 2.2—2.32 (1H, m), 2.45—2.60 (1H, m), 3.1 (3H, s, OCH_3), 3.27 (1H, dt, J = 4.7, 10.6 Hz), 7.12—7.37 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ = 25.0 (CH_2), 26.1 (CH_2), 31.5 (CH_2), 34.5 (CH_2), 51.1 (CH), 56.7 (OCH_3), 83.2 (CH), 126.0 (CH), 127.6 (CH), 128.2 (CH), 145.0 (C); MS *m*/*z* 190 (M^+; 47%), 158 (36%), 130 (66%), 129 (42%), 117 (34%), 104 (37%), 91 (65%), 71 (100%).

***cis*-1-Methoxy-2-phenylcyclohexane (3b):** Colorless oil; ^{1}H NMR ($CDCl_3$) δ = 1.25—2.2 (8H, m), 2.65 (1H, dt, J = 3.5, 11.7 Hz), 3.1 (3H, s, OCH_3), 3.5 (1H, br), 7.1—7.4 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ = 19.8 (CH_2), 26.26 (CH_2), 26.31 (CH_2), 29.2 (CH_2), 48.0 (CH), 56.9 (OCH_3), 79.8 (CH), 125.9 (CH), 127.9 (CH), 128.1 (CH), 145.0 (C); MS *m*/*z* 190 (M^+; 51%), 158 (44%), 130 (69%), 129 (44%), 117 (36%), 104 (40%), 91 (69%), 71 (100%).

***trans*-1-Methoxy-2-phenylcycloheptane (2c):** Colorless oil; ^{1}H NMR ($CDCl_3$) δ = 1.45—1.95 (10H, m), 2.69 (1H, dt, J = 3.5, 9.4 Hz), 3.07 (3H, s, OCH_3), 3.36 (1H, dt, J = 4.7, 9.4 Hz), 7.13—7.33 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ = 22.2 (CH_2), 27.8 (CH_2), 29.0 (CH_2), 30.9 (CH_2), 32.8 (CH_2), 53.3 (CH), 56.9 (OCH_3), 87.0 (CH), 125.7 (CH), 127.4 (CH), 128.2 (CH), 147.7 (C); MS *m*/*z* 204 (M^+; 8%), 172 (27%), 104 (100%), 91 (42%), 81 (29%), 71 (81%).

***cis*-1-Methoxy-2-phenylcycloheptane (3c):** Colorless oil; ^{1}H NMR ($CDCl_3$) δ = 1.45—1.85 (8H, m), 2.0—2.2 (2H, m), 2.75 (1H, dt, J = 2.3, 10.6 Hz), 3.15 (3H, s, OCH_3), 3.54 (1H, dt, J = 2.3, 5.9 Hz), 7.13—7.37 (5H, m, Ph); ^{13}C NMR δ = 22.7 (CH_2), 27.4 (CH_2), 27.5 (CH_2), 29.5 (CH_2), 31.5 (CH_2), 50.6 (CH), 57.0 (OCH_3), 83.5 (CH), 125.7 (CH), 127.8 (CH), 128.0 (CH), 147.4 (C); MS *m*/*z* 204 (M^+; 8%), 172 (27%), 104 (100%), 91 (41%), 81 (29%), 71 (77%).

Results and Discussion

Production of Anti-Markovnikov Adducts 2 and 3.

a. Effect of Ring Size of 1. As can be seen in Table 1, the isomer ratio of **2**/**3** formed in MeCN for **1a** and **1c** was approximately 50 : 50, while the ratio was approximately 20 : 80 for **1b**, regardless of the sensitizers used. It was confirmed that the adducts **2a**, **b** and **3a**, **b** were photostable under the conditions employed. However, the isomer ratio of **2c**/**3c** changed with irradiation time under the conditions used; therefore, the ratio was determined before the photoreaction reached 5% conversion. These results suggest that **1a** and **1c** have similar product selectivity for the nucleophilic addition of MeOH through PET reaction.

b. Effect of Solvent Polarity. It is noteworthy that the isomer ratio of **2**/**3** in PhH, in contrast to that in MeCN, was independent of the ring size of **1**. The *trans*-isomer **2** was formed as the predominant product (**2**/**3** = 94/6—56/44; Table 1). Mizuno et al. have found that the isomer ratio of *cis*- and *trans*-adducts of MeOH to 1-phenyl-3,4-dihydronaphthalene through PET reaction was significantly affected by the polarity of the solvent used; *trans*-isomer/*cis*-isomer = 21/79 in MeCN and 76/24 in PhH.[4] This change in the ratio due to solvent polarity is in close agreement with that for **1b**; **2**/**3** = 19/81 in MeCN and 74/26 in PhH when DCNB is used as a sensitizer.

These effects on the formation of the adducts **2** and **3** suggest both that there are differences in the reactive key intermediates in MeCN and PhH, and that their structures and stabilities in MeCN depend on the ring size of **1**.

Quenching of Fluorescence. Electrochemical and kinetic data for **1** and $\mathbf{1}^{\bullet+}$ are shown in Table 2. Free energy changes (ΔG) for photoinitiated electron transfer between the sensitizers in the excited singlet state and the ground state **1** in MeCN can be calculated from the data by using Weller's equation (Eq. 2), where $E(\mathbf{1}^{\bullet+}/\mathbf{1})$ is the oxidation

Table 1. Effects of Ring Size of **1**, Solvent Polarity, and Sensitizers on the Formation of anti-Markovnikov Adducts (**2** and **3**) through Photoinduced Electron Transfer Reaction[a)]

1	Ring size	Sensitizers[b)]	Conversion of 1/%		Yield of adducts 2 and 3/%		Isomer ratio, 2/3	
			MeCN	PhH	MeCN	PhH	MeCN	PhH
1a	n=5	CN	75	24	26	5	53/47	75/25
		DCNB	50	31	9	13	53/47	87/13
		CA	13	4	2	—	43/57	—
		DCA	46	14	1	7	49/51	71/29
1b	n=6	CN	85	26	57	10	22/78	56/44
		DCNB	15	16	41	48	19/81	74/26
1c	n=7	CN	96	54	54	6	60/40[c)]	90/10
		DCNB	31	80	15	5	53/47	94/6

a) For deaerated MeCN and PhH solutions containing **1** (0.1 M), a sensitizer, and MeOH (1.0 M). b) CN = 1-cyanonaphthalene, 0.05 M; DCNB = 1,4-dicyanobenzene, 0.01 M; CA = 9-cyanoanthracene, 0.001 M; DCA = 9,10-dicyanoanthracene, 0.001 M. c) The isomer ratio of **2c/3c** changed with irradiation time under the conditions used; therefore, the ratio was determined before the photoreaction reached 5% conversion.

Table 2. Electrochemical and Kinetic Data for 1-Phenylcycloalkenes and their Cation Radicals

1	$E(\mathbf{1}^{\bullet+}/\mathbf{1})$/V[a)]	ΔG / eV[b)]				$k_q\tau$[d)]	k_q[e)]	k_o[f)]	k_{MeOH}[g)]
		CN (-1.93)[c)]	DCNB (-1.57)[c)]	CA (-1.40)[c)]	DCA (-0.89)[c)]	M^{-1}	$M^{-1}\,s^{-1}$	s^{-1}	$M^{-1}\,s^{-1}$
1a	1.61	−0.27	−1.08	−0.01	−0.44	108	1.6×10^{10}	6.9×10^{6}	7.7×10^{8}
1b	1.64	−0.22	−1.03	0.04	−0.39	105	1.6×10^{10}	5.7×10^{6}	1.4×10^{8}
1c	1.63	−0.25	−1.06	0.01	−0.42	107	1.6×10^{10}	6.3×10^{6}	2.4×10^{8}

a) Irreversible oxidation potentials of **1** vs. Ag/AgCl in MeCN. b) Free energy change (ΔG) in the electron transfer process between singlet sensitizers and **1**, calculated using Weller's equation (Ref. 9), and excited singlet state energies of sensitizers [Ref. 16: E_{Sens}/eV = 3.75 (CN), 4.2 (DCNB), 2.96 (CA), and 2.88 (DCA)]. c) Reduction potentials of sensitizers [E(Sens/Sens$^{\bullet-}$)/V] vs. Ag/AgCl in MeCN [Ref. 16: E(Sens/Sens$^{\bullet-}$)/V = −1.98 (CN), −1.60 (DCNB), −1.39 (CA), and −0.89 (DCA) vs. SCE in MeCN]. d) Slope of linear Stern–Volmer plot for fluorescence lifetime (τ) of CN measured in MeCN vs. concentration of **1**. e) Quenching rate constants of excited singlet CN by **1**, calculated using τ = 13.1 ns in MeCN. f) Observed decay rate constants of $\mathbf{1}^{\bullet+}$ in the absence of MeOH. g) Reaction rate constants of MeOH with $\mathbf{1}^{\bullet+}$ generated by pulse radiolysis of **1** in n-BuCl at room temperature, obtained by plotting decay rate constants of $\mathbf{1}^{\bullet+}$ observed (k_{obsd}) vs. initial concentration of MeOH (See Fig. 2).

potential of **1**, E(Sens/Sens$^{\bullet-}$) is the reduction potential of a sensitizer, and E_{Sens} is the energy of the excited singlet state of the sensitizer.[9)] The results indicate that the first electron transfer process is largely exothermic, except for CA (ΔG = −0.01—+0.04 eV). Therefore, CA would have been the most inefficient sensitizer for the present PET reaction. By contrast, excited singlet CN, the most efficient sensitizer used in this study, was quenched by **1** at the diffusion controlled rate (1.6×10^{10} $M^{-1}\,s^{-1}$) regardless of the ring size of **1**.

$$\Delta G = E(\mathbf{1}^{\bullet+}/\mathbf{1}) - E(\text{Sens}/\text{Sens}^{\bullet-}) - E_{Sens} - 0.06\ \text{eV}. \quad (2)$$

Mechanism for the Photoreaction in MeCN. The reaction mechanism for the formation of anti-Markovnikov adducts **2** and **3** in MeCN, shown in Eqs. 3, 4, 5, and 6, follows that originally proposed by Arnold et al.[1)] PET reaction between the excited singlet sensitizer (^{1}Sens*) and the ground state **1** gives $\mathbf{1}^{\bullet+}$ and an anion radical of the sensitizer (Sens$^{\bullet-}$), followed by the addition of MeOH to $\mathbf{1}^{\bullet+}$ to generate free radical **4** as the second intermediate. The reduction of **4** by Sens$^{\bullet-}$ might produce carbanion **5** as the third intermediate. Finally, protonation of **5** produces **2** and **3**.

$$\mathbf{1} + {}^1\text{Sens}^* \xrightarrow{\Delta G} \mathbf{1}^{\bullet+} + \text{Sens}^{\bullet-} \quad (3)$$

$$\mathbf{1}^{\bullet+} + \text{MeOH} \longrightarrow \underset{\mathbf{4}}{\text{Ph}(\bullet)\text{-}(\text{CH}_2)_{n-3}\text{-CH(OMe)}} \quad (4)$$

$$\mathbf{4} + \text{Sens}^{\bullet-} \xrightarrow{\Delta G'} \underset{\mathbf{5}}{\text{Ph}(\ominus)\text{-}(\text{CH}_2)_{n-3}\text{-CH(OMe)}} \quad (5)$$

$$\mathbf{5} + \text{H}^+ \longrightarrow \mathbf{2} + \mathbf{3} \quad (6)$$

a. Effect of Sensitizers. The isomer ratio of **2/3** in MeCN is independent of the sensitizers used for the same alkene. The adducts **2** and **3** were the major products and with our methods of analysis no other products were detected. With respect to the yields of the adducts, CN and DCNB proved to be more efficient sensitizers than CA and DCA, as can be seen in the case of **1a**. In particular, the amount of **1a** converted in the presence of CA was definitely lower than for the other sensitizers; however, the production of **2a** and **3a** was nevertheless a major reaction. On the other hand, the quantity of **1a** converted in MeCN with DCA was almost the same as that with DCNB (46 and 50%, respectively);

although the yield of the adducts for DCA was considerably lower than that for DCNB (1 and 9%, respectively), probably due to the formation of polymeric products.

The free energy change ($\Delta G'$) associated with the second electron transfer process between **4** and $Sens^{\bullet -}$ to give **5** (Eq. 5) was estimated using the reduction potential of 1-methyl-1-phenylethyl radical ($E_{red} = -1.73$ V vs. SCE)[10] and Eq. 7. According to $\Delta G'$ calculated, the second electron transfer process must be largely endothermic for DCA ($\Delta G' = +0.78$ eV) and only the anion radical of CN would be able to reduce the free radicals ($\Delta G' = -0.31$ eV). This result shows that the quantity of **1a** converted in the presence of DCA was relatively high (46%) while yield of **2a** and **3a** was quite low (1%), because the first electron transfer process between excited singlet DCA and **1a** is largely exothermic ($\Delta G = -0.44$ eV).

$$\Delta G' = E(\text{Sens}/\text{Sens}^{\bullet -}) - E_{red} - 0.06 \text{ eV}. \quad (7)$$

b. Reactive Intermediates. On the basis of the mechanism shown in Eqs. 3, 4, 5, and 6, we studied the reactivities and stereoselectivity of the three kinds of reactive intermediates ($\mathbf{1}^{\bullet +}$, **4**, and **5**) producing **2** and **3**, using pulse radiolysis for $\mathbf{1}^{\bullet +}$ and semiempirical MO calculation for **4** and **5**. As far as we know there has as yet been no attempt to explain the stereoselectivity for PET nucleophilic addition using MO calculation, although studies of the regioselectivity for the addition using AM1 calculation have been reported.[11]

(i) Reaction of Cation Radical $\mathbf{1}^{\bullet +}$ with MeOH. Transient absorption spectra of $\mathbf{1}^{\bullet +}$ were measured in *n*-BuCl by means of pulse radiolysis as shown in Fig. 1. It was found that the plots of the observed rate constants (k_{obsd}) for the decay of $\mathbf{1}^{\bullet +}$ vs. the initial concentration of MeOH ([MeOH]) gave a linear correlation (Fig. 2), as reported for the case of the styrene cation radical with MeOH.[12] According to Eq. 8, the slope of the plots represents the quenching rate constant (k_{MeOH}) for $\mathbf{1}^{\bullet +}$ by MeOH and the intercept represents the rate constant (k_o) for the decay in the absence of MeOH

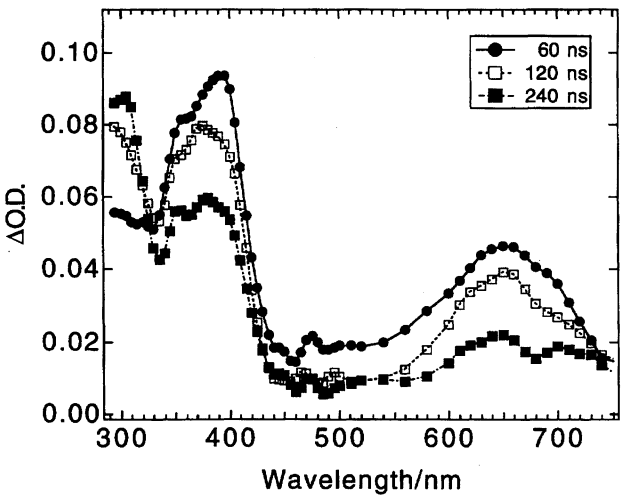


Fig. 1. Transient absorption spectra of $\mathbf{1c}^{\bullet +}$ in *n*-BuCl obtained by pulse radiolysis. The spectra of $\mathbf{1a}^{\bullet +}$ and $\mathbf{1b}^{\bullet +}$ have been reported in Ref. 13.

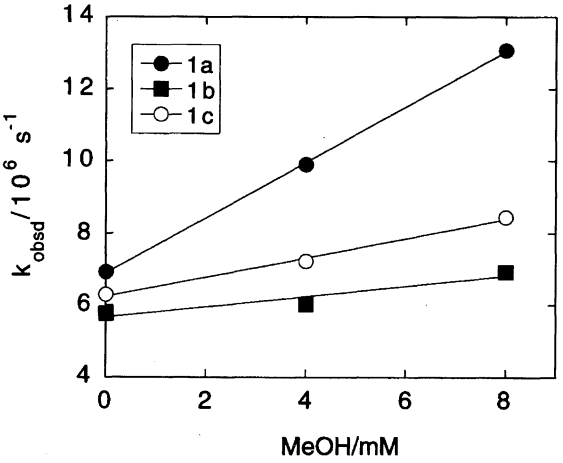


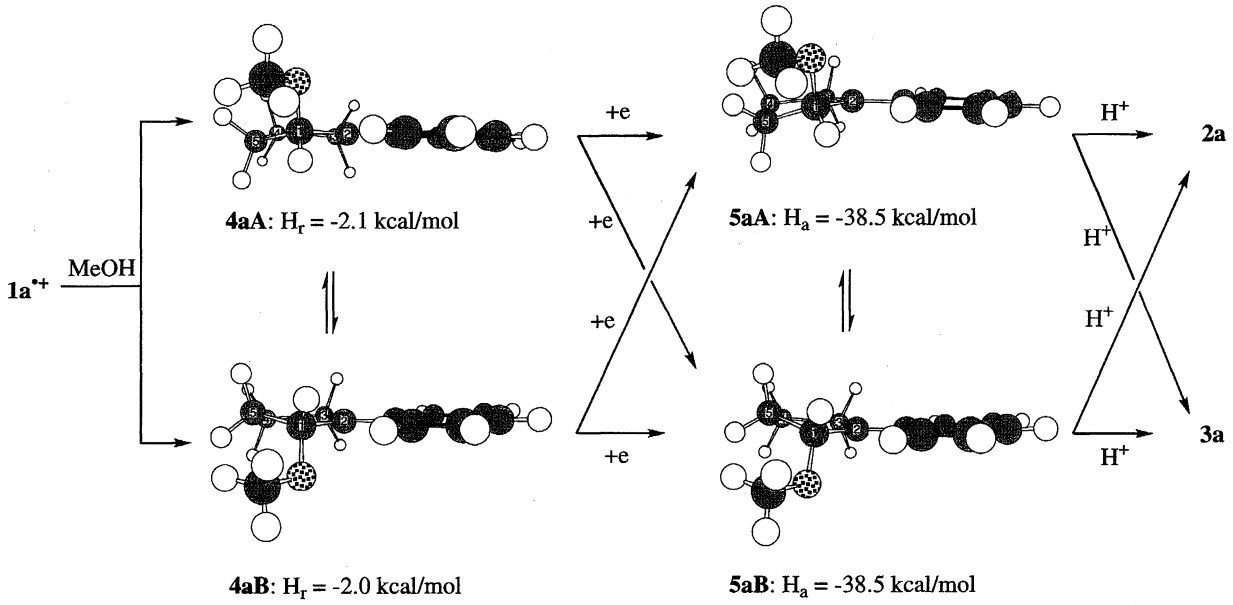
Fig. 2. Linear plot for the decay rate constant (k_{obsd}) of $\mathbf{1}^{\bullet +}$ observed vs. the concentration of MeOH.

due to the reaction with neutral precursors and/or the nucleophiles generated in *n*-BuCl e.g. Cl^-. It should be noted that the neutral alkenes **1** have similar oxidation potentials as shown in Table 2. However, k_{MeOH} depended on the ring size [**1a** (7.7×10^8 M^{-1} s^{-1}) > **1c** (2.4×10^8 M^{-1} s^{-1}) > **1b** (1.4×10^8 M^{-1} s^{-1}), Table 2]. This is probably because the cation radicals have different structures as reported for the case of the ring-size dependent dimerization of 1-phenylcycloalkene cation radicals.[13] These experiments, as well as a more detailed study of $\mathbf{1}^{\bullet +}$ and other aromatic cycloalkene cation radicals, will be reported separately.[14]

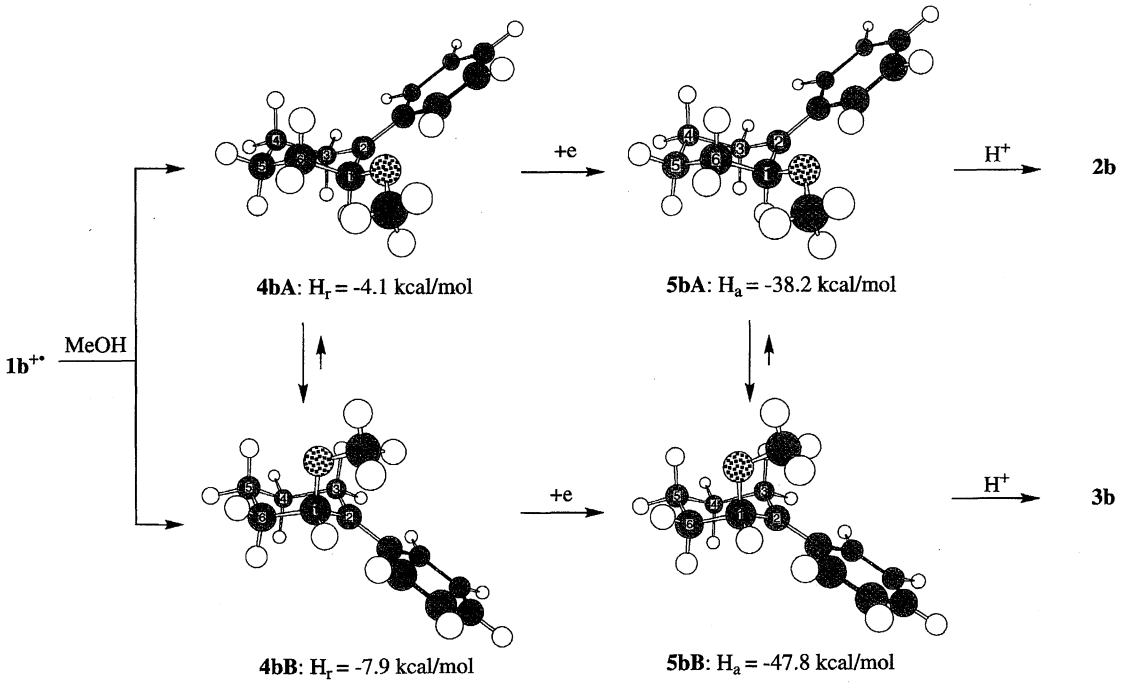
$$k_{obsd} = k_o + k_{MeOH}[\text{MeOH}]. \quad (8)$$

(ii) Free Radical 4 and Carbanion 5. As shown in Schemes 1, 2, and 3 and Table 3, the optimum structures and heat of formation (*H*) for free radicals **4** and carbanions **5** were calculated, using the PM3 method, from the optimum structures of adducts **2** and **3**. The other conformers for **4** and **5** were obtained from the structures of **5** and **4**, respectively, optimized by the above procedure. On the basis of the bond angles for the optimum structures, it seems probable that regardless of the ring size, the radical carbon and the anion carbon (C-2) attached to the phenyl group are sp^2 hybrids. Therefore, as discussed below, it is likely that the stereoselectivity for the production of **2** and **3** is due to the molecular structures of **4** and **5** dependent on the ring size, and not to hybridization of the C-2.

For **1a**, it is interesting that as can be seen in Scheme 1, the optimum structures of the corresponding free radicals (**4aA** and **4aB**) and carbanions (**5aA** and **5aB**) are markedly planar; namely the phenyl group and the cyclopentane ring exist almost on the same plane. Furthermore, it should be noted that there is no significant difference either in the stabilities of **4aA** and **4aB**, or **5aA** and **5aB** ($\Delta H_r = 0.1$ kcal mol^{-1} and $\Delta H_a = 0$ kcal mol^{-1}, respectively). Steric hindrance caused by the methoxy group might influence, to some extent, the second electron transfer from $Sens^{\bullet -}$ to **4a** to generate **5a** (Eq. 5) and the subsequent protonation of **5a** to give final products **2a** and **3a** (Eq. 6). However, it is to be expected,



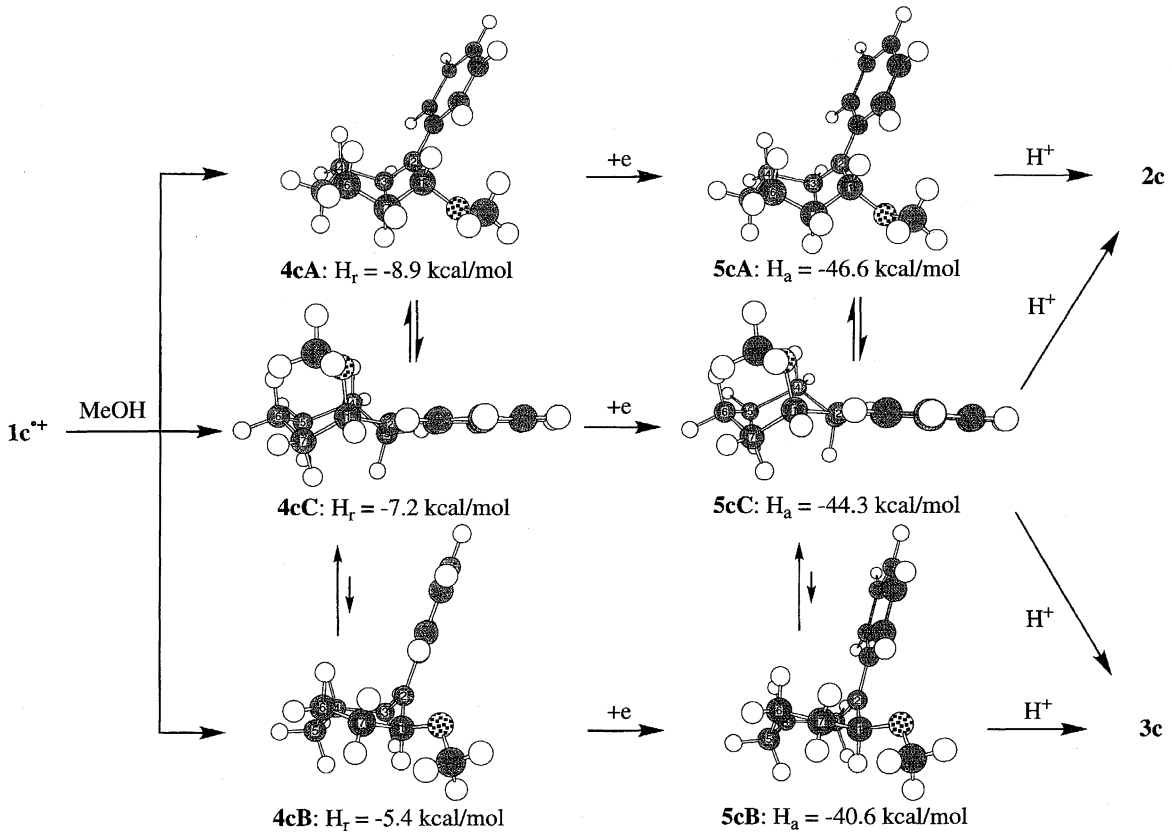
Scheme 1.



Scheme 2.

due to the markedly planar structures of **4a** and **5a**, that both processes occur either from the upper or the lower side of the phenyl group. As a result, the isomer ratio of **2a/3a** probably becomes approximately 50 : 50.

For **1b**, however, the optimum structures calculated for **4b** and **5b** show that the phenyl group causes steric repulsion toward the cyclohexane ring (Scheme 2), as suggested for the case of the PET amination of 1-phenyl-3,4-dihydronaphthalene.[15] Besides radicals **4bA** and **4bB**, other radical conformers were determined by calculation and seemed to have energy minimums between $H_r = -4.1$ and -7.9 kcal mol^{-1}. As in the case of the radicals, beside carbanions **5bA** and **5bB**, other carbanion conformers were found to have energy minimums between $H_a = -38.2$ and -47.8 kcal mol^{-1}. We have not determined the energy barriers between the conformers; however, it was noticed that, except for **5bA**, the other carbanion conformers have a methoxy group in an axial position, the configuration of which favors finally the formation of **3b**. Moreover, it is noteworthy that there are significant differences in the heat of formation between **4bA** and **4bB** ($\Delta H_r = 3.8$ kcal mol^{-1}) and between **5bA** and **5bB** ($\Delta H_a = 9.6$ kcal mol^{-1}). On the basis of the optimum structures calculated for **4b** and **5b**, it is suggested that for any conformers the second electron transfer for producing **5b** and the subsequent protonation probably occur on the carbon (C-2) attached to the phenyl group from the side with less steric



Scheme 3.

Table 3. Heat of Formation (kcal mol^{-1}) for Alkenes **1** (H_n), Cation Radicals **1**$^{\bullet+}$ (H_c), Adducts **2** and **3** (H_p), Free Radicals **4** (H_r), and Carbanions **5** (H_a)

	H_n	H_c	ΔH_c[a]	H_p		ΔH_p[b]	H_r			ΔH_r[c]	H_a			ΔH_a[d]
	1	**1**$^{\bullet+}$		**2**	**3**		**4A**	**4B**	**4C**		**5A**	**5B**	**5C**	
1a	26.9	218.9	192	−30.8	−25.4	−5.4	−2.1	−2.0	—	−0.1	−38.5	−38.5	—	0
1b	19.5	211.5	192	−36.0	−33.9	−2.1	−4.1	−7.9	—	3.8	−38.2	−47.8	—	9.6
1c	19.7	211.9	192	−35.8	−33.7	−2.1	−8.9	−5.4	−7.2	1.7[e]	−46.6	−40.6	−44.3	2.3[f]

a) $\Delta H_c = H_c - H_n$. b) $\Delta H_p = H_p(\mathbf{2}) - H_p(\mathbf{3})$. c) $\Delta H_r = H_r(\mathbf{4A}) - H_r(\mathbf{4B})$. d) $\Delta H_a = H_a(\mathbf{5A}) - H_a(\mathbf{5B})$. e) $\Delta H_r = H_r(\mathbf{4C}) - H_r(\mathbf{4A})$. f) $\Delta H_a = H_a(\mathbf{5C}) - H_a(\mathbf{5A})$.

hindrance from the cyclohexane ring and the methoxy group. From these results, we conclude that the difference in the stabilities of **5bA** and **5bB** probably determines the isomer ratio of **2b/3b** in MeCN, but not that of **2b** and **3b** ($H_p = -36.0$ and -33.9 kcal mol^{-1}, respectively).

For **1c**, as shown in Scheme 3, three significant optimum structures for **4c** and **5c** with different energy minimums were obtained by calculation. The results suggest that free radical **4cA** ($H_r = -8.9$ kcal mol^{-1}; dihedral angle (θ) of C1–C2–C3–C4 $\approx 86°$; the numbers denoting carbon atoms are shown in Scheme 3) and carbanion **5cA** ($H_a = -46.6$ kcal mol^{-1}; $\theta \approx 88°$) inclined by their structures to yield **2c** as the final product are more stable than isomer radical **4cB** ($H_r = -5.4$ kcal mol^{-1}; $\theta \approx 81°$) and carbanion **5cB** ($H_a = -40.6$ kcal mol^{-1}; $\theta \approx 81°$), the structures of which prefer to form **3c**. However, the third isomer radical **4cC** and carbanion **5cC** with relatively more planar structure ($\theta \approx 45°$ and 41°, respectively) and with energy minimums ($H_r = -7.2$ and $H_a = -44.3$ kcal mol^{-1}, respectively) between those for the above two radicals (**4cA** and **4cB**) and carbanions (**5cA** and **5cB**) were determined by calculation. The differences in the stabilities between **4cA** and **4cC** ($\Delta H_r = 1.7$ kcal mol^{-1}) and between **5cA** and **5cC** ($\Delta H_a = 2.3$ kcal mol^{-1}) are estimated to be extremely small, and it therefore seems likely that two kinds of conformers (**4cA** and **4cC**, and **5cA** and **5cC**) are significant intermediates for the PET reaction of **1c**. However, it also seems that, due to the more planar structures of **4cC** and **5cC** compared to **4cA** and **5cA**, the second electron transfer from Sens$^{\bullet-}$ to **4cC** to generate **5cC** and the subsequent protonation of **5cC** might occur faster than for **4cA** and **5cA**. Hence, as in the case of **1a**, the ratio of **2c/3c** might become approximately 50 : 50.

Mechanism for the Photoreaction in PhH. It is likely that exciplex formation of the sensitizer with **1** occurs in non-polar solvent. For DCA we actually observed the weak exciplex emission in PhH, but not in MeCN, as in the case

of 1-phenyl-3,4-dihydronaphthalene.[4] At the present stage, however, we have no further evidence with which to discuss the mechanism in detail. Therefore, we tentatively propose the following scheme. First, MeOH probably attacks the electron deficient **1** constituting the exciplex from the opposite side of the sensitizer due to steric hindrance. Secondly, if protonation of the carbanion generated takes place from the same side on which the first attack of MeOH occurred, while the sensitizer still exists near the carbanion, *trans*-isomer **2** would be formed as the predominant adduct.

Conclusion

On the basis of the results obtained by semiempirical MO calculation (PM3), we have concluded that the stereoselectivity of anti-Markovnikov adducts **2** and **3** produced through PET reaction of **1** with MeOH in MeCN probably depends on the optimum structures and stabilities of the corresponding radical and carbanion intermediates (**4** and **5**, respectively), but not on the stabilities of adducts **2** and **3**. For **1a** and **1c** the isomer ratio of **2/3** is approximately 1 : 1 because the corresponding radical and carbanion intermediates have highly planar structures; as a result, the second electron transfer from $Sens^{\bullet -}$ to **4** and the subsequent protonation of **5** generated probably occur either from the upper or the lower side of the phenyl group. In contrast, for **1b** *cis*-isomer **3** is yielded stereoselectively because carbanion **5bB** is probably more stable than its isomer carbanion **5bA** ($\Delta H_a = 9.6$ kcal mol^{-1}).

In PhH, on the other hand, steric hindrance in exciplex comprising an excited singlet sensitizer and **1**, forced *cis* addition of MeOH to **1** to give *trans*-isomer **2** as the major product.

The authors are grateful to Prof. S. Takamuku (Fukui University of Technology) and Prof. S. Yanagida (Osaka University) for their helpful discussion.

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