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Mechanism of the *cis*- and *trans*-anti-Markovnikov Addition of Methanol to 1-Phenylcycloalkenes through Photoinduced Electron Transfer

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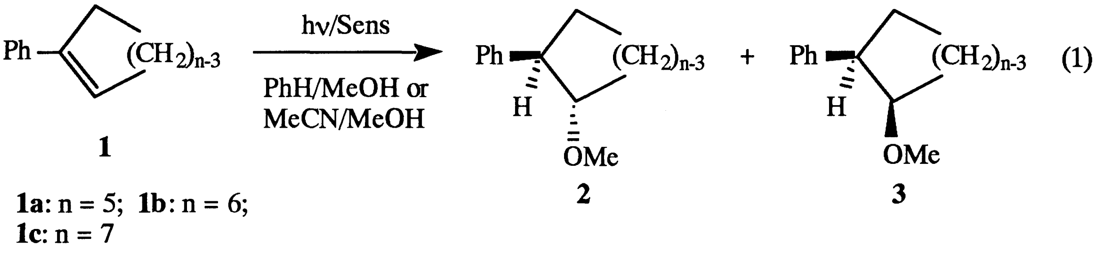
Irradiation of 1-phenylcycloalkenes with cyanoaromatics in methanol/acetonitrile and methanol/benzene solutions gives *cis*- (**2**) and *trans*-anti-Markovnikov type adducts (**3**), the ratio of which depends on both solvent polarity and the ring size of the starting olefins. The results of a semiempirical molecular orbital calculation show that the isomer ratio of **2**/**3** in acetonitrile would be determined by the stability of anion intermediates intervening in the reaction.

Photoinduced addition of nucleophiles to aromatic olefins in the presence of electron acceptors has been suggested to give anti-Markovnikov type adducts through three kinds of intermediates: the first cation radical, the second free radical, and the third anion intermediates.[1)] In the case of the cyclic olefins, *cis*- and *trans*-addition was observed; however, there have been arguments about the factors that determine the isomer ratio.[1b)] Recently, it was reported that photoaddition of nucleophiles to 1-phenyl-3,4-dihydronaphthalene in the presence of cyanoaromatics depends on the solvent polarity and the bulkiness of the nucleophiles.[2,3)] Herein we wish to report that the *cis*- and *trans*-addition of methanol to 1-phenylcycloalkenes through photoinduced electron transfer reaction depends on both solvent polarity and the ring size of the cyclic olefins, which affects the stability of anion intermediates formed in the reaction.

When 1-phenylcyclopentene (**1a**, 0.1 M; M = mol/dm^3) was irradiated using a 400-W high pressure mercury lamp in acetonitrile containing 1.0 M methanol with cyanoaromatics such as 1-cyanonaphthalene (CN, 0.05 M), 1,4-dicyanobenzene (DCNB, 0.01 M), 9,10-dicyanoanthracene (DCA, 0.001 M), and 9-cyanoanthracene (CA, 0.001 M), *cis*- and *trans*-adducts **2a** and **3a** were produced at the ratio of ca. 50/50,



1a: n = 5; **1b**: n = 6;
1c: n = 7

Table 1. Effects of Solvent Polarity, Sensitizers, and the Ring Size of Cycloolefins on the Formation of anti-Markovnikov Type Adducts (**2** and **3**) of Methanol to 1-Phenylcycloalkenes[a]

Olefin **1**	Sensitizer[b]	Conv./%		Yield of Adducts/%		Isomer Ratio (**2**/**3**)	
		MeCN	PhH	MeCN	PhH	MeCN	PhH
1a	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	CN	85	26	57	10	22/78	56/44
	DCNB	15	16	41	48	19/81	74/26
1c	CN	96	54	54	6	60/40[c]	90/10
	DCNB	31	80	15	5	53/47	94/6

a) 1.0 M MeOH was contained in the solution. b) CN= 1-cyanonaphthalene, 0.05 M; DCNB= 1,4-dicyano-benzene, 0.01 M; CA= 9-cyanoanthracene, 0.001 M; DCA= 9,10-dicyanoanthracene, 0.001 M. c) See Ref. 4.

which is similar to that obtained from 1-phenylcycloheptene (**1c**),[4] while formation of *trans*-adduct **3b** was preferred to *cis*-adduct **2b** (**2b**/**3b** ≅ 20/80) in the case of **1b** [Eq. (1) and Table 1]. By contrast, irradiation of 1-phenylcycloalkenes (**1**) in benzene under the similar conditions gave *cis*-adduct **2** more selectively than *trans*-adduct **3**, regardless of the ring size of the olefins and sensitizers used (Table 1).

Olefins **1** have substantially the same oxidation potentials (Eox = 1.61 - 1.64 V vs. Ag/AgCl). The

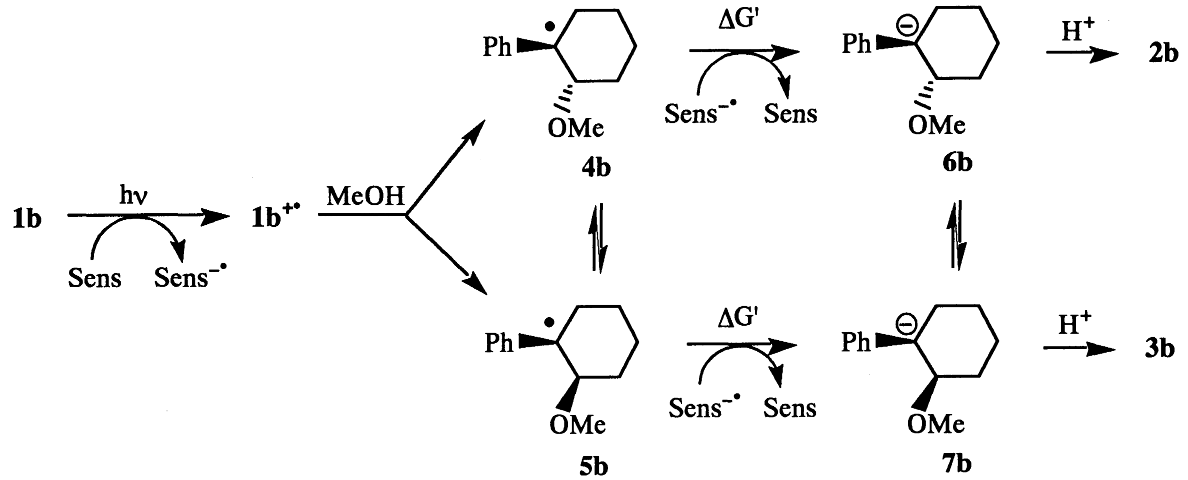
Table 2. Electrochemical, Photophysical, and Kinetic Data of Sensitizers

Sensitizer	Es/eV[a]	Ered/V		τ/ns[b]		ΔG/eV[c]	10^{-9}kq/$M^{-1}s^{-1}$[d]	
		vs. Ag/AgCl	vs. SCE[a]	MeCN	PhH		MeCN	PhH
CA	2.96	-1.40	-1.39	13.1	12.1	-0.01	3.4	1.7
DCA	2.88	-0.89	-0.89	16.2	14.6	-0.44	15.3	2.5
CN	3.75	-1.93	-1.98	6.6	8.2	-0.27	16.4	9.4
DCNB	4.2	-1.57	-1.60	-	-	-1.08	-	-

a) Ref. 7. b) Measured with a single photon counting apparatus.

c) The free energy change (ΔG) in the electron transfer process between excited singlet sensitizers and **1a**.

d) The quenching rate constant (kq) of excited singlet sensitizers by **1a** in acetonitrile and benzene.



Scheme 1. Mechanism of the addition of methanol to **1b** through photoinduced electron-transfer reaction.

free energy change in the first electron-transfer process (ΔG) between excited singlet sensitizers and **1** was estimated using a Weller's equation to be strongly exothermic, except for CA.[5] In fact, the quenching processes of the singlet excited sensitizers by **1** in acetonitrile were measured to be the diffusion-controlled rate in the cases of CN and DCA (Table 2).[6]

The olefin cation radicals ($\mathbf{1}^{+\bullet}$), generated in acetonitrile by the electron transfer reaction, react with methanol to give free radical intermediates **4** and **5** (Scheme 1). As shown in Tables 1 and 2, CN is the most effective sensitizer in the above reaction to yield adducts **2** and **3**, although ΔG is estimated to be more exothermic in the cases of DCA and DCNB rather than CN. It is probably because CN is a sole sensitizer to have a reduction potential enough to reduce free radicals **4** and **5** (Ered ≅ -1.73 V vs. SCE).[8] If the second electron transfer process is endothermic (ΔG' > 0), polymerization of **1** would be initiated by free radicals **4** and **5**, in stead of the formation of anion intermediates **6** and **7**.

Semiempirical molecular orbital calculations using the MOPAC system (the MNDO/PM3 method) were carried out to estimate the stability and the optimized structure of the adducts, the free radicals, and the anions.[9]

Table 3. The Heat of Formation (kcal/mol) for the Adducts (H), the Free Radicals (H_r), and the Anions (H_a)

	H		$\Delta H^{a)}$	H_r		$\Delta H_r^{b)}$	H_a		$\Delta H_a^{c)}$
	2	**3**		**4**	**5**		**6**	**7**	
1a	-30.8	-25.4	-5.4	-2.1	-2.0	-0.1	-38.5	-38.5	0
1b	-36.0	-33.9	-2.1	-4.1	-7.9	3.8	-38.2	-47.8	9.6
1c	-36.1	-30.6	-5.5	-6.1	-7.7	1.6	-44.3	-44.3	0

a) ΔH = H (adduct **2**) -H (adduct **3**). b) ΔH_r = H_r (radical **4**) - H_r (radical **5**).
c) ΔH_a = H_a (anion **6**) - H_a (anion **7**).

As shown in Table 3, there is no difference in the heat of formation (H_r, kcal/mol) between **4a** and **5a** as well as in that (H_a) between **6a** and **7a**; furthermore, the optimized structure of the radicals and the anions is almost planer, which suggests that they are not indistinguishable. Therefore, anti-Markovnikov type adducts **2a** and **3a** would be obtained in acetonitrile at the ratio of ca. 50/50 in the case of **1a**, although **2** is expected to be more stable than **3** in the cases of all the olefins used. It should be noticeable that similar results are given for **1c**. By contrast, a remarkable difference in H_a between **6b** and **7b** is revealed in the case of **1b** (ΔH_a = 9.6 kcal/mol), while ΔH_r between **4b** and **5b** (3.8 kcal/mol) is smaller than the ΔHa. These results indicate that the higher stability of **7b** than **6b** would favor the formation of *trans*-isomer **3b** in the polar solvent.

In fluorescence quenching of DCA by **1a**, formation of weak exciplex was observed in benzene, but not in acetonitrile, as well as in the case of DCA and 1-phenyl-3,4-dihydronaphthalene reported by Mizuno et al.2) Although emissive exciplex of CN and DCNB with **1** was not formed in benzene, there is the possibility that non emissive exciplex would exist. Thus, it would be explained that the addition of methanol to polarized exciplex or a geminate ion radical pair in solvent cage, which would have a sandwich configuration,10) occur from the opposite side of the sensitizer, because of less steric hindrance, followed by protonation to the anion intermediate from the same side, finally to give **2**.

Further studies concerning the structure and the reactivity of $\mathbf{1}^{+\bullet}$ in a polar solvent are now in progress.

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