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Photodimerization Mechanism of *m*-Methoxystyrene *via* Its Cation Radical. Open Type Dimer Cation Radical as Its Intermediate

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Synopsis. Two isomeric tetralin type dimers were obtained by UV excitation of *m*-methoxystyrene in the presence of an electron acceptor. Stepwise electrophilic dimerization mechanism through the dimer cation radical was confirmed. The scheme was analyzed with the aid of MO calculation.

Photodimerization of vinyl compounds conjugated to an aromatic nucleus (electron donors) has been studied extensively by direct photoexcitation,[1] or in the presence of electron acceptors.[2–10] In the presence of electron acceptors, vinyl compounds are photoionized in polar solvents to produce the cation radicals when either the ground state EDA complexes are photoexcited or the exciplexes are formed. The cation radical thus produced gives either [2+2] cyclobutane type dimers[2–6] or [2+4] tetrahydronaphthalene (tetralin) type dimers.[7–10] It has been shown that the dimerizations *via* cation radicals are nonconcerted and stepwise: the intermediates are 1,4-cation radicals.[2,10] However, the factor to determine the path to either cyclobutane type dimer or tetralin type dimer is still ambiguous: *N*-vinylcarbazole,[3] *p*-methoxystyrene,[5] *N,N*-dimethylaminostyrene,[6] *etc.* give mainly the former cyclobutanes; 1,1-diphenylethylene,[7] styrene, α-methylstyrene,[8] *etc.* give the latter tetralin type dimer. In this work, the reactivity of *m*-methoxystyrene cation radical was studied and this was found to give two isomers of tetralin type dimer: the one is predominant compared with the other. The mechanism is explained by the intramolecular electrophilic reaction of the 1,4-cation radical, which is supported by MO analysis.

Photoirradiation of *m*-methoxystyrene (**1**) in the presence of *m*-dicyanobenzene (**2**) in various solvents gave two isomeric tetralin type dimers:[11] 8-methoxy-1-(3-methoxyphenyl)-1,2,3,4-tetrahydronaphthalene (**3**) and 6-methoxy-1-(3-methoxyphenyl)-1,2,3,4-tetrahydronaphthalene (**4**) as shown in Table 1. Quantum yield of the dimerization in MeCN solvent (Run 1) was 0.016 with excitation wavelength of 313 nm. Effect of solvent polarity on the dimer yield and the fraction of the dimers are shown in Table 1, Runs 1, 2, and 3. In polar solvent MeCN, the rate is faster than those in less polar solvents, THF and CH_2Cl_2, and the ratio of **3**/**4** is smaller than those in less polar solvents. Runs 4, 5, and 6 show the time course of photodimerization. Dimer yields increase with irradiation time, but the ratios of **3**/**4** decrease with time. This decrease seems to be due to the variation of the partitioning between **3** and **4** with reaction time. In the limit of $t=0$, the ratio of **3**/**4** is 7.7. As for other exciplex acceptors, *p*-dicyanobenzene and dimethyl terephthalate are also effective and gave the same products with approximately the same rates and product ratios. Temperature dependence of the dimer yield was hardly observed in the range from −30 to +30 °C.

Table 1. Dimerization yields and fractions

Run	**1** / mM	**2** / mM	Solvent	Time/h	Dimer yield / %	Fraction/% **3**	Fraction/% **4**
1	37	22.4	MeCN	20	37.4	55.6	44.4
2	37	22.4	THF	20	2.2	92.1	7.9
3	37	22.4	CH_2Cl_2	20	3.0	80.9	19.1
4	149	22.4	MeCN	0.75	0.113	85.1	14.9
5	149	22.4	MeCN	1	0.378	79.9	20.1
6	149	22.4	MeCN	2	1.43	72.7	27.3

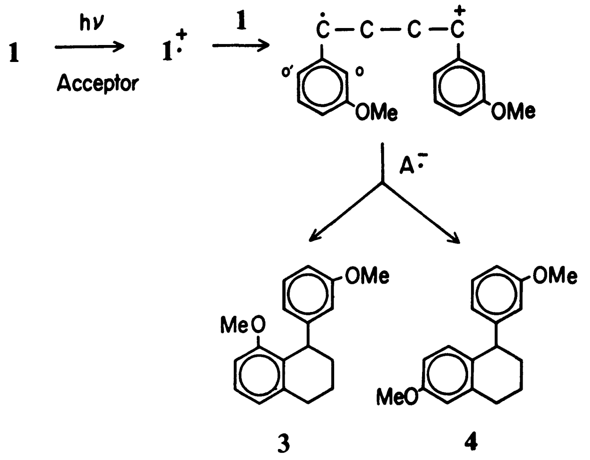

Fig. 1. Scheme.

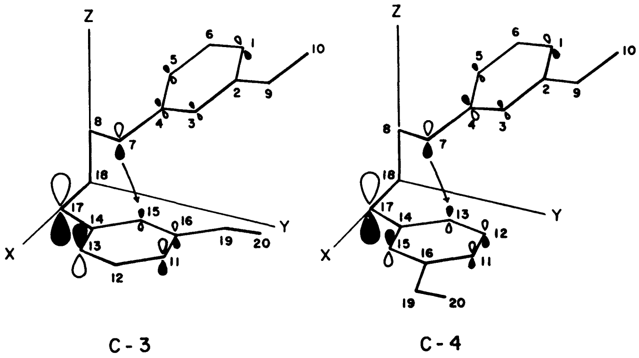

Fig. 2. 1,4-Cation radical intermediates **C-3** and **C-4** prior to $\mathbf{3}^{+\cdot}$ and $\mathbf{4}^{+\cdot}$.

The reaction scheme is shown in Fig. 1. The monomer cation radical $\mathbf{1}^{+\cdot}$ which is produced by the interaction of **1** with **2** (fluorescence quenching constant $k_q=9\times10^9\ M^{-1}\ s^{-1}$ in MeCN solvent), reacts with the monomer to form an open type dimer cation radical. Electrophilic attack of the carbenium ion to ortho-positions *o* or *o′* of phenyl ring and subsequent intramolecular proton migration give $\mathbf{3}^{+\cdot}$ and $\mathbf{4}^{+\cdot}$, respectively.[12] Back electron transfer from $\mathbf{2}^{-\cdot}$ to the dimer cation radicals gives either **3** or **4**. Yamaguchi[13] showed

Table 2. Formal charge and spin density for **C-3** and **C-4** conformations

Atom No.	**C-3**		**C-4**	
	Formal charge	Spin density	Formal charge	Spin density
C 7	0.158	0.182	0.140	0.183
C11	−0.065	0.061	−0.046	0.025
C12	0.072	−0.019	0.048	0.002
C13	−0.030	0.089	−0.052	0.016
C14	0.082	−0.035	0.085	−0.029
C15	−0.093	0.022	−0.070	0.084
C16	0.253	−0.006	0.268	−0.012
C17	0.010	0.647	0.019	0.635

by theoretical analysis that the dimerization of olefin cation radical with neutral olefin proceeds *via* open type cation radical.

Preferred formation of **3** to **4** can be estimated by the MO analysis. In this calculation, a reaction path to tetralin is assumed: **C-3** and **C-4** in Fig. 2 correspond to two conformations just before C7–C15 and C7–C13 bond formations, which lead to **3** and **4**, respectively. In Fig. 2, the coefficients of HOMO are also roughly shown by the size of lobes. Formal charge density, and total spin density of the dimer cation radical are given in Table 2. The carbenium ion was found to be at carbon 7, while the radical was at site C17 as can be seen from Table 2. The carbenium ion (C7) attacks *o* position (C15 in **C-3**) or *o*′ position (C13 in **C-4**).[12] Electron density of *o* position (C15) for **C-3** (−0.093) is higher than that of *o*′ position (C13) for **C-4** (−0.052). Formal charge at C7 for **C-3** (+0.158) is more positive than that for **C-4** (+0.140). Furthermore the AO bond population[14] between C7 and C15 in **C-3** is 0.250 and the one between C7 and C13 in **C-4** is 0.236. Therefore, it can be understood that the dimer **3** is produced more favorably than the dimer **4**. This result supports the stepwise electrophilic dimerization. In the LUMO of the styrene cation radical **1**$^{+\cdot}$, the α- and β-carbons have the same sign, but in the HOMO of styrene **1** the signs of the β- and *o*-carbons are opposite, hence these do not interact in a concerted way and the products **3** and **4** are not produced by a concerted mechanism.

Experimental

^{1}H-NMR spectra were taken on a Varian HA-100 spectrometer with TMS as an internal standard. Mass spectra were taken on a Hitachi RMU-60 mass spectrometer. Photolysis was carried out through Pyrex vessel wall with a 300 W high-pressure mercury lamp (Toshiba 300H) at room temperature. Analysis of the sample solutions was performed with a Shimadzu GC-3BF with a 1 m column packed with Apiezon grease L (230 °C), using phenanthrene as an internal standard.

8-Methoxy-1-(3-methoxyphenyl)-1,2,3,4-tetrahydronaphthalene(3): After photolysis of degassed MeCN solution of **1** and **2**, the dimer fraction was collected by silica gel column eluted with dichloromethane–hexane (1 : 1) and the fraction of **3** was collected by GLPC. Recrystallization from CCl_4–dichloromethane gave an analytical sample **3**: mp 87—90 °C; IR (KBr-pellet) 1600, 1580, 1480 (phenyl), 1245 (C–O), 870 (isolated ring H atom), 790, 770 cm^{-1} (three adjacent ring H atoms); NMR (CCl_4) δ=1.44—2.86 (m, CH_2, 6H), 3.53 (s, OCH_3, 3H), 3.67 (s, OCH_3, 3H), 4.27 (m, CH, 1H), 6.36—7.10 (m, phenyl, 8H). MS (70 eV), *m/e*: 268 (M^+, main), 160 (M^+—anisole).

6-Methoxy-1-(3-methoxyphenyl)-1,2,3,4-tetrahydronaphthalene(4): In the final separation procedure of **3** from the dimer fraction, **4** was also collected. Uncrystallized. IR (neat) 1605, 1580, 1500 (phenyl), 1250 (C–O), 870, 855 (isolated ring H atom), 830 (two adjacent ring H atoms), 780 cm^{-1} (three adjacent ring H atoms); NMR (CCl_4) δ=1.20—2.90 (m, CH_2, 6H), 3.66 (s, OCH_3, 3H), 3.69 (s, OCH_3, 3H), 3.97 (m, CH, 1H), 6.40—7.20 (m, phenyl, 8H); MS (70 eV), *m/e*: 268 (M^+, main), 160 (M^+—anisole).

Method of Calculation. The calculation was carried out with the unrestricted SCF INDO method.[15] It is assumed that the effect of the contaminating spin components of the S^2 operator is negligible. The geometry of the dimer cation radical in Fig. 2 is as follows: R(C$\overset{\cdots}{-}$C of aromatic ring)=1.40 Å, R(C4–C7)=1.47 Å, R(C7–C8)=1.51 Å, R(C8–C18)=1.54 Å, $R(\text{C–H}_{\text{aromatic}})$=1.08 Å, $R(\text{C–H}_{\text{aliphatic}})$=1.09 Å, R(C–O)=1.36 Å, ∠C17–C14–C15=110° (**C-3**), ∠C17–C14–C13=130° (**C-3**), ∠C18–C17–C14=110°, ∠C17–C18–C8=90°, ∠C18–C8–C7=100°, C7 and C17 have sp^2 shape, R(C7–C15 or C7–C13)=2.283 Å. In Fig. 2, atoms 9 and 19 are oxygen, and hydrogen atoms are not shown. The calculations were carried out on the FACOM-230-75 computer at the Computer Center of Kyoto University.

References

1) G. Kaupp, "Methoden der Organischen Chemie, Vol. IV/5a, Photochemie I (Houben-Weyl)," Georg Thieme Verlag, Stuttgart (1975), p. 278; H. F. Kauffmann, *Makromol. Chem.*, **180**, 2649, 2665, 2681, 2695 (1979).

2) S. L. Mattes and S. Farid, *Acc. Chem. Res.*, **15**, 80 (1982).

3) A. Ledwith, *Acc. Chem. Res.*, **5**, 133 (1972).

4) S. Kuwata, Y. Shigemitsu, and Y. Odaira, *J. Org. Chem.*, **38**, 3803 (1973).

5) M. Yamamoto, T. Asanuma, and Y. Nishijima, *J. Chem. Soc., Chem. Commun.*, **1975**, 53.

6) T. Asanuma, M. Yamamoto, and Y. Nishijima, *J. Chem. Soc., Chem. Commun.*, **1975**, 56.

7) R. A. Neunteufel and D. R. Arnold, *J. Am. Chem. Soc.*, **95**, 4080 (1973): T. R. Evans, R. W. Wake, and O. Jaenicke, "The Exciplex," ed by M. Gordon and W. R. Ware, Academic, New York (1975), p. 345.

8) T. Asanuma, M. Yamamoto, and Y. Nishijima, *J. Chem. Soc., Chem. Commun.*, **1975**, 608.

9) T. Asanuma, T. Gotoh, A. Tsuchida, M. Yamamoto, and Y. Nishijima, *J. Chem. Soc., Chem. Commun.*, **1977**, 485.

10) T. Gotoh, M. Yamamoto, and Y. Nishijima, *J. Polym. Sci., Polym. Lett. Ed.*, **17**, 143 (1979).

11) In the absence of **2**, the main product is *cis*-1,2-bis(3-methoxyphenyl)cyclobutane.

12) The open type cation radical could be trapped as its methoxylation product which supports electrophilic reaction. The ratio of **3**/**4** is better explained in terms of formal charge rather than spin density.

13) K. Yamaguchi, *Chem. Phys.*, **25**, 215 (1977).

14) The AO bond population proposed by Mulliken, $N_{rs}=2\sum_{j}^{occ}c_r^j c_s^j S_{rs}$ was calculated from the bond order population and the overlap integral although the overlap integral S_{rs} is not explicitly included in INDO calculation.

15) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**,2026 (1967).