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Direct and Sensitized Photoreactions of Allyl Phenyl Ether

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It has been reported that UV irradiation of allyl phenyl ether gives rearrangement products (*o*- and *p*-allylphenol) and phenol.[1-4] Although the mechanism of the photo-rearrangement has been proposed,[4] little investigation has been carried out on the excited states responsible for the formation of photo-rearrangement products and phenol. The present work deals with the effects of solvents and additives (sensitizers and quenchers) for the elucidation of the character of the excited states in the photoreaction.

Results and Discussion

Unsensitized photoreaction of allyl phenyl ether in transparent solvents is explained by reaction paths a,b,c,d, and e in Scheme 1.

The formation of a radical pair in a solvent cage is concluded from the effect of the viscosity of the solvents. Cage reactions are dependent on the viscosity (η) of solvent. The following equation was presented:[5]

$$\frac{\phi_1 + \phi_2}{\phi_1} = K_1 + \frac{K_2}{\eta} \qquad (1)$$

where ϕ_1 and ϕ_2 are the quantum yields of the reaction within and outside a solvent cage, and K_1 and K_2 are constants. In the unsensitized photoreactions of allyl phenyl ether, the equation was satisfied when allylphenols and phenol were taken as the products within and outside a solvent cage, respectively (Fig. 1).

As shown in Table 1, the quantum yields of the reactions within and outside a cage were almost independent of the presence of 1,3-pentadiene (a triplet quencher). This suggests that the unsensitized photoreaction occurs *via* excited singlet state. Photo-Fries rearrangement has been reported to proceed from excited singlet state of aryl esters.[6,7]

In the photosensitized reaction it was observed that aromatic hydrocarbons acted as sensitizers in a different way from carbonyl compounds. The photoreaction of allyl phenyl ether in aromatic hydrocarbons such as benzene and toluene satisfies Equation (1) as shown in Fig. 1. Addition of naphthalene to the cyclohexane solution of ether slightly affected the ratio of the quantum yields of the reactions within and outside a solvent cage. The reaction in benzene solution was not quenched by the addition of 1,3-pentadiene. Thus, sensitization by aromatic hydrocarbons should proceed through singlet-singlet energy transfer.

In contrast to aromatic hydrocarbons, the presence of carbonyl sensitizers (benzaldehyde, acetophenone, benzophenone and substituted benzophenones) increased the formation of phenol.

Carbonyl compounds are photo-reactive and undergo photo-induced reactions such as hydrogen abstraction

TABLE 1. EFFECTS OF ADDITIVES

Additive (mol/*l*)		E_t kcal/mol	Solv.[a]	Irr. time (hr)	ϕ_{PhOH}[b]	ϕ_o[b]	ϕ_p[b]	$\frac{\phi_o+\phi_p}{\phi_{PhOH}}$
—	—	—	C	2	0.058	0.061	0.055	2.0
—	—	—	B	5	0.045	0.036	0.038	1.7
Acetophenone	5.5×10^{-2}	74	C	2	0.054	0.0057	0.0025	0.13
Acetophenone	5.9×10^{-2}	74	B	2	0.049	0.0070	0.0064	0.28
Benzaldehyde	5.6×10^{-2}	72	C	2	0.051	0.0055	0.0029	0.17
Benzophenone	5.1×10^{-2}	69	C	2	0.026	+	+	<0.1
Benzophenone	5.0×10^{-2}	69	B	2	0.042	0.012	0.012	0.57
p,p'-Dimetoxybenzophenone	2.5×10^{-2}	70	B	2	0.076	0.019	0.012	0.41
p-Hydroxybenzophenone	1.0×10^{-1}	68	B	2	0.044	0.021	0.017	0.86
Michler's ketone	2.5×10^{-2}	61	B	2	0.027	0.0058	0.0053	0.42
Naphthalene	5.1×10^{-2}	61	C	5	0.012	0.0088	0.0089	1.5
1,3-Pentadiene	2.5×10^{-1}	59	C	5	0.033	0.028	0.030	1.8
1,3-Pentadiene	2.5×10^{-1}	59	B	5	0.043	0.032	0.028	1.4
Oxygen	—	—	C	5	0.011	0.012	0.011	2.0

a) B: 0.1 M Benzene solution, C: 0.1 M Cyclohexane solution
b) ϕ_{PhOH}, ϕ_o and ϕ_p represent the quantum yields of phenol, *o*-allylphenol and *p*-allylphenol, respectively.

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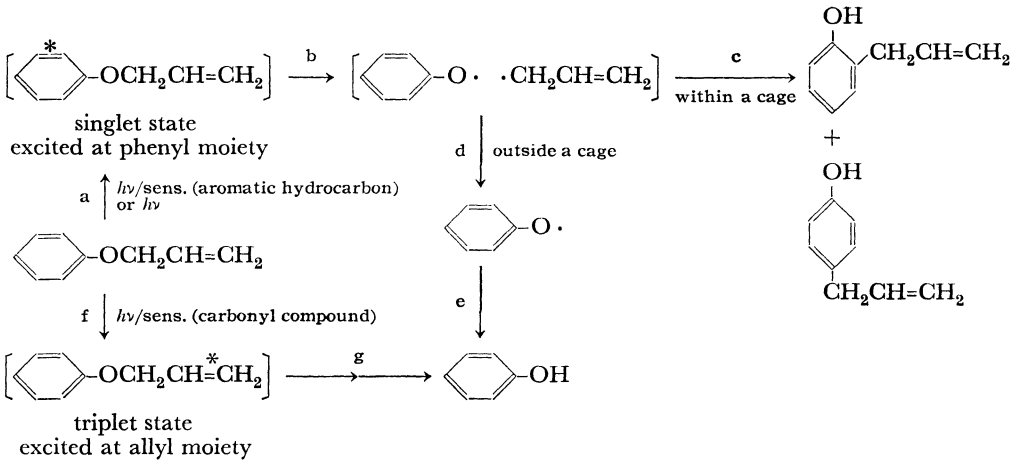

Scheme 1

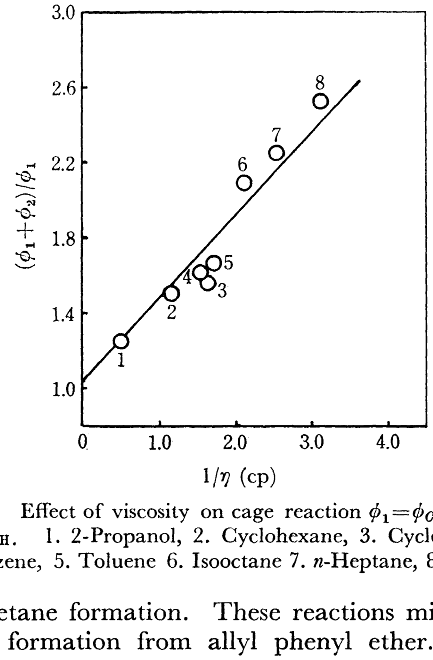

Fig. 1. Effect of viscosity on cage reaction $\phi_1 = \phi_C + \phi_P$, $\phi_2 = \phi_{PhOH}$. 1. 2-Propanol, 2. Cyclohexane, 3. Cyclohexene, 4. Benzene, 5. Toluene 6. Isooctane 7. *n*-Heptane, 8. *n*-Hexane

and oxetane formation. These reactions might induce phenol formation from allyl phenyl ether. (In this case the consumption of sensitizers is expected.) However, this sort of "sensitization" is not probable: (i) UV absorption and gas-chromatographic examination of the acetophenone and benzophenone sensitized reactions in benzene revealed that no sensitizer was consumed in the course of the reaction; (ii) sensitization was observed with Michler's ketone and *p*-hydroxybenzophenone which are known to be photo-unreactive; (iii) thermal decomposition of benzoyl peroxide in benzene containing allyl phenyl ether did not give allylphenols or phenol.

The results can be interpreted by the mechanism of energy transfer from *n*-π* triplet state of carbonyl compounds to olefins proposed by Yang, Cohen, and Shani.[8] The mechanism consists of two steps: (i) addition of excited carbonyl compounds to olefinic double bonds; (ii) elimination of ground state carbonyl compounds to give excited olefins. This suggests that the triplet energy of carbonyl compounds can be transferred selectively to the double bond of allyl moiety rather than phenyl moiety of allyl phenyl ether, while the excess energy of aromatic hydrocarbons is transferred to phenyl moiety of the ether. Excitation of allylic double bond would bring about phenol formation, the mechanism of which is still unknown.

The photoreactions of allyl phenyl ether are summarized in Scheme 1.

Experimental

Materials. Ally phenyl ether was synthesized from phenol and allyl bromide and purified by distillation, bp 92°C/25 mmHg. The purity determined by gas-chromatography was 98.6%. Benzophenone, *p,p'*-dimethoxybenzophenone, 3,4-dimethylphenol (G.R. grade of Tokyo Kasei Co.), *p*-hydroxybenzophenone, Michler's ketone (E.P. grade of Tokyo Kasei Co.), naphthalene (E.P. grade of Showa Kagaku Co.), and benzoyl peroxide (T.G. grade of Wako Junyaku Co.) were used without further purification. Benzaldehyde, acetophenone (E.P. grade of Yoneyama Yakuhin Co.), and 1,3-pentadiene (T.G. grade of Tokyo Kasei Co.) were purified by distillation.

Solvents. Commercially available *n*-hexane, *n*-heptane, and isooctane of spectral quality (Dotite Spectrosol) were used without further purification. Benzene, toluene, and 2-propanol (each E.P. grade of Junsei Kagaku Co.) were purified by fractional distillation. Cyclohexane was purified by treatment with nitric acid, followed by treatment with a silica gel column. Cyclohexane, *n*-hexane, *n*-heptane, and isooctane used had no or a slight absorption at 254 nm.

UV Irradiation. Degassed 0.1 M solution of ally phenyl ether in a quartz tube was irradiated externally with a low pressure mercury lamp (16W spiral type lamp made by Taika Kogyo Co.) with or without sensitizers and quenchers. The solution was stirred with a magnetic stirrer. The reaction vessel and the mercury lamp were immersed in a thermostat kept at 25°C. Up to 5 hours the products increased nearly in proportion to irradiation time. Prolonged irradiation caused a decrease in the quantum yields of the products probably because of the contamination of the wall of the vessel by photolysis products.

Analysis of the Products. The reaction products were analyzed gas-chromatographically with Yanagimoto Gas Chromatograph Model GCG 550 F (column, 1.2 m, 20% Carbowax on Celite; temperature, 180°C).

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[8] N. C. Yang, J. I. Cohen, and A. Shani, *J. Amer. Chem. Soc.*, **90**, 3264 (1968).

In the experiment of photosensitization by carbonyl compounds, the quantities of carbonyl compounds after irradiation were estimated by UV absorption spectroscopy and gas-chromatography. Absorption of acetophenone at 320 nm and absorption of benzophenone at 345 nm were used for the estimation.

Actinometry. Actinometry was performed with potassium ferrioxalate actinometer.[9] In the reaction condition above, the intensity of light was 2.9×10^{17} quanta/sec for 20 m*l* of solution.

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[9] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.* (London), **A 235**, 518 (1956).