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PHOTOCYCLOREVERSION-REACTION OF A CAGE MOLECULE AND RELATED CYCLOBUTANES WITH CATIONIC SENSITIZERS[1]

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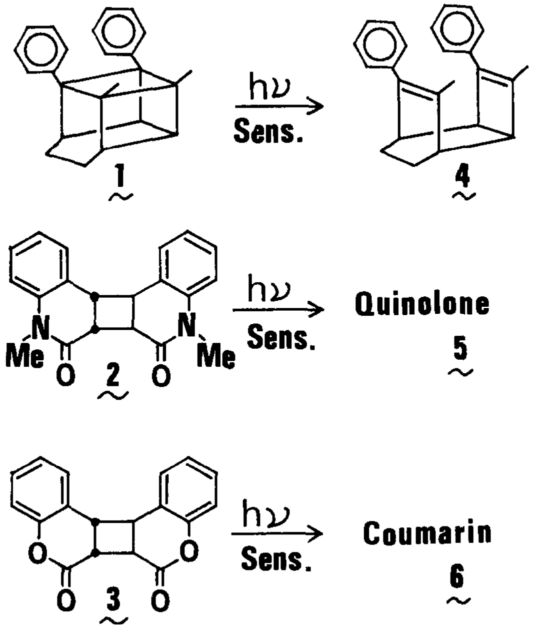
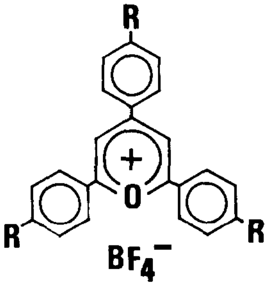
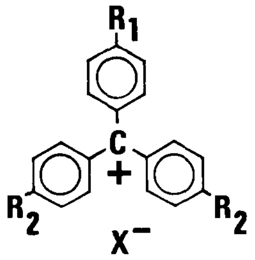
Summary: Irradiation of 1, 2, or 3 in acetonitrile in the presence of cationic sensitizer 7 or 8 afforded the cycloreversion product 4, 5 or 6, respectively. A wide range in quantum yields were found and these were dependent on the substrates and sensitizers.

Recently, photochemical reactions initiated with visible light excitation[2] have attracted considerable attention in connection with the solar energy storage problem. We now report the induction of photocycloreversion in a cage molecule 1 as well as cyclobutane derivatives 2 and 3, using cationic sensitizers such as pyrylium salts 7a and 7b, and trityl salts 8a, 8b, 8c, and 8d. All of these have strong absorption in the visible region (Table 1).





7a: R=H
7b: R=OMe



8a: $R_1=R_2=H$ $X=BF_4$
8b: $R_1=R_2=OMe$ $X=BF_4$
8c: $R_1=R_2=OMe$ $X=Cl$
8d: $R_1=H$ $R_2=NMe_2$ $X=Cl$

Table 1 Maximum wave length of VIS-spectra and the reduction potential of sensitizers.

Compound	**7a**	**7b**	**8a**	**8b**	**8c**	**8d**
λ_{max}^{nm} (CH_3CN)	354, 404	410, 450	405, 433	482	482	618
$E_{1/2}^{red}$ (CH_3CN, V vs SCE)	-0.32	-0.51	+0.29	-0.14	-0.15	-0.50

When 2-5 ml of an acetonitrile solution of cage molecule **1** or dimer **2** or **3** in the presence of a small amount (2-3 mg) of sensitizer was irradiated with a 300-W Xenon lamp (3-74 Corning glass filter)[3] at 25°C, the diene **4** or the olefin **5** or **6**, respectively, was produced in high yield (Table 2). The high quantum yield (greater than unity in some cases) strongly suggests that the process involves a chain reaction.

Table 2 Photosensitized cycloreversion of cage molecule **1** and dimers **2** and **3** in the presence of sensitizers **7a**, **7b**, **8a**, **8b**, **8c**, and **8d**.

Compound($E_{1/2}^{ox}$)^a	Sensitizer	Reaction Time	Chemical Yield	Quantum Yield^b	$K_q\tau$(M^{-1})
1 (+1.40)	**7a**	5min	100%	45	114
1	**7a**	5min	100%	59^c	
1	**7a**	5min	100%	76^d	
1	**7b**	5min	100%	12	116
1	**8a**	5min	100%	9^e	
1	**8b**	20min	100%	0.5	
1	**8c**	120min	61%	0.03	
1	**8d**	9000min	86%	small	
2 (+1.30)	**7a**	5min	100%	16	100
2	**7b**	5min	100%	10	116
2	**8a**	f	f	f	
2	**8b**	60min	100%	0.2	
2	**8c**	120min	1%	small	75
3 (+1.92)	**7a**	20min	96%	0.3	6
3	**7b**	120min	0%	0	
3	**8a**	120min	0%	0	
3	**8b**	120min	0%	0	
3	**8c**	120min	0%	0	

a: V vs SCE in CH_3CN b: [substrate] = 1.86×10^{-2}M, [sens] = 2.51×10^{-4}M

c: [substrate] = 2.24×10^{-2}M, [sens] = 2.51×10^{-4}M d: [substrate] = 3.75×10^{-2}M, [sens] = 2.51×10^{-4}M e: [substrate] = 1.86×10^{-2}M, [sens] = 3.82×10^{-3}M

f: Decolorization of sensitizer disturbed the cycloreversion.

In order to obtain more insight into the reaction mechanism, the quenching of the fluorescence of the sensitizer by 1, 2, 3, and some electron donors was studied (Figure 1). The fact that $k_q\tau$ increased and approached a constant value as the oxidation potential of the substrate decreased strongly suggests an electron transfer mechanism, since according to the Rehm-Weller equation,[4] the value for electron transfer to a given sensitizer (k_q) can be considered to increase linearly and approach the diffusion rate constant as the oxidation potential of the quencher decreases. The electron transfer mechanism is suggested by experiments in which the cycloreversion of 1 was efficiently quenched by tetramethoxybenzene ($E^{ox}_{1/2}$ = +0.81 V vs SCE)[5], but not by trimethoxybenzene ($E^{ox}_{1/2}$ = +1.49 V vs SCE).[5] We thus propose the electron transfer chain mechanism shown in Scheme 1.[6,7]

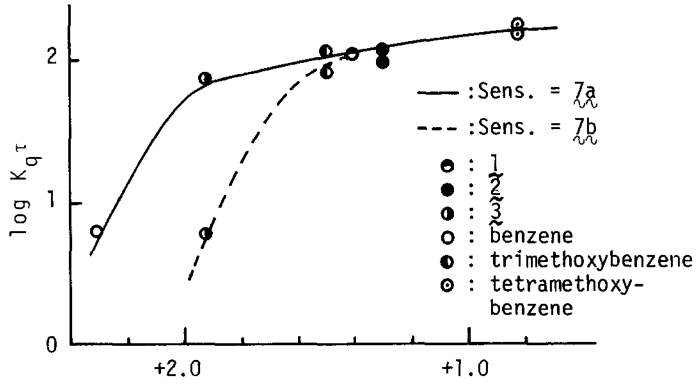


Figure 1 Relationship between the $K_q\tau$ values and the oxidation potentials of substrates.

$$7a \xrightarrow{h\nu} 7a^{*} \qquad \text{eq.1)}$$

$$7a^{*} \longrightarrow 7a \qquad \text{eq.2)}$$

$$7a^{*} + 1 \longrightarrow 7a^{\cdot -} + 1^{\cdot +} \qquad \text{eq.3)}$$

$$1^{\cdot +} \longrightarrow 4^{\cdot +} \qquad \text{eq.4)}$$

$$4^{\cdot +} + 1 \longrightarrow 4 + 1^{\cdot +} \qquad \text{eq.5)}$$

$$7a^{\cdot -} + 1^{\cdot +} \longrightarrow 7a + 1 \qquad \text{eq.6)}$$

$$7a^{\cdot -} + 4^{\cdot +} \longrightarrow 7a + 4 \qquad \text{eq.7)}$$

Scheme 1

As would be expected from eq 5), the quantum yield increases when higher concentrations of 1 were used (Table 2). The electron transfer step, eq 3) appears to occur efficiently as is indicated by the fluorescence quenching and the free energy difference (-23.9 Kcal/mol) calculated by the Rehm-Weller equation.[4] The following two steps, eq 4) and 5), represent the chain propagation steps. Because the oxidation potentials of 1 and 4 were nearly the same[8] and because the enthalpy change in the release of strain (eq 4) was estimated (MINDO/3)[9] to be exothermic by at least 9 Kcal/mol. Thus owing to the efficient electron transfer from 1 to the excited sensitizer in the initiation step and subsequent efficient propagation cycle, the photocycloreversion of 1 proceeded to completion, even when an acetonitrile solution of 1 containing the pyrylium salt 7a was exposed to sun-light for 20 min on a fine day.

These results may be rationalized by an electron transfer mechanism as follows. 1) Compound **7b** was not a good sensitizer in comparison with **7a**, although the substrate **1** or **2** quenched the fluorescence with nearly the same efficiency. This may be due to a more rapid back electron transfer step (eq 6) for **7b** than for **7a**, probably in a solvent cage. The difference in the reduction potential between **7a** and **7b** accords with that the back electron transfer is more exothermic for **7b** than for **7a**. 2) Considerably different quantum yields were obtained for sensitizers **8b** and **8c**, although both of them have nearly the same reduction potential. This may be derived from the difference in oxidation potential between **8b** ($E^{ox}_{1/2} > + 2.00$ V vs SCE) and **8c** ($E^{ox}_{1/2} = + 1.00$ V vs SCE). This would induce the intramolecular electron transfer from chloride anion to the excited trityl cation. The subsequent recombination of the resulting radicals, yielding the ground state of sensitizer results in the deactivation of the excited **8c** (eq 2).

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3) The filter cuts the light shorter than 400 nm wave-length.
4) D. Rehm and A. Weller, *Isr. J. Chem.*, **8**, 259(1970). Coulombic stabilization energy was omitted for the calculation of the free energy change (-23.9 Kcal/mol).
5) C. K. Mann and K. K. Barns, "Electrochemical Reaction in Nonaquous System" Marcel Dekker, New York 1970.
6) Other termination step, for example, trapping of cation radicals with unknown impurities in the solvent can not be ruled out.
7) Although, as for the trityl salt, the reaction mechanism of the initial step concerning the reactive excited state is ambigious, the fact that addition of n-propyl bromide considerably decreased the yield of diene **4** in trityl salt (**8b**)-sensitized reaction as well as in pylylium salt (**7a**)-sensitized one, suggests that the reactive excited state would be singlet. Cf. H. G. Lewis and E. D. Owen, *Ber. Bunsenges. Phisk. Chem.*, **72**, 277(1968).
8) The oxidation potentials (V vs SCE) of **4**, **5**, and **6** were +1.42, +1.62, +2.13, respectively.
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